Dipole-Dipole Coupling and Other Interaction Effects in Polar Dielectrics and Magnetic Relaxation of Single Domain Ferromagnetic Nanoparticles

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Summary

The main purpose of this thesis is to provide the precise details of the very onerous calculations underlying our two published papers [19] and [21]. Thus, the latter can be better understood and utilised later for future research as the details form an invaluable archive which for space reasons could not be published in the journals. These details which are essential for understanding the effect of two body interactions are provided in the thesis via my comprehensive appendices written in Chapters 5 and 7. In addition, through the use of Wolfram Mathematica, the results are corroborated by calculating the complex electrical susceptibility in Figures 2-4 of [19] as well as the integral relaxation time and complex magnetic susceptibility in Figures 2-4 of [21]. The published papers may be summarised as follows:

In the Budó paper [19] a fractional Smoluchowski equation for the orientational distribution of dipoles incorporating two body interactions with continuous time random walk *Ansatz* for the collision term is obtained for polar molecules. This equation is written via the non-inertial Langevin equations for the evolution of the relevant Eulerian angles and their associated Smoluchowski equation for the orientational probability distribution function. These equations govern the normal rotational diffusion of an assembly of non-interacting dipolar molecules with similar internal interacting polar groups hindering their rotation owing to their mutual potential energy. The resulting fractional Smoluchowski equation is then explicitly solved in the frequency domain using scalar continued fractions yielding the linear dielectric response as a function of the fractional parameter for extensive ranges of the interaction parameter and friction ratios. Thus, the main result is that Budó's treatment can possibly be extended to disordered materials.

In the magnetic paper [21], the magnetisation response including dipole-dipole interactions of a pair of macrospins (single-domain ferromagnetic particles) following the sudden alteration of a dc magnetic field is calculated from the stochastic Landau-Lifshitz-Gilbert equation for the magnetisation by reducing the overall task

to an infinite hierarchy of differential-recurrence relations in the time domain for the statistical moments (averaged products of spherical harmonics in this case). This is exactly solved in the frequency domain by matrix continued fractions. The greatest relaxation time and dynamic susceptibility are then compared with the corresponding results for two exchange-coupled spins using the same exact method. I believe that this is effectively the first exact treatment of dipole-dipole effects in the relaxation of macrospins. Generally, both the dielectric and magnetic calculations are essential as a starting point for the understanding of the effects of two body interactions on relaxation processes.

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Contents

1. Introduction

Long ago Debye proposed a model [1] of dielectric relaxation of an assembly of rigid non-interacting dipoles which yields a qualitatively acceptable microscopic explanation of the microwave absorption of polar fluids. It was initially posed as an extension of the work of Einstein [2] (concerning the translational Brownian motion of particles in a one dimensional extension) to *rotation* of a typical dipole of the polar assembly about a space-fixed axis [1] subject to a weak alternating (ac) electric field at microwave (GHz) frequencies. The calculation was later extended to rotation [3] in space. We shall call this *the first Debye model* [3]. Here, the rotation of a typical polar molecule in a liquid regarded microscopically as an assembly of non-interacting rigid rotators under the influence of both deterministic and random torques imposed by the surrounding heat bath is treated as rotational Brownian motion [3]. The theory then qualitatively predicts the observed dispersion and absorption of microwave (GHz) radiation of polar fluids. This is the principle underlying the operation of the microwave oven as there the dipoles are unable to keep in phase with the fast applied field, with the ensuing phase lag causing the dissipation of the rotational energy contained in the dipoles manifested as friction in the bath. This energy is dissipated as heat.

The second model considered by Debye is a solid-state like mechanism of relaxation which is mainly associated with dielectric relaxation in solids and latterly with magnetic relaxation of single domain ferromagnetic particles. Here a typical dipole can stay in either of two directions (parallel or anti-parallel to the applied field direction) and reverse its direction by crossing over an internal potential barrier through the action of thermal agitation which is again modelled by rotational Brownian motion. However the relaxation time, which is the time to cross the barrier from one orientation to another is effectively an Arrhenius process and so is exponentially long [4]. More details on the theory of dielectric relaxation, the work of Debye and others will be provided in Chapter 2 of the thesis.

Although the Debye model has been largely successful in accounting for the behaviour of the complex susceptibility of polar fluids at *low* frequencies (GHz), there remain two limitations. The first is the prediction of *infinite* integrated absorption occurring at THz (10^{12} Hz) frequencies and higher, giving rise to the infamous Debye plateau in the loss spectrum ($\omega\chi''(\omega)$), where $\chi''(\omega)$ is the imaginary part of the complex susceptibility, leading to the "black water" phenomenon. This flaw was eliminated by Rocard [5], who showed in a semi-heuristic fashion that the solution to this problem lies in the neglect of dipole inertial effects on the dynamics which cause them to become deterministic at very high frequencies. Rocard's calculations were later put on a rigorous basis by Sack [6, 7].

The second limitation of the Debye theory is that in formulating it all interactions between the dipolar rotators are ignored, with the sole exceptions being the Brownian torques due to the bath and the (external) interaction between a typical dipole of the polar assembly and the applied external time-dependent field. The inclusion of other interactions poses a very challenging problem in the stochastic dynamics of rigid bodies. To address this, a heuristic attempt at treating dipolar interactions combined with inertial effects was made via the itinerant oscillator (cage) model [8–10], where the interaction of a typical dipolar molecule with its polar cage of neighbours is represented by a cosine potential which has a rotating centre of torsion oscillation. This model has been reasonably successful in reproducing the main features of the GHz - THz absorption spectrum which are computed from the observed data [11]. Simply put the model predicts both the Debye (GHz) and far-infrared resonance absorption (THz) of polar fluids as well as the necessary return to transparency at very high frequencies. Despite this success however, the original form of the model is restricted to rotators which may rotate about a space-fixed axis only. Therefore a better and more rigorous approach would be to utilise a molecular model where we address the following:

1. Coupling [11–14] between a pair of dipoles [12] so as to account for their

hindered rotation.

2. Restriction to molecules rotating about a fixed axis can be removed.
3. Inertial effects can be fully accounted for.
4. Collision mechanisms other than the Brownian *Stosszahlansatz* (Boltzmann's collision number hypothesis that only interactions between two particles are ever of any importance i.e., molecular chaos) can be taken into consideration.

Now Budó's work [15, 16] (See the Appendix of Chapter 2 of the thesis, for an English translation of the paper, "Anomale Dispersion und freie Drehbarkeit," Physik. Zeits., vol. 39, p. 706, 1938. by A. Budó [15]) on the dielectric relaxation of molecules containing rotating polar groups may provide a framework for solving these problems. Budó has demonstrated how the original Debye theory for the complex susceptibility $\chi(\omega)$ valid in the non-inertial limit, is modified for assemblies of non-interacting molecules containing such groups. His main result [12,16] is that the inclusion of the interaction between two groups embedded in a given polar molecule yields a discrete set of Debye-type relaxation mechanisms for the susceptibility $\chi(\omega)$ with relaxation times given by the eigenvalues of the Sturm-Liouville equation appropriate to the potential considered. His results were later corroborated by Zwanzig [17,18]. He studied in the non-inertial limit, the complex susceptibility $\chi(\omega)$ of an assembly of permanent dipoles at relatively high temperatures coupled by dipole-dipole interactions and arranged at the sites of a simple cubic lattice.

Our purpose is to report progress that has been made in addressing problems 1, 2 and 4 mentioned earlier and to provide an indication of how potential future research into addressing 3 as well as providing precise details of all the intricate calculations involved. In doing so we shall also demonstrate how Budó's [15, 16] hindered rotation treatment can be generalised to include an anomalous diffusion *Stosszahlansatz* in a weak microwave field in the non-inertial limit [19] (More details on how anomalous diffusion arises and Brownian motion will be given in Chapter 2). In our treatment [19], a fractional Smoluchowski equation based on the continuous-time random walk *Ansatz* is written via the non-inertial (pertaining to anomalous diffusion in configuration space) Langevin equations for the dynamics of a molecule consisting of two similar polar groups. However the groups cannot rotate freely relatively to one another owing to their mutual potential energy (more details on the Smoluchowski equation and methods for its solution are provided in Chapter 4). The fractional Smoluchowski equation is shown to be fruitful in describing the dynamics of complex non-inertial systems governed by anomalous diffusion. Mathematically, all that is being done is that differentiation with respect to time in a normal Smoluchowski equation is replaced by fractional derivatives of non-integer order, representing a Boltzmann *Stosszahlansatz* for a system interacting with a thermal bath. Generally speaking interactions between polar molecules, even for the simple hindered rotation configuration envisaged by Budó, appear to have been ignored [20] for anomalous diffusion.

In general the (fractional) Smoluchowski equation obtained is converted to a scalar differential recurrence relation for the statistical moments and then solved in the frequency domain by use of continued fractions, allowing for the calculation through successive convergents of the fraction of the linear dielectric response as a function of the fractional parameter for various ranges of damping, dipole moment and interaction parameters. Therefore, both the dipole correlation functions and complex susceptibility are obtained. The latter then comprises a low frequency band with width depending on the anomalous parameter (more details on linear response theory are provided in Chapter 2). The solution explained here will expand the scope of the Budó model for describing the dynamical effects of hindered rotation. Thus we determine the numerically exact solution for the linear response of that model for anomalous diffusion [19] and compare it with the previous exact results [12, 16] for normal diffusion.

In addition to this dielectric relaxation problem, we can also apply our methods to the solution of the magnetic relaxation of single domain ferromagnetic particles as used in recording [21]. This in essence uses Debye's second model to demonstrate how interactions in the two-magnet-dipole problem (a system with four degrees of freedom) may be treated analytically via the formally exact solution of the relevant Langevin or Fokker-Planck equations for the desired observables. These are the characteristic relaxation times and decay functions. This will be achieved through extending the exact method of Titov, Kachachi, et al. [22] to study the effect of magnetic dipole-dipole interaction on the magnetisation relaxation over the internal (to the particle) anisotropy Zeeman energy barrier (note that in [22] exchange interactions alone were treated). The dipole-dipole coupling is very useful for structural studies (because it depends only on known physical constants and the dipole separation) and for its effect on spin relaxation. Thus, magnetic dipole-dipole interactions are exactly treated for the two-spin model hence representing a system with more than two configurational degrees of freedom [21]. These results are compared with those of the two-spin system with exchange interaction only [22]. Now *unlike* exchange interactions, dipole-dipole interactions are *anisotropic*. However, as a first step towards including this anisotropy only parallel easy axes (also parallel to the direction of the applied dc field) are analysed, because the resulting circularly symmetric Hamiltonian drastically simplifies the calculations. For all other orientations of the anisotropy axes which of course is the most interesting case the calculations are much more complicated and will lead to varying results arising from the anisotropic nature of the dipole-dipole interaction. Our calculations are effected by first rewriting the governing (vector) stochastic Landau-Lifshitz-Gilbert (Langevin) equation governing the time-dependent magnetisation as scalar Langevin equations for the products of the spherical harmonics, statistical averages of which are the desired observables, specifying the orientation of each of the spins [21]. Next (using the theory of angular momentum in the manner of [2]) averaging them over their realisations in configuration space in an infinitesimal time given a sharp set of initial orientations. This time is taken following Einstein [2] as shorter than any characteristic time of the system but long compared to the time of an adiabatic collision. Thus the time evolution equation of the sharp values in the form of a partial differential-recurrence relation in space and time may be determined. Next by postulating an appropriate spatial distribution of the sharp values and then ensemble averaging over this distribution one has a hierarchy of differential-recurrence relations for the statistical moments yielding the observables via rapidly convergent matrix continued fractions in the frequency domain [2]. Hence, one has in analytic fashion the relaxation time for effectively all values of the interaction, anisotropy, and applied field parameters as well as other relevant observables (spectra of the relaxation functions, the complex susceptibility, etc.). The observables so calculated [21] will then be compared with the corresponding ones for exchange interaction available in Ref. [22]. It should be emphasised that uniaxial anisotropy with the external field applied parallel to the easy Z-axis is supposed. The advantage of this particular anisotropy potential is that (although obviously subject to many symmetry restrictions) it ultimately results in a (tractable) recurrence relation (for the observables) in three indexes only.

2. Dielectrics, Polarisation and Dielectric Response

A *dielectric* or *dielectric material* is an electrical insulator that can be polarised by an applied external field. However upon being placed in an electric field, electric charges do not flow through the material as we would observe in an *electrical conductor* (e.g. metals), rather what happens is that they shift from their average equilibrium positions, resulting in the phenomenon known as *dielectric polarisation*, where the positive charges within the dielectric are shifted slightly in the direction of the electric field, while the negative charges shift in the opposite direction, which creates an internal electric field within the dielectric which reduces the overall field within the dielectric itself. Dielectrics are primarily used in the manufacture of capacitors because they have a permittivity ε that is higher than the permittivity ε_0 of a vacuum (free space, $\varepsilon_0 = 1/36\pi \times 10^{-9}$F/m), which leads to a higher capacitance. Most commercially available capacitors make use of solid materials with high permittivity. Almost all materials we encounter are dielectrics, some examples include glass, porcelain, most plastics, gases such as nitrogen, and liquids such as mineral oil [23].

The measurement of dielectric response is a non-invasive technique that has been used for the characterisation of materials throughout most of the 20th century. As such there are a number of books that cover the technique from different perspectives. The most noteworthy of which include *Debye* [3], *Smyth* [24], *McCrum* et al. [25], *Daniels* [26], *Böttcher* and *Bordewijk* [27], *Jonscher* [28] *Scaife* [29] and *Fröhlich* [30].

In this chapter, we shall examine the concept of dielectric polarisation on both a molecular and macroscopic level, then we will discuss the concept of susceptibility and dielectric response from the perspective of linear response theory. Then it will be expedient to explore the historical background of the research associated with the analysis of dielectric response, from the work of Debye [1,3] to one of the topics of this thesis, the work of Budó [15,16].

2.1 Polarisation and Susceptiblity

As mentioned earlier, dielectric polarisation of polar molecules is due to the particular phenomenon whereby an assembly of dipole moments may rotate due to an external applied electrical field. But how does polarisation generally occur? To answer this we need to first consider what happens to an atom when it is placed under the influence of an external electric field **E**. An atom consists of a positively charged nucleus with protons (positively charged) and neutrons (neutral), and a cloud of negatively charged electrons which surround and orbit it. As a whole, without the influence of an electric field, the positions of the nucleus and electron are such that their centres are aligned leading to the atom in its entirety being electrically neutral. Under the influence of an electric field however, what we observe is a displacement in the positions of the nucleus and the cloud of electrons, where the nucleus is pulled in the direction of the field, while the cloud of electrons goes in the opposite direction. As they are pulled apart, they exert a mutual attractive force due to being polar opposites in order to keep from being separated, eventually if the field is not strong enough to overcome this attractive force and split them apart, forming an ion, there will be an equilibrium reached where the nucleus and electron have their centres kept apart by the field, while their mutual attractive forces prevent them from separating. This leads to the atom now having a dipole moment **p** pointing in the direction of the field **E**. **p** and **E** are related by [31]

$$\mathbf{p} = \alpha\mathbf{E}, \tag{2.1}$$

where α is the atomic polarisability, whose value depends on the structure of the atom. So here we see that polarisation occurs in the atom due to a *displacement* between the centres of the oppositely charged elements of the atom. However, what if we are dealing with the polarisation of a *molecule*? In that case we have to now take into consideration the orientation of the molecule with respect to the direction of the electric field, as we will find that molecules tend to have different magnitudes of polarisation depending on the angle they make with the electric field. In that case we must now generalise Eq. (2.1) into its components along the molecular axes xyz [31]

$$\begin{aligned} p_x =& \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z, \\ p_y =& \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z, \\ p_z =& \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z, \end{aligned} \tag{2.2}$$

where the constants α_{ij} are the polarisabilty tensors for the molecule in question.

So far we have dealt with atoms and molecules where a dipole moment is induced on them through exposure to an electric field $\mathbf{E}$, where they had none before. But what about molecules (common examples include $\mathrm{H_2O}, \mathrm{CH_2Cl_2}$) which have their own inherent permanent dipole moments, such as electrets [32] and ferroelectrics? Such *polar molecules* under the influence of an electric field will experience a torque which if they were free to rotate, will swing around until it aligns itself in the direction of the applied field. In the absence of an electric field, the dipole moments of the molecules all point in random directions, which leads to the average dipole moment being zero. The torque applied to the polar molecules in question is illustrated in Figure 2.1, where if the field is uniform, the force on the positive end of the molecule, given by $\mathbf{F}_+ = q\mathbf{E}$, will cancel the force on the negative end of the molecule, given by $\mathbf{F}_- = -q\mathbf{E}$, but there will be a torque $\mathbf{N}$ given by [31]

$$\begin{aligned} \mathbf{N} =& (\mathbf{r}_+ \times \mathbf{F}_+) + (\mathbf{r}_- \times \mathbf{F}_-) \\ =& \left[\frac{\mathbf{d}}{2} \times q\mathbf{E}\right] + \left[-\frac{\mathbf{d}}{2} \times -q\mathbf{E}\right] = q\mathbf{d} \times \mathbf{E}. \end{aligned} \tag{2.3}$$

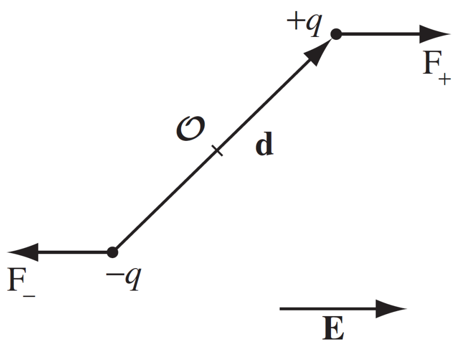

Figure 2.1: Torque applied to a polar molecule by the field **E**. (aft. [31])

So ultimately, looking at the phenomena we have just described that occur on an atomic and molecular level (for both neutral and polar molecules), we can see that the same basic result is observed, the dipoles end up pointing along the direction of the electric field being applied to them, i.e., the dielectric material becomes *polarised*. So now we can define polarisation **P** as *the dipole moment per unit volume.*

Now we can take a look at the relationship between the polarisation of the dielectric in question and the electric field. For many substances, the polarisation is proportional to the field provided that it is not too strong through the relationship,

$$\mathbf{P} = \chi \mathbf{E}, \tag{2.4}$$

where $\chi = \varepsilon_0(\varepsilon_r - 1)(\varepsilon_0 = 1/36\pi \times 10^{-9}\text{F/m})$ is the electrical susceptibility of the dielectric in question and ε_r is the relative permittivity. It should be noted that **E** in Eq. (2.4) is the *total* field that we observe which can occur in part from free charges and in part from the polarisation itself. In the presence of a field $\mathbf{E}_0$, **P** cannot be obtained from Eq. (2.4) because the polarisation of the material will itself produce its own field, and this field contributes to the total field **E** and we end up with an infinite regress of the external field polarising the material, the polarisation in the material producing its own field, which contributes to the total field, which polarises the material etc. A simple approach to this problem is to analyse the *electric displacement field* **D** of the material in question. Consider a broad sample of dielectric material of thickness d with electrodes of area A placed on each opposite surface. The material being a dielectric will mean that effectively this system behaves as a capacitor storing charges $\pm Q$ on the surfaces which have a potential V applied. The charge Q on a plate is then given by [33]

$$Q = CV, \tag{2.5}$$

where C is called the *capacitance* of the system in question, which for parallel plate capacitor considered is given by

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}, \tag{2.6}$$

where ε_0 is the permittivity of free space, and of course ε_r is still the permittivity of the material relative to the permittivity of free space (i.e., the relative permittivity). The susceptibility χ in Eq. (2.4) is given by

$$\chi = \varepsilon_0(\varepsilon_r - 1). \tag{2.7}$$

The electric field for the parallel electrode geometry just described has magnitude $E = V/d$, and the magnitude of the electric displacement field $\mathbf{D}$ of the material is given by $D = Q/A$, then Eqs. (2.5) and (2.6) can be rewritten as

$$\mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E} = \varepsilon_0 \mathbf{E} + \chi \mathbf{E}. \tag{2.8}$$

This relation is valid for any geometry and is true for linear media.

So far the focus has been on the polarisation $\chi\mathbf{E}$ of the material if we apply a *static* electric field where the frequency $f = 0$. Suppose now that the static field is replaced with an electric field that oscillates with an angular frequency $\omega = 2\pi f$, then the formula for the polarisation becomes

$$\mathbf{P}(\omega) = \chi(\omega)\mathbf{E}(\omega), \tag{2.9}$$

where $\mathbf{E}(\omega) = \mathbf{E}_0 e^{i\omega t}$. Hence the polarisation $\mathbf{P}(\omega)$ is now dependent upon the frequency of the electric field (ac field). If we have our material in thermal equilibrium without an applied electric field, and we were then to suddenly apply the electric field, what we would observe is the alteration in the net dipole moment density as discussed earlier. However, this change in the internal arrangement of positive and negative charges is not instantaneous. What happens instead is that it will evolve according to some equation of motion appropriate to the type of charges and dipole moments that are present. Therefore there is a time period required before the system can reach equilibrium with the applied field. Formally this time will tend to infinity (equivalent to an ac frequency of zero), but to all intents and purposes it can be assumed that the system reaches equilibrium fairly rapidly after some relevant time scale, τ, with the polarisation approaching the static value $P = P(0)$ for $t \gg \tau$. What if then the electric field reverses sign before equilibrium is reached, such reversal occurring in an ac field at a time $t = 1/2f$? In such a scenario, it would be clear that the polarisation will not have reached its equilibrium value before the field is reversed, thus $P(\omega) \lesssim P(0)$ and $\chi(\omega) \lesssim \chi(0)$. As such the frequency dependence of the dielectric susceptibility $\chi(\omega)$ is determined via the equation of motion which governs the evolution of the ensemble of electric dipole moments following excitation. Generally speaking, $\chi(\omega)$ may be expressed as a complex function with a real component $\chi'(\omega)$, which defines the component of $P(\omega)$ that is in phase with the applied ac field $E_0 \cos(\omega t)$, and an imaginary component $-\chi''(\omega)$ defining the component which is 90° out of phase. The conventional form is given by [2, 33, 34]

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega). \tag{2.10}$$

$\chi'(\omega)$ corresponds to the net separation of charge with the dielectric in the form of a macroscopic capacitor. $\chi''(\omega)$ also determines the real component of the *polarisation current density* in phase with the electric field, i.e., $J_{pol}(\omega)$ which is [33]

$$\begin{aligned} J_{pol}(\omega) =& \chi''(\omega)\omega E_0 \cos(\omega t) \\ =& \sigma_{AC}(\omega) E_0 \cos(\omega t), \end{aligned} \tag{2.11}$$

where $\chi''(\omega)\omega = \sigma_{AC}$ is the contribution to the ac conductivity that occurs due on account of the polarisation response to the electric field. From Joule's law for the dissipation of power thermally by an electric current ($P = IV$), it is evident that $(1/2)\chi''(\omega)\omega(E_0)^2$ is the dissipated power per unit volume as a result of the generation of a net polarisation by the electric field, in other words, the power dissipation density. Thus, $\chi''(\omega)$ is often called the power dissipation component, which arises due to the work that the electric field has to exert on the dielectric so as to produce a net dipole moment density. A part of this energy is stored in the charge separations, and can be recovered in a manner similar to how elastic energy stored in a spring can be recovered. The remaining energy however which is used to overcome the friction which goes against the establishment of the net dipole density, cannot be recovered, is dissipated in the dielectric.

2.2 Linear Response Theory and Dielectric Relaxation

Linear response theory [35] is of fundamental importance to the calculation of the time behaviour of statistical averages from microscopic evolution equations such as the Langevin or Fokker-Planck equation in order to obtain the linear response of a system to a weak applied stimulus. When talking about dielectric relaxation, we are interested in the linear approximation in a small applied electric field. The origin of the response is due to the permanent dipoles existing in many molecules (e.g. H_2O) due to the asymmetry of their structure. Moreover atoms exist which while not possessing a permanent dipole moment, have ion pairs which will also act as dipoles. Thus an ensemble of permanent dipoles can also exist in such a system and will obey the laws of statistical mechanics. However, the orientation of the permanent dipoles in this system in the absence of an electric field will be random, effectively leading to the net dipole moment of system being zero as discussed earlier in the thesis. However, the description of the thermodynamic ensembles is done through the use of distributions that allow for fluctuations about the defined average values. For example *canonical* ensembles allow for fluctuations in energy about a *defined average energy content*, and *grand canonical* ensembles allow for fluctuations in the number of effective units. With regard to dipole responses, we are observing fluctuations involving the orientations of the permanent dipoles, leading to the formation of a net dipole moment density. As mentioned earlier, the application of an electric field to the system leads to the coupling of the permanent dipoles to the field, whereby a torque applied to the dipoles tries to align them with the electric field vector at the lowest energy position. This results in an increase in the population of the permanent dipole fluctuations with a component oriented in the field direction in comparison to the ones having components oriented in other directions. Hence we have a net dipole moment density driven by the frequency of the electric field [36]. For example we will presently show how the after-effect (i.e., the time behaviour following the removal of a dc field) and alternating field solutions of the Smoluchowski equation for the rotational Brownian motion of electrical dipoles can be obtained. Moreover these can be related via a method given by Scaife [18, 37] which is also presented in detail in Section 2.8 of the book "The Langevin Equation: With Applications to Stochastic Problems in Physics, Chemistry and Electrical Engineering" [2]. In addition we will further expand upon and explain the individual steps of Section 2.8 of [2] in order to illustrate the procedure which will be utilised later in the thesis.

Consider a causal, linear time-invariant system, with input $x(t)$ and output $y(t)$. Let $h(t)$ and $a(t)$ denote the impulse and unit-step responses respectively. These functions are related by

$$a(t) = u(t) * h(t), \tag{2.12}$$

where $*$ denotes the convolution operator and $u(t)$ denotes the unit step function. Using the commutative property of mathematical convolution, we can rewrite Eq. (2.12) in the opposite manner as

$$\begin{aligned} a(t) =& h(t) * u(t) \\ =& \int_{-\infty}^{\infty} h(t')\, u(t-t')\, dt'. \end{aligned} \tag{2.13}$$

We note that the impulse response $h(t) = 0$ for $t < 0$, which means the integral can be rewritten as

$$a(t) = \int_{0}^{\infty} h(t')\, u(t-t')\, dt'. \tag{2.14}$$

Since the shifted unit step function $u(t-t') = 0$ for $t' > t$, the integral may be written as

$$a\left(t\right) = \int_{0}^{t} h\left(t'\right) dt'. \tag{2.15}$$

The response $y(t)$ to the input $x(t)$ is obtained by convolving $x(t)$ and $h(t)$

$$y\left(t\right) = \int_{-\infty}^{\infty} x\left(\tau\right) h\left(t-\tau\right) d\tau = \int_{-\infty}^{t} x\left(\tau\right) h\left(t-\tau\right) d\tau, \tag{2.16}$$

since $h\left(t-\tau\right) = 0$ for $\tau > t$. As mathematical convolution is a commutative operation, we may also obtain $y(t)$ by convolving $h(t)$ and $x(t)$

$$y\left(t\right) = \int_{-\infty}^{\infty} h\left(\tau\right) x\left(t-\tau\right) d\tau = \int_{0}^{\infty} h\left(\tau\right) x\left(t-\tau\right) d\tau, \tag{2.17}$$

since $h(\tau)$ is causal. If $x(t) = 0$ for $t < 0$, then

$$y\left(t\right) = \int_{0}^{t} x\left(\tau\right) h\left(t-\tau\right) d\tau = \int_{0}^{t} h\left(\tau\right) x\left(t-\tau\right) d\tau. \tag{2.18}$$

Since $h(t)$ is obviously related to $a(t)$ by

$$h\left(t\right) = \frac{d}{dt} a\left(t\right), \tag{2.19}$$

we can rewrite Eq. (2.18) as

$$y\left(t\right) = \int_{0}^{t} \frac{da\left(\tau\right)}{d\tau} x\left(t-\tau\right) d\tau. \tag{2.20}$$

If we consider at time $t = 0$ a unit electric field applied to a dielectric body, an electric dipole moment $a(t)$ will be induced on the body. The unit step response $a(t)$ is then called the response function of the body. Let $\mathbf{m}(t)$ denote the instantaneous dipole moment of the body. The response to $\mathbf{E}_0 u(t)$, where $\mathbf{E}_0$ is a constant vector and $u(t)$ is the unit-step function, is $\mathbf{m}(t) = \mathbf{E}_0 a(t)$. The response to the field being switched on at time $t = 0$ is called the rise transient. It can be postulated that when the field is switched on, there is no instantaneous response, so that $a\left(0\right) = 0$. Since the system is time-invariant, the response to $\mathbf{E}_0 u(t - t_0)$ is $\mathbf{E}_0 a(t - t_0)$ where t_0 is a constant. $\mathbf{E}_0 a(t - t_0)$ is the response of the body to the electric field being switched on at time $t = t_0$.

We shall now consider the case where the electric field is switched on at time $t_0 = -\infty$, $\mathbf{E}(t) = \mathbf{E}_0 u(t - (-\infty)) = \mathbf{E}_0 u(t + \infty)$, $\mathbf{m}(t)$ will be equal to $\mathbf{E}_0 a(t + \infty)$. For $t \geq 0$ we have $\mathbf{m}\,(t) = \mathbf{E}_0 a\,(\infty)$. If the field is switched on at time $t = -\infty$ and switched off at time $t = 0$, we have $\mathbf{E}\,(t) = \mathbf{E}_0\,[u\,(t + \infty) - u\,(t)]$ and the response $\mathbf{m}(t)$ for $t \geq 0$ is equal to $\mathbf{E}_0\,[a\,(\infty) - a\,(t)]$. The *after-effect* function $b(t)$ is defined by the relation

$$b(t) = \begin{cases} a(\infty) - a(t), & t \geq 0, \\ 0, & t < 0, \end{cases} \tag{2.21}$$

therefore $\mathbf{m}\,(t) = \mathbf{E}_0 b\,(t)$ for $t \geq 0$.

By superposition the (linear) response of the body to a time-varying field $\mathbf{E}(t)$ that is zero for $t < 0$ is

$$\mathbf{m}\,(t) = \int_0^t \mathbf{E}\,(t - \tau)\,\frac{d}{d\tau} a\,(\tau)\,d\tau. \tag{2.22}$$

Consider now the a.c. response where $\mathbf{E}(t)$ is expressed as

$$\mathbf{E}(t) = \begin{cases} \mathbf{E}_m \cos(\omega t), & t \geq 0, \\ 0, & t < 0, \end{cases} \tag{2.23}$$

such that

$$\mathbf{m}\,(t) = \int_0^t \mathbf{E}\,(t - \tau)\,\frac{d}{d\tau} a\,(\tau)\,d\tau = \int_0^t \mathbf{E}_m \cos\left(\omega(t - \tau)\right)\frac{d}{d\tau} a\,(\tau)\,d\tau. \tag{2.24}$$

Using the trigonometric identity $\cos\,(u - v) = \cos\,(u)\cos\,(v) + \sin\,(u)\sin\,(v)$ Eq. (2.24) can be rewritten as

$$\mathbf{m}\,(t) = \int_0^t \mathbf{E}_m\left[\cos\,(\omega t)\cos\,(\omega\tau) + \sin\,(\omega t)\sin\,(\omega\tau)\right]\frac{d}{d\tau} a\,(\tau)\,d\tau, \tag{2.25}$$

which can be split into two integrals

$$\mathbf{m}\left(t\right)=\int_{0}^{t}\mathbf{E}_{m}\cos\left(\omega t\right)\cos\left(\omega\tau\right)\frac{d}{d\tau}a\left(\tau\right)d\tau+\int_{0}^{t}\mathbf{E}_{m}\sin\left(\omega t\right)\sin\left(\omega\tau\right)\frac{d}{d\tau}a\left(\tau\right)d\tau. \tag{2.26}$$

Taking the constants out from the integrals we obtain,

$$\mathbf{m}\left(t\right)=\cos\left(\omega t\right)\mathbf{E}_{m}\int_{0}^{t}\cos\left(\omega\tau\right)\frac{da\left(\tau\right)}{d\tau}d\tau+\sin\left(\omega t\right)\mathbf{E}_{m}\int_{0}^{t}\sin\left(\omega\tau\right)\frac{da\left(\tau\right)}{d\tau}d\tau. \tag{2.27}$$

If t becomes very large, $da(\tau)/d\tau$ becomes negligibly small for $1 \ll t \leq \tau \leq \infty$, thus the integrals

$$\int_{t}^{\infty}\frac{da\left(\tau\right)}{d\tau}\cos\left(\omega\tau\right)d\tau\ \text{and}\ \int_{t}^{\infty}\frac{da\left(\tau\right)}{d\tau}\sin\left(\omega\tau\right)d\tau, \tag{2.28}$$

become negligible as well and so we can write

$$\mathbf{m}\left(t\right)=\mathbf{E}_{m}\alpha'\left(\omega\right)\cos\left(\omega t\right)+\mathbf{E}_{m}\alpha''\left(\omega\right)\sin\left(\omega t\right), \tag{2.29}$$

where

$$\alpha'\left(\omega\right)=\int_{0}^{\infty}\frac{da\left(\tau\right)}{d\tau}\cos\left(\omega\tau\right)d\tau, \tag{2.30}$$

$$\alpha''\left(\omega\right)=\int_{0}^{\infty}\frac{da\left(\tau\right)}{d\tau}\sin\left(\omega\tau\right)d\tau. \tag{2.31}$$

The complex polarisability $\alpha\left(\omega\right)=\alpha'\left(\omega\right)-i\alpha''\left(\omega\right)$ can now be defined as

$$\begin{aligned}\alpha\left(\omega\right)&=\int_{0}^{\infty}\frac{da\left(t\right)}{dt}\cos\left(\omega t\right)dt-i\int_{0}^{\infty}\frac{da\left(t\right)}{dt}\sin\left(\omega t\right)dt\\&=\int_{0}^{\infty}\frac{da\left(t\right)}{dt}\left[\cos\left(\omega t\right)-i\sin\left(\omega t\right)\right]dt.\end{aligned} \tag{2.32}$$

Using Euler's formula, we can rewrite this as

$$\alpha\left(\omega\right)=\int_{0}^{\infty}\frac{da\left(t\right)}{dt}e^{-i\omega t}dt. \tag{2.33}$$

The derivative of the after-effect function $b(t)$ in Eq. (2.21) with respect to t is given by

$$\frac{db\left(t\right)}{dt}=-\frac{da\left(t\right)}{dt}, \tag{2.34}$$

which we can substitute back into Eq. (2.33) to get

$$\alpha\left(\omega\right)=-\int_{0}^{\infty}\frac{db\left(t\right)}{dt}e^{-i\omega t}dt. \tag{2.35}$$

We can observe from Eqs. (2.30) and (2.31) that $\alpha^{*}\left(-\omega\right)=\alpha'\left(\omega\right)+i\alpha''\left(\omega\right)$, where $*$ denotes complex conjugate. Evaluating Eq. (2.35) through integration by parts where the formula is

$$\int uv'=uv-\int u'v, \tag{2.36}$$

and letting $v'=db\left(t\right)/dt$ and $u=e^{-i\omega t}$, we get

$$\begin{aligned}\int_{0}^{\infty}\frac{db\left(t\right)}{dt}e^{-i\omega t}dt&=b\left(t\right)e^{-i\omega t}\Big|_{0}^{\infty}-\int_{0}^{\infty}-i\omega e^{-i\omega t}b\left(t\right)dt\\&=\left[0-b\left(0\right)\right]+i\omega\int_{0}^{\infty}e^{-i\omega t}b\left(t\right)dt\\&=-b\left(0\right)+i\omega\int_{0}^{\infty}e^{-i\omega t}b\left(t\right)dt,\end{aligned} \tag{2.37}$$

which we substitute back into Eq. (2.35) to get

$$\alpha\left(\omega\right)=b\left(0\right)-i\omega\int_{0}^{\infty}e^{-i\omega t}b\left(t\right)dt. \tag{2.38}$$

Dividing both sides of Eq. (2.38) by $b(0)$, we get

$$\frac{\alpha\left(\omega\right)}{\alpha_{s}}=1-i\omega\int_{0}^{\infty}R\left(t\right)e^{-i\omega t}dt, \tag{2.39}$$

where $R(t)=b(t)/b(0)$ and $\alpha_{s}=\alpha'\left(0\right)=b\left(0\right)$ is the static polarisability. The alternating and after effect solutions are connected by Eq. (2.39) on the condition that the response is *linear*.

In Eq. (2.39), α_s is closely connected with the dissipative part of the frequency dependent polarisability $\alpha''(\omega)$. The proof for this comes when we utilise the Kramers-

Kronig dispersion relations [30].

$$\alpha'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\alpha''(\mu)\mu d\mu}{\mu^2 - \omega^2}, \tag{2.40}$$

$$\alpha''(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\alpha'(\mu)\omega d\mu}{\omega^2 - \mu^2}, \tag{2.41}$$

where P indicates that the Cauchy principal value [38] of the integral is to be taken. In Eq. (2.40), let $\omega = 0$, since ω and μ are interchangeable we get

$$\alpha_s = \alpha'(0) = \frac{2}{\pi} \int_0^\infty \frac{\alpha''(\omega) d\omega}{\omega}, \tag{2.42}$$

which gives a fundamental link between the equilibrium and the nonequilibrium properties of the body and gives a demonstration of one of the most fundamental theorems of statistical mechanics, called the *fluctuation-dissipation theorem* [35,39,40]. The latter is explained through the use of Scaife's method [18,37] as presented in [2]. The static polarisability of a dielectric body can be given by $\alpha_s = \langle M^2 \rangle_0 / 3kT$, where $\langle M^2 \rangle_0 = \langle \mathbf{M} \cdot \mathbf{M} \rangle_0$ is the ensemble average of the square of the fluctuating dipole moment $\mathbf{M}$ of the body in the absence of an external field [30]. It would be opportune at this point to briefly talk about what is called the *ergodic (energy path) hypothesis* as is described in detail in [2]. Maxwell and Boltzmann [41] hoped to justify the methods of statistical mechanics through showing that the *time average* [42] of any quantity pertaining to any *single* system of interest should agree with the *ensemble average* for that quantity calculated from statistical mechanics. The postulate leading to this conclusion was called the *ergodic hypothesis* by Boltzmann, and by Maxwell was called the assumption of *continuity in phase* [2]. It states that the phase point for any isolated system should pass in succession through every point compatible with the energy of the system before finally returning to its original position in phase space. Note that in the form postulated by the founders of statistical mechanics, this is not strictly true (see pages 63 - 70 of [43]). Consequently, when calculating average values one has to distinguish between an *ensemble average* and a *time average*. However for a *ergodic* process where by definition all time dependent averages are functions only of time difference, in other words the basic mechanisms underlying the process do not change with the course of time, these two methods of averaging will always give the same result. For example, consider the autocorrelation function (ACF) $C_x(\tau) = \overline{x(t)x(t+\tau)}$ which we define as the time average of a two-time product over an arbitrary range time T' [2]

$$C_x(\tau) = \lim_{T'\to\infty} \frac{1}{T'} \int_{-\frac{T'}{2}}^{\frac{T'}{2}} x(t)x(t+\tau)dt, \tag{2.43}$$

where for the cases of negative values for τ, it is to be interpreted as $|\tau|$. Ergodicity therefore means that for a stationary process where

$$\overline{x(t)x(t+\tau)} = \overline{x(t)x(t-\tau)}, \tag{2.44}$$

we may also consider *ensemble* averages where we simultaneously repeat the same measurement for all copies of the system [44] and calculate averages which yields a result identical to that seen in Eq. (2.43), i.e.,

$$\langle x(t)x(t+\tau)\rangle = \overline{x(t)x(t+\tau)}. \tag{2.45}$$

So now through the ergodic hypothesis we get [2] (applying it to dipole moments)

$$\langle M^2\rangle_0 = \lim_{T'\to\infty} \frac{1}{T'} \int_{-\frac{T'}{2}}^{\frac{T'}{2}} \mathbf{M}(t)\cdot\mathbf{M}(t)dt, \tag{2.46}$$

then we write the Fourier transform pair

$$\tilde{\mathbf{M}}(\omega) = \int_{-\infty}^{\infty} \mathbf{M}(t)e^{-i\omega t}dt, \quad \mathbf{M}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{\mathbf{M}}(\omega)e^{i\omega t}d\omega. \tag{2.47}$$

Through inserting Eq. (2.47) into Eq. (2.46), we obtain from Parseval's theorem [42] and the ergodic hypothesis [2]

$$\langle M^2\rangle_0 = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{M}(\omega)d\omega, \tag{2.48}$$

where since $\mathbf{M}(t)$ is a real *causal* function of time

$$\mathrm{M}(\omega) = \lim_{T'\to\infty} \frac{1}{T'}|\tilde{\mathbf{M}}(\omega)|^2, \tag{2.49}$$

is the *spectral density* of the fluctuations in the dipole moment $\mathbf{M}(t)$. Note that $\mathrm{M}(\omega)$ is an even function of ω. From Eqs. (2.42) and (2.48) we get

$$\alpha_s = \frac{2}{\pi}\int_0^\infty \frac{\alpha''(\omega)d\omega}{\omega} = \frac{1}{3\pi kT}\int_0^\infty \mathrm{M}(\omega)d\omega, \tag{2.50}$$

whence

$$6kT\alpha''(\omega) = \omega\mathrm{M}(\omega). \tag{2.51}$$

Effectively, the dissipative part of the frequency-dependent complex polarisability and the spectral density of the spontaneous fluctuations in the dipole moment of the body at equilibrium have been related to one another. The autocorrelation function (ACF) of the dipole moment is the time average of $\mathbf{M}(t')$ with $\mathbf{M}(t'+t)$ given by

$$C_m(t) = \lim_{T'\to\infty}\frac{1}{T'}\int_{-\frac{T'}{2}}^{\frac{T'}{2}} \mathbf{M}(t')\cdot\mathbf{M}(t'+t)dt'. \tag{2.52}$$

However, we have also the Wiener-Khinchin theorem [2] which states that the ACF and the spectral density are each other's Fourier cosine transforms, therefore with Eq. (2.51) we get

$$C_m(t) = \frac{1}{\pi}\int_0^\infty \mathrm{M}(\omega)\cos(\omega t)d\omega = \frac{6kT}{\pi}\int_0^\infty \frac{\alpha''(\omega)}{\omega}\cos(\omega t)d\omega, \tag{2.53}$$

so that on inversion

$$\alpha''(\omega) = \frac{\omega}{3kT}\int_0^\infty C_m(t)\cos(\omega t)dt. \tag{2.54}$$

From Eqs. (2.39) and (2.54), we thus have since $b(t) = C_m(t)/(3kT)$

$$\alpha(\omega) = \frac{1}{3kT}\left[\langle\mathbf{M}\cdot\mathbf{M}\rangle_0 - i\omega\int_0^\infty \langle\mathbf{M}(t')\cdot\mathbf{M}(t'+t)\rangle_0 e^{-i\omega t}dt\right], \tag{2.55}$$

where the subscript zero denotes that the average is to be evaluated in the absence of the driving field (at the equilibrium or stationary state). This is the Kubo relation [35] and the generalisation of the Fröhlich relation [30] to the dynamical behaviour of the dielectric.

We find that there are many situations where $\langle \mathbf{M}(0) \rangle_0$ will not vanish, where for example if the dielectric is in equilibrium under the action of a steady d.c. field and that field is then altered by a *small* perturbation to maintain linearity of the response. Here the normalised ACF $C_m(t)$ and static polarisability α_s are defined as

$$C_m(t) = \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle_0 - \langle \mathbf{M}(0) \rangle_0^2}{\langle \mathbf{M}^2(0) \rangle_0 - \langle \mathbf{M}(0) \rangle_0^2}, \tag{2.56}$$

and

$$\alpha_s = \frac{\langle \mathbf{M}^2(0) \rangle_0 - \langle \mathbf{M}(0) \rangle_0^2}{3kT}. \tag{2.57}$$

So now Eq. (2.55) can be rewritten as

$$\frac{\alpha(\omega)}{\alpha_s} = 1 - i\omega \int_0^\infty C_m(t) e^{i\omega t} dt. \tag{2.58}$$

The basic results of linear response theory have been illustrated here via its application to dielectric relaxation of a system of electric dipoles. However, linear response theory can also apply to many other phenomena, where knowledge of the linear response of a system to a weak external force is required [35, 45, 46]. In particular all of the above results can be modified to magnetic relaxation of a system of magnetic dipoles, where the main quantities of interest are the magnetisation, its characteristic relaxation times, and complex magnetic susceptibility.

2.3 History of Research in the Dielectric Response

In the context of this thesis, it is expedient to briefly highlight the historical research and results in the theory of the static and dynamic dielectric response of polar molecules over the past decades, starting with the work of Debye [1, 3], then Kirkwood [47], Fröhlich [30], and Budó [15, 16] (Note that in the Appendix of Chapter 2 of the thesis, we have provided an English translation of the paper, "Anomale Dispersion und freie Drehbarkeit," Physik. Zeits., vol. 39, p. 706, 1938 by A. Budó [15]). Upon doing so we can then discuss the more recent advances which have been made in the analysis of anomalous relaxation. An overview of the classical theory of the dielectric response of an assembly of polar molecules is provided by Coffey [48].

2.3.1 The Debye Theory of the Static Permittivity

Following Langevin's treatment of paramagnetism in 1905, Debye was the first investigator to give a relation between the static susceptibility χ_s of a polar substance and the permanent dipole moment $\boldsymbol{\mu}$ of a molecule of the substance.

We select from a macroscopic specimen of dielectric of relative permittivity ε_s e.g. the dielectric material between the plates of a capacitor as seen in Figure 2.2, a spherical region which is large enough to have the same physical properties as the macroscopic specimen.

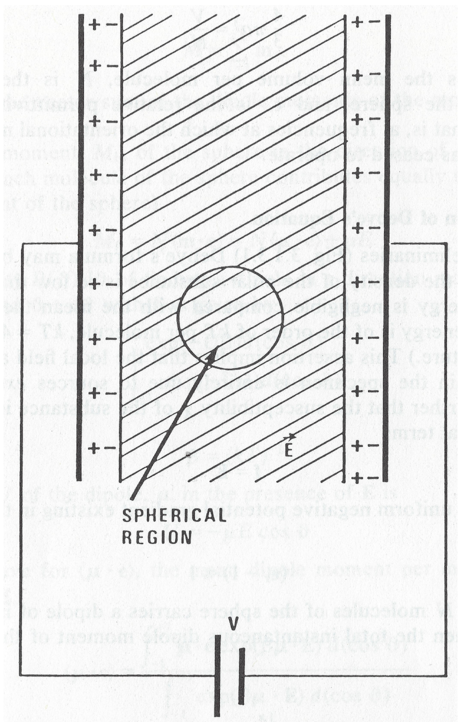

Figure 2.2: Spherical region in a dielectric sample. (aft. [49])

A constant negative potential gradient is then produced within the macroscopic specimen via a battery which will influence a dipolar molecule inside the spherical region in two ways. First it will perturb the rotational motion of the molecule and cause it to have a preferred orientation in the direction of the imposed potential gradient. Secondly it will enlarge the dipole moment of the molecule via elastic displacement of the constituent charges. The induced dipole moment is denoted by $\alpha\mathbf{f}$, where α is the polarisability of the molecule and $\mathbf{f}$ is the field which acts on the molecule due to all sources except the molecule itself. Furthermore, the total dipole moment of a molecule of the substance may be written as follows:

$$\mathbf{m} = \boldsymbol{\mu} + \alpha\mathbf{f}, \tag{2.59}$$

where $\boldsymbol{\mu}$ is the permanent moment of a molecule when isolated. Suppose now that the molecules are isotropic, then α can be obtained via the relation [50]

$$\begin{aligned} \alpha &= \frac{3V}{4\pi N}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right), \\ \frac{4}{3}\pi a^3 &= \frac{V}{N}, \end{aligned} \tag{2.60}$$

where $(4/3)\pi a^3$ is the mean volume per molecule, N is the number of molecules in the sphere, V is the potential, and ε_∞ is the relative permittivity at optical frequencies, which means frequencies where the orientational mechanism of polarisation has ceased to operate. Using the preliminaries presented in Figure 2.3, Debye's formula can be derived by assuming that the density of the polar substance is so low that the dipolar interaction energy can be considered negligible in comparison to the mean thermal energy which is of the order of the thermal energy kT per molecule, where kT is equal to $4.2 \times 10^{-21} J$ at room temperature.

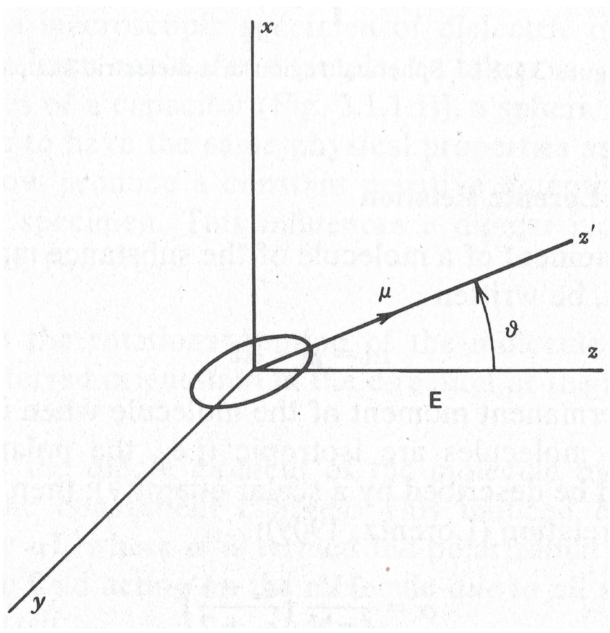

Figure 2.3: Notation for molecule with permanent moment $\boldsymbol{\mu}$ in presence of $\mathbf{E}$. (aft. [49])

The assertion above implies that the local field acting on any molecule within the specimen is entirely due to sources external to the sphere. It also implies that the susceptibility χ of the substance is small. Therefore, in mathematical terms

$$\mathbf{f} = \mathbf{E}, \tag{2.61}$$

where $\mathbf{E}$ is the uniform negative potential gradient existing in the specimen and $\varepsilon_s - 1 \ll 1$. If each of the N molecules of the sphere carries a dipole of instantaneous moment $\mathbf{m}_i$, then the total instantaneous dipole moment of the sphere, $\mathbf{M}$, is

$$\mathbf{M} = \sum_{i=1}^{N} \mathbf{m}_i, \tag{2.62}$$

which implies that $\mathbf{m}_i$ is the vector sum of the dipole moments of the molecules of the sphere. The derivation is explained in more detail in Section 3.1.3 of the book "Molecular Dynamics and the Theory of Broadband Spectroscopy" [49] where the total susceptibility χ_s of a polar substance is given by Eq. (3.1.3.14) as

$$\chi_s = N\left(\frac{\mu^2}{3kT} + \alpha\right), \tag{2.63}$$

where $n = N/V$ is the molecular number density.

2.3.2 The Debye Theory of Dielectric Relaxation

In 1913, Debye [3] in order to treat time dependent fields (as alluded to in the introduction) applied the Smoluchowski equation to the dielectric relaxation of an assembly of polar molecules, which were each conceived of as a rigid body rotating about a fixed axis, with the only interaction being due to the external applied field with the individual dipoles imagined to be rigid Brownian rotators. Later he extended the theory to rotation in space where the appropriate Smoluchowski equation is

$$\frac{\partial W}{\partial t} = D_R \Delta W + \frac{1}{\zeta}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta W\frac{\partial V}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial}{\partial\varphi}\left(W\frac{\partial V}{\partial\varphi}\right)\right], \tag{2.64}$$

where $D_R = kT/\zeta$ is the rotational diffusion coefficient, $\zeta = 8\pi\eta a^3$ is the viscous drag coefficient on a spherical rotator, η is the viscosity and a is the radius of the spherical Brownian particle. A spatially uniform field $\mathbf{E}_m e^{i\omega t}$ is applied along the polar axis so that the potential V is

$$V(\vartheta, t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t) = -\mu E_m e^{i\omega t} \cos\vartheta. \tag{2.65}$$

Eq. (2.64) represents the random walk of the tip of the dipole vector $\boldsymbol{\mu}$ on a sphere of constant radius $|\boldsymbol{\mu}|$ in the diffusion limit where a dipole undergoes a small angular displacement Δ in an infinitesimal time τ (Einstein's hypothesis). Solving Eq. (2.64) in the linear approximation in the field parameter ($\xi = \mu E_m/kT \ll 1$) yields the mean dipole moment of a sphere which contains N molecules

$$N\langle \boldsymbol{\mu} \cdot \mathbf{e} \rangle = N\mu\langle \cos\vartheta \rangle = \frac{N\mu^2}{3kT} \frac{E_m e^{i\omega t}}{1 + i\omega\tau_D}, \;\; \xi \ll 1. \tag{2.66}$$

Thus the mean dipole moment lags behind the applied field by an angle $\tan^{-1}\omega\tau_D$ and is reduced in amplitude by the frequency dependent factor $1/\sqrt{1+\omega^2\tau_D^2}$. The quadrature part of Eq. (2.66) exhibits a pronounced maximum at $\omega = 1/\tau_D$ where $\tau_D = \zeta/2kT$ is called the Debye relaxation time and the drag coefficient ζ is calculated from Stokes' law for the viscous drag torque on a rotating body in a liquid with the assumption that it can be applied to molecules so that

$$\zeta = 8\pi\eta a^3, \tag{2.67}$$

where η is the viscosity and a is the radius of the spherical Brownian particle.

The Debye theory was later extended to the non-linear response to an applied a.c. field by Coffey and Paranjape [51] and the non-linear behaviour was experimentally verified by Jadzyn et al. [52]. So effectively, the Debye theory applies [30] when we have the following conditions:

1. A dilute solution of dipolar molecules in a non-polar liquid.
2. Axially symmetric molecules - Perrin later generalised to ellipsoidal molecules [53, 54].

3. Isotropy of the liquid, even on an atomic scale in the time average over an interval, is small compared with the Debye relaxation time τ_D.

2.3.3 Onsager's Theory of the Relative Permittivity of Dipolar Fluids

The static Debye formula (seen in Eq. (2.63)) due to the assumptions made in its derivation, holds only for polar gases at low densities thus it cannot be applied to liquids with any accuracy. Onsager was the first to successfully calculate the static permittivity of a polar liquid. One of the consequences of the assumption that the interaction energy of the molecules could be neglected in comparison to the mean thermal energy was that the local field acting on the molecule was equal to the negative potential gradient (field) imposed on the dielectric. This assumption was modified by Onsager to account for the effect of the surroundings of a molecule on the local field at a molecule. The model used by Onsager can effectively take into account the long-range dipolar interaction, which is a component of the molecular interaction. To calculate the static relative permittivity of the liquid in question, Onsager made use of a model which was originally proposed by Bell [55] for a spherical dipolar molecule. The model consists of a point dipole situated at the centre of an empty spherical cavity in a continuous dielectric with permittivity equal to the bulk permittivity ε_s of the dielectric. The model is shown in Figure 2.4.

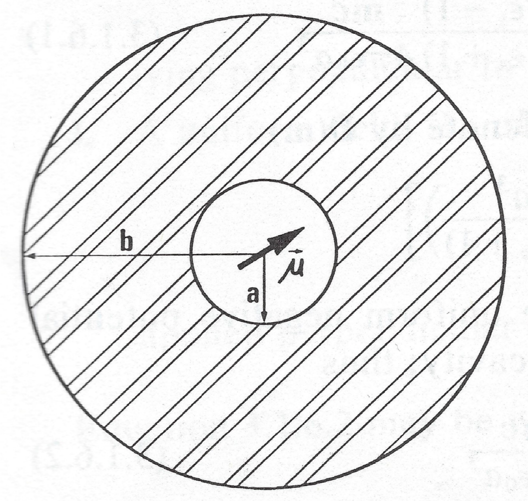

Figure 2.4: Onsager's model. (aft. [49])

The radius of the cavity is defined by the relation

$$\frac{4}{3}\pi n a^3 = 1, \tag{2.68}$$

where n is the molecular number density. Therefore, the volume of the cavity is defined as the the volume available to each molecule. However the field of the dipole in the cavity polarises its surroundings. This polarisation of the surroundings leads $\boldsymbol{\mu}$ to induce a homogenous field in the cavity which is referred to as the reaction field $\mathbf{R}$. Since the cavity is spherical, $\mathbf{R}$ has the same direction as $\boldsymbol{\mu}$. If the dipole is polarisable and possesses a polarisability α, then the reaction field polarises the dipole and therefore alters the dipole moment. Onsager's assumptions for the theory are succinctly stated by Fröhlich [56] as follows:

1. A molecule occupies a sphere of radius a, its polarisability is isotropic and no saturation effects can take place.
2. The short-range molecular interaction energy is negligible in comparison to kT.

The second assumption means that the surroundings of the molecule are treated as a continuous dielectric of relative permittivity ε_s, equal to the bulk relative permittivity of the liquid because only long range forces are considered. In order to describe Onsager's formula, it will be convenient to imagine the dipole with its cavity of radius a to be placed at the centre of a very large dielectric sphere of outer radius b and relative permittivity ε_s (see Figure 2.5).

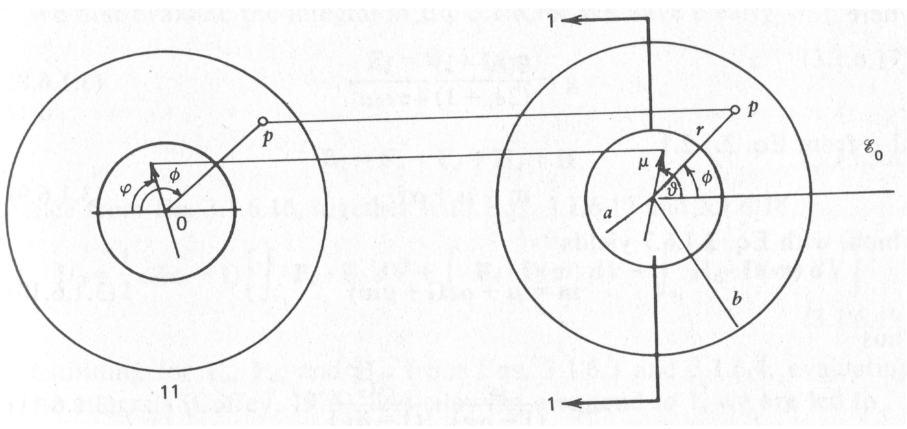

Figure 2.5: Dipole in a spherical cavity. (aft. [49])

The field within the cavity of this sphere upon being subjected to both a uniform external field $\mathbf{E}_0$, which is parallel to the Z-axis, and to the field of a *polarisable* point dipole $\mathbf{m}$, which is situated at the centre of the cavity and making an angle ϑ with the Z-axis consists of a uniform field given by [18, 57]

$$\mathbf{f} = \mathbf{G} + \mathbf{R} = \frac{9\varepsilon_s \mathbf{E}_0 c}{(2\varepsilon_s + 1)(\varepsilon_s + 2)} + \frac{2(\varepsilon_s - 1)}{(2\varepsilon_s + 1)} \frac{\mathbf{m}c}{4\pi\varepsilon_0 a^3}, \tag{2.69}$$

where $\mathbf{G}$ is referred to as the cavity field because if a macroscopic uniform negative potential gradient $\mathbf{E}_0$ is imposed on the dielectric through external sources, then a calculation in electrostatics shows that the field $\mathbf{G}$ in an empty cavity in the dielectric will not be equal to $\mathbf{E}_0$. $\mathbf{R}$ is the reaction field due to $\mathbf{m}$ [49]. Note that

$$c^{-1} = 1 - \frac{2(\varepsilon_s - 1)^2 a^3}{b^3(\varepsilon_s + 2)(2\varepsilon_s + 1)}. \tag{2.70}$$

The details of the derivation are again presented in the book [49] in Section 3.1.6 where Onsager's equation reads as

$$(\varepsilon_s - \varepsilon_\infty) = \left(\frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty}\right)\left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \frac{N}{V\varepsilon_0}\frac{\mu^2}{3kT}. \tag{2.71}$$

2.3.4 Fröhlich's Theory

Kirkwood obtained a general formula for the relative permittivity of a polar liquid by treating the interactions between the molecules of a large sphere of dielectric by the methods of classical statistical mechanics. In this thesis, the results of Kirkwood will be presented in the manner of Fröhlich, who gave general expressions for the relative permittivity of any substance that is not permanently polarised. Fröhlich's general expression for the relative permittivity of a polar substance may be derived through again taking a very large sphere, and selecting from it a smaller sphere of radius a. This small (but still macroscopic) sphere is such that it's just large enough to have the same properties as the large sphere, while at the same time must be far removed from the boundaries of the large sphere. Therefore if b is the radius of the large sphere, then the ratio $(a/b)^3 \ll 1$. The inner sphere is treated on a discrete basis, whereas the surrounding shell is treated as a continuous dielectric medium. It is assumed that this system consisting of the inner sphere and its surrounding shell obeys the laws of classical statistical mechanics.

We suppose that the inner sphere contains charges and denote the i^{th} charge by e_i. In any given energy state of the system, other than the ground state, all the charges of the system are displaced from the positions they occupied in the ground state. The displacements of the charges in the inner sphere are collectively denoted by $\mathbf{X}$, which is the set

$$\{\mathbf{r}_1, ..., \mathbf{r}_i, ..., \mathbf{r}_N\} = \{\mathbf{r}_i\}_{i=1}^{N}\,, \tag{2.72}$$

and $\mathbf{r}_i$ is the displacement of the i^{th} charge. If it is assumed that the dipole moment of the substance vanishes in the lowest energy state, then the dipole moment of the inner sphere when its constituent charges undergo a set of displacements $\mathbf{X}$ is

$$\mathbf{M}(\mathbf{X}) = \sum_{i=1}^{N} e_i \mathbf{r}_i. \tag{2.73}$$

An atom or molecule contains several elementary charges. Through following Fröhlich, we term an atom or a molecule a cell and label such a cell j. If the cell j contains

s elementary charges, they are then denoted by the set

$$\{e_{jk}\}_{k=1}^{s}, \tag{2.74}$$

then the collective displacements of these charges are denoted by the set

$$\mathbf{m}(\mathbf{x}_j) = \sum_{k=1}^{s} e_{jk}\mathbf{r}_{jk}, \tag{2.75}$$

and the total dipole moment of the inner sphere is

$$\mathbf{M}(\mathbf{X}) = \sum_{j} \mathbf{m}(\mathbf{x}_j) = \sum_{k=1}^{s} e_{jk}\mathbf{r}_{jk}. \tag{2.76}$$

The rest of the derivation is explained in Section 3.2 of [49], where the final result is presented in Eq. (3.2.15) as

$$(\varepsilon_s - 1) = \left(\frac{3\varepsilon_s}{2\varepsilon_s + 1}\right)\left(\frac{1}{v\varepsilon_0}\right)\frac{\langle M^2\rangle_0}{3kT}. \tag{2.77}$$

This equation is a perfectly general result as it expresses the permittivity of the specimen in terms of the mean square fluctuations $\langle \mathbf{M}^2\rangle_0$ in the instantaneous dipole moment $\mathbf{M}(\mathbf{X})$ of a spherical (macroscopic) specimen of the dielectric embedded in a large volume of the same dielectric. These fluctuations in the instantaneous dipole moment are the total fluctuations in the dipole moment from all causes, because in a dielectric several mechanisms of polarisation may be operative. Refer to Section 3.2 of [49] for more details.

2.3.5 The Kirkwood-Fröhlich Equation

This equation provides a general expression for the relative permittivity of liquids which consist of polar molecules which possess a permanent dipole $\boldsymbol{\mu}$ and a polarisability α which is given by the Lorenz-Lorentz relation, which means that the effect of α is accounted for by considering the liquid as a continuous dielectric of relative permittivity ε_∞ in which are embedded dipoles with permanent dipole moments $\boldsymbol{\mu}$. In order to derive this equation, following the methodology of [49], we consider a cell j, (this is discussed in more detail in Section 3.2.3 of the book [49]) such that it contains just one dipolar molecule, leading to the moment $\mathbf{m}$ of the cell being $\boldsymbol{\mu}$. Hence, the orientations of the dipoles are then the only variables. We define

$$\mathbf{m}^* = \boldsymbol{\mu}^* \quad \text{(notation used in [49])}, \tag{2.78}$$

where $\boldsymbol{\mu}^*$ is the average moment of the sphere when the dipole $\boldsymbol{\mu}$ is held in a fixed orientation. If

$$\langle \mathbf{m} \cdot \mathbf{m}^* \rangle_0 = \langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}^* \rangle_0, \tag{2.79}$$

then in a liquid without an applied field all dipolar interactions are equivalent and

$$\langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}^* \rangle_0 = \boldsymbol{\mu} \cdot \boldsymbol{\mu}^*, \tag{2.80}$$

so that with Eq. (3.2.3.15) in [49] we have

$$\varepsilon_s - \varepsilon_\infty = \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty} \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 \left(\frac{N}{v\varepsilon_0} \right) \frac{\boldsymbol{\mu}_v^2}{3kT} \left(1 + z \langle \cos \gamma \rangle \right), \tag{2.81}$$

where z is the average number of *nearest neighbours* and $\langle \cos \gamma \rangle$ is the average of the cosine of the angle between neighbouring dipoles. More often the equation is written as follows

$$\varepsilon_s - \varepsilon_\infty = \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty} \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 \frac{N}{v\varepsilon_0} g \boldsymbol{\mu}_v^2, \tag{2.82}$$

where g is the Kirkwood correction factor written as:

$$g = 1 + z \langle \cos \gamma \rangle . \tag{2.83}$$

2.3.6 Generalisation of Fröhlich's Equations to the Frequency-Dependent Case

The concept of the autocorrelation function (A.C.F), which as we saw earlier is the time average $\mathbf{M}(t)$ with $\mathbf{M}(t+t')$ or $\mathbf{M}(t-t')$, that is

$$C_m(t) = \overline{\mathbf{M}(t') \cdot \mathbf{M}(t+t')} = \overline{\mathbf{M}(t-t') \cdot \mathbf{M}(t')}. \tag{2.84}$$

Through the use of the Wiener-Khinchin theorem (details in [49]) we have Fröhlich's relation for the frequency dependent case viz.,

$$\begin{aligned} \alpha(\omega) =& \frac{1}{3kT}\left(\overline{\mathbf{M}\cdot\mathbf{M}} - i\omega\int_0^\infty \overline{\mathbf{M}(t')\cdot\mathbf{M}(t+t')}e^{i\omega t}dt\right) \\ =& \frac{1}{3kT}\left[\langle\mathbf{M}\cdot\mathbf{M}\rangle_0 - i\omega\int_0^\infty \langle\mathbf{M}(t')\cdot\mathbf{M}(t+t')\rangle_0 e^{i\omega t}dt\right]. \end{aligned} \tag{2.85}$$

This is often called the Kubo relation, and is the generalisation of the Fröhlich relation

$$\alpha_s = \frac{\langle\mathbf{M}^2\rangle_0}{3kT}, \tag{2.86}$$

to cover the dynamical behaviour of the dielectric.

2.4 Budó's Treatment of Dipole-Dipole Coupling

We have discussed the limitations of the simple dynamical theory of Debye in explaining the complex susceptibility of polar fluids at low frequencies (GHz) in the introduction, more specifically the fact that virtually all interactions between the dipolar molecules are ignored. The sole exceptions are the Brownian torques due to the bath and the interaction between a typical dipole of the polar assembly and the applied external field. Here we shall describe how Budó [15, 16], addressed the neglect of interactions by showing how the results of the original Debye theory valid in the non-inertial limit are modified for assemblies of non-interacting molecules containing interacting rotating polar groups. This was published as a full paper in the Journal of Chemical Physics [16].

The Brownian motion model used by Budó is shown in Figure 2.6

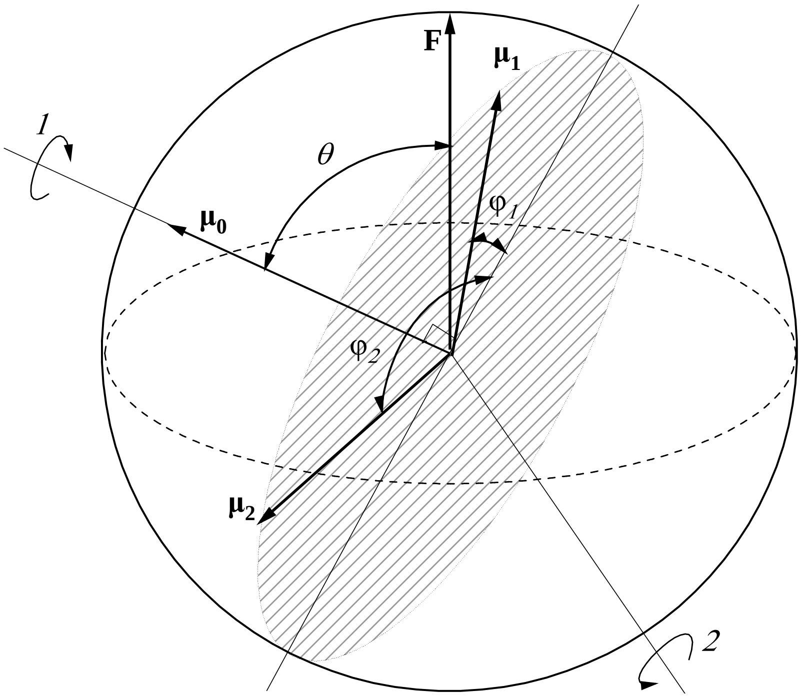

Figure 2.6: Geometry of the problem. Notation for Euler angles is that of Landau-Lifshitz. (aft. [58])

He supposes that the dielectric consists of an assembly of dipoles that do not interact with each other electrically, with only internal dipole-dipole coupling between the members 1 and 2 included. From this can be written the Smoluchowski equation for the variation in configuration space of the probability distribution function $f(\theta, \varphi_1, \varphi_2, t)$ which is associated with the orientation of the molecule under the influence of a time varying electric field. Following Budó, it shall be supposed that the molecule consists of two groups of equal size with common rotational axis, which is marked 1 in Figure 2.6. The coefficient of friction arising from the thermal energy of the surroundings acting on the molecule as a whole he denoted as ζ, which leads to ζ_1 denoting rotations about axis 1, and ζ_2 denoting rotations about axis 2. The components of the dipole moments of the group perpendicular to the molecular axis (axis 1) will be denoted by $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$ respectively and $\boldsymbol{\mu}_0$ denotes the components of the dipole moment in the direction of axis 1. We shall obtain the simplest form of the theory through assuming that $\boldsymbol{\mu}_0 = 0$. In the light of the above assumptions, along with the coordinate system presented in the figure, one can obtain the Smoluchowski equation for the variation in configuration space of the distribution function f for a time t after the sudden removal of unidirectional electric field of magnitude E, which had been steady up to the time $t = 0$. The equation is presented as follows (a detailed derivation is given in the Appendices)

$$\begin{aligned}\frac{\partial f}{\partial t} =& \frac{kT}{\zeta}\left[\frac{\partial^2 f}{\partial \theta^2} + \cot\theta\frac{\partial f}{\partial \theta} + \left(\cot^2\theta + \frac{\zeta}{\zeta_1}\right)\left(\frac{\partial^2 f}{\partial \varphi_1^2} + \frac{\partial^2 f}{\partial \varphi_2^2}\right) + 2\cot^2\theta\frac{\partial^2 f}{\partial \varphi_1 \partial \varphi_2}\right] \\ &+ \frac{\partial}{\partial \varphi_1}\left(\frac{f\sin\theta}{\zeta_1}\frac{\partial V}{\partial \varphi_1}\right) + \frac{\partial}{\partial \varphi_2}\left(\frac{f\sin\theta}{\zeta_1}\frac{\partial V}{\partial \varphi_2}\right). \end{aligned} \tag{2.87}$$

Here, $f \sin\theta d\theta d\psi d\varphi_1 d\varphi_2 = f\, d\Omega$ refers to the number of molecules of dipole moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ in the domain Ω, $\Omega + d\Omega$ at time t, θ and ψ are the polar angles which specify the direction of the molecular axis relative to that of $\mathbf{E}$, and φ_1 and φ_2 are the azimuthal angles of $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ measured from the plane which contains the axes 1 and 2. Note that f has no dependence on the angle ψ due to the rotational symmetry about axis 1. $V(\varphi_1 - \varphi_2) = V$ is the mutual potential energy of the dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ due to dipole-dipole coupling. It should be noted at this point that the Eq. (2.87) in the way it is written has the assumption that the only portion of the dipole-dipole interaction taken into account is that between the groups 1 and 2, meaning that we only take into account the coupling between pairs of dipoles. If this were not done, then one would be forced into considering an intractable many-body problem.

The principal result of his investigation is that including dipole-dipole interaction between two groups in a given molecule gives rise to a discrete set of Debye-type dipole relaxation mechanisms. In the book "Molecular Diffusion and Spectra" by Coffey, Evans and Grigolini in Section 3.2 [8], it is shown how this equation can be solved for the relaxation mechanisms of the dipoles and how the problem of calculating the relaxation times and so on may always be reduced to the solution of a Sturm-Liouville problem. The summary of the main features of Budó's treatment is as follows [8]:

1. The analysis only takes into account the coupling between pairs of dipoles in a rotating group. Note that the groups are not supposed to interact with one another.
2. The potential depends only on the relative longitudes of the dipoles.
3. It seems that the effect of dipole–dipole coupling always leads to a denumer-

able set of relaxation times and a corresponding denumerable set of relaxation mechanisms.

4. Both dipolar autocorrelation and dipolar cross-correlation functions contribute to the polarisation.
5. In the situation where the dipole-dipole coupling is very strong, the coupling torque $B \sin 2\eta$, where B is constant, may be replaced by $2B\eta$ to give closed-form expressions for the dipolar auto-correlation and cross-correlation functions.
6. Because the theory is based on the Smoluchowski equation, it excludes inertial effects, so that it is invalid at high frequencies.
7. The solution to calculating the relaxation times, etc. can always be reduced to a Sturm-Liouville problem.
8. The harmonic approximation potential yields a much narrower set of relaxation mechanisms than the cosine one.

The principal result that including dipole-dipole interaction between two groups in a given molecule yields a discrete set of Debye-type dipole relaxation mechanisms was further corroborated by that of Zwanzig in 1963 [17, 18] who studied, in the non-inertial limit, the complex susceptibility of an assembly of permanent dipoles coupled by dipole-dipole interactions and arranged on a simple cubic lattice. More details on the Smoluchowski equation will be provided in Chapter 4 of the thesis.

2.5 Anomalous Diffusion and Anomalous Dielectric Relaxation

It is opportune to briefly discuss the phenomenon of diffusion, which is generally described as the net movement of (e.g. atoms, ions, molecules) from a region of higher concentration to a region of lower concentration. Thus, it is driven by a gradient in concentration which falls into one of two categories, normal and anomalous diffusion. Normal diffusion processes are often described as resulting from microscopic random walks with independent and identically distributed steps, where the distribution of step sizes has finite variance and where a characteristic time between steps can be defined. Here, the central limit theorem [2] implies that the resulting distribution of the particle positions, provided via the accumulated sum of steps, converges to a Gaussian distribution. Hence, the mean squared displacement of the particles which move in a one dimensional extension x scales linearly with time according to [35].

$$\left\langle \left(x\left(t\right)-x\left(0\right)\right)^{2}\right\rangle =2Dt, \tag{2.88}$$

where $x(t)$ is the position of a particle at time t, D is the diffusion coefficient and $\langle\rangle$ is the ensemble average operation. Anomalous diffusion is likely to occur if one of the conditions for the validity of the central limit theorem is violated, due to either the occurrence of step distributions with infinite variance [59,60] or to the occurrence of steps that are not statistically independent [61,62] as happens in disordered media. The deviation from normal diffusion may be characterised by either a vanishing (sub-diffusion) or a diverging (super-diffusion) coefficient [63]

$$D=\lim_{t\to\infty}\frac{1}{2t}\left\langle x^{2}\right\rangle , \tag{2.89}$$

where $\langle x^2\rangle \propto 2Dt^{\alpha}$ (asymptotically). With this formal statement, we can only define anomalous regimes asymptotically, which leads to limited practical applications. An alternative is to characterise an unknown diffusive process through expressing its variance as a non-linear function of time, with a constant diffusion coefficient for a fractional (or non-linear) diffusion equation, such that

$$\left\langle x^{2}\right\rangle =2Dt^{\alpha}. \tag{2.90}$$

With this generalisation, we can cover both sub-diffusion ($\alpha < 1$) and super-diffusion ($\alpha > 1$) (see Figure 2.7).

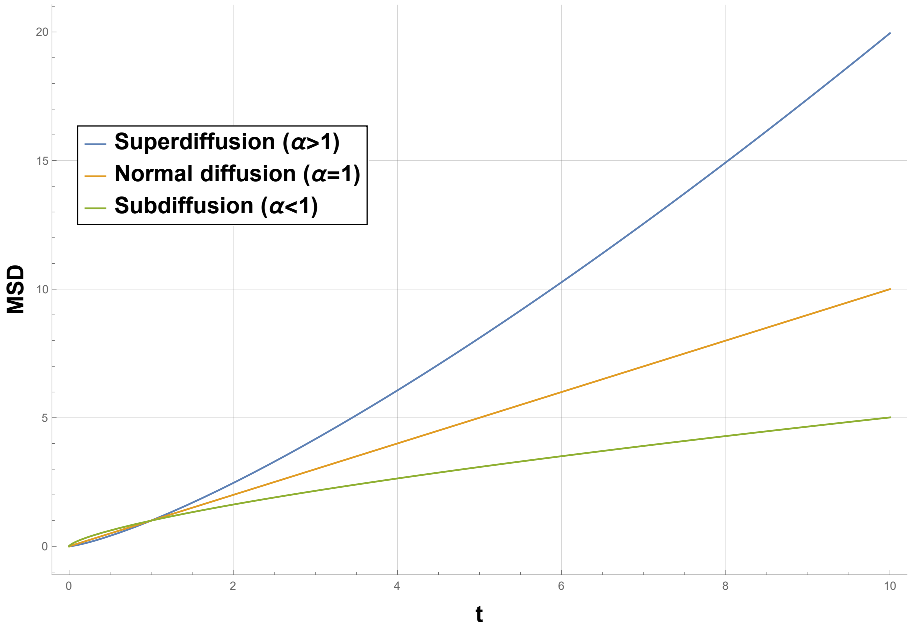

Figure 2.7: Mean squared displacement for different types of anomalous diffusion.

This expression has been applied to studies of both sub-diffusive [64–68] and super-diffusive behaviours [69–72].

Anomalous diffusion allows one to model diverse physical phenomena in dense systems or porous media. The mechanisms that underlie anomalous diffusion have been explored extensively in the literature, including but not limited to, continuous-time random walks [73–75], fractional Brownian motion [76, 77], diffusion in disordered media [2, 78] etc.

It has been shown earlier how the Debye equation can successfully describe the low frequency behaviour of the complex susceptibility, but we end up with the situation where there are a number of amorphous materials which show significant departure from Debye-like behaviour (in other words, we end up with anomalous relaxation). As such there have been a number of empirical formulas which have been used to describe the experimentally observed complex susceptibility. These include the Cole-Cole formula [29]

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{1 + (i\omega\tau_D)^{\alpha}}, \quad 0 < \alpha \leq 1, \tag{2.91}$$

the Cole-Davidson formula [29]

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{(1+i\omega\tau_D)^o}, \quad 0 < o \leq 1, \tag{2.92}$$

and the Havriliak-Negami formula [29]

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{(1+(i\omega\tau_D)^\alpha)^o}. \tag{2.93}$$

These three empirical formulas exhibit anomalous relaxation behaviour, and they may also be regarded as arising from a distribution of relaxation mechanisms if we suppose that the complex susceptibility may be written as

$$\frac{\chi(\omega)}{\chi'(0)} = \int_0^\infty \frac{f(\tau)}{1+i\omega\tau} d\tau. \tag{2.94}$$

This superposition integral [29] embodies the idea that the dielectric behaves as though it were a collection of individual Debye time mechanisms with relaxation time τ and distribution function $f(\tau_D)$. Clearly for the Debye equation [29]

$$f_D(\tau) = \delta(\tau - \tau_D), \tag{2.95}$$

meaning that only *one* relaxation mechanism is involved, while for the Cole-Cole equation

$$f_{CC}(\tau) = \frac{\sin \pi\alpha}{\pi\tau \left[(\frac{\tau}{\tau_D})^\alpha + (\frac{\tau}{\tau_D})^{-\alpha} + 2\cos \pi\alpha \right]}, \tag{2.96}$$

for the Cole-Davidson equation

$$f_{CD}(\tau) = \begin{cases} (\pi\tau)^{-1}(\frac{\tau_D}{\tau - 1})^{-o} \sin \pi o, & \tau < \tau_D, \\ 0, & \tau > \tau_D, \end{cases} \tag{2.97}$$

and for the Havriliak-Negami formula

$$f_{HN}(\tau) = \frac{\left(\frac{\tau}{\tau_D}\right)^{o\alpha} \left| \sin\left(o \arctan\left\{ \left[\left(\frac{\tau}{\tau_D}\right)^\alpha + \cos \pi\alpha \right]^{-1} \sin \pi\alpha \right\} \right) \right|}{\pi\tau \left[\left(\frac{\tau}{\tau_D}\right)^{2\alpha} + 2\left(\frac{\tau}{\tau_D}\right)^\alpha \cos \pi\alpha + 1 \right]^{\frac{o}{2}}}. \tag{2.98}$$

Therefore, the anomalous relaxation behaviour may be characterised by a superposition of an infinite number of Debye-like relaxation mechanisms with the relaxation times given by Eqs. (2.95) - (2.98). It is important to investigate whether it is possible to derive these formulas from a *microscopic* model of the underlying processes such as suitable adaptations of the Einstein theory of the Brownian motion underlying the work of Debye. If indeed it is possible to achieve this, it would constitute significant progress in the theory as one then could include both the effects of the inertia of the molecules and an external potential arising from crystalline anisotropy or indeed any other mechanism. This topic has in part been investigated for the Cole-Cole equation by Coffey, Kalmykov and Titov [2], who have shown that the Cole-Cole equation may be derived from a kinetic equation based on the concept of a continuous time random walk that is, a walk with a long-tailed distribution of waiting times between the elementary jumps. This was later extended to include both inertial effects and an external mean-field potential [2]. An overview of advances that have been made in the study of anomalous relaxation and the use of fractional diffusion equations is given by Coffey [2, 48].

2.6 Fractional Diffusion Equations

In order to generalise the various diffusion equations of Brownian dynamics for explaining anomalous relaxation phenomena, we exploit the fact that the temporal occurrence of the motion events performed by the random walker is so broadly distributed that no characteristic waiting time exists [79]. The resulting equations are called *fractional* diffusion equations since they generally involve *fractional derivatives* of the PDF with respect to time. As an example, in fractional diffusion, the diffusion equation for the Brownian motion of a free particle, (see Eq. (1.4.6) in [2]) becomes

$$\frac{\partial f}{\partial t} = \left(\frac{kT}{\zeta}\right)^{\alpha} \frac{\partial^2}{\partial x^2} D_t^{1-\alpha} f, \tag{2.99}$$

where α is the anomalous exponent, the fractional operator ${}_0D_t^{1-\alpha} \equiv \frac{\partial}{\partial t}\, {}_0D_t^{-\alpha}$ in Eq. (5.8) is defined via the convolution (the Riemann-Liouville definition) [79–82]

$$ {}_0D_t^{-\alpha} f(\,\mathbf{\Omega}, t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{f(\mathbf{\Omega}\,, t')dt'}{(t-t')^{1-\alpha}}, \tag{2.100} $$

$\Gamma(\alpha)$ denoting the gamma function [83]. In Eq. (2.99), if $0 < \alpha < 1$ we have *sub-diffusion*, if $\alpha = 1$ *normal diffusion* and if $1 < \alpha < 2$ *super diffusion* ($\alpha = 2$ defines the ballistic limit).

Appendices

2.A Translation of "Anomalous Dispersion and Free Rotation", Physik. Zeits., *39*, 706 (1938) by A. Budó (Budapest)

In dispersion phenomena in polar molecules subjected to high frequency alternating electric fields, the mean dipole moment can be found from the equation

$$\overline{m} = \frac{\mu^2}{3kT}\frac{F_0 e^{i\omega t}}{1+i\omega\tau}. \tag{1}$$

Here μ is the magnitude of the dipole moment, F_0 is the amplitude of the electric field of angular frequency ω and τ is the relaxation time of a molecule. This result only holds for a rigid dipole and therefore cannot be applied to molecules containing rotating groups with their own embedded dipole moments.

However, one can following Zahn [1], divide molecules containing rotating groups into two general classes: molecules where the axis of rotation does not change with time and molecules where the rotating axis's *location* changes with time. Here we wish to deal with the first class based on elementary model considerations, namely the case in which the axes of rotation of groups are directed *parallel* to one another. We are only concerned with free rotation; therefore, we can disregard any interactions between individual moments. Already electrostatic interactions between dipoles in equilibrium under the influence of a constant field as treated by Meyer [2] have led to far reaching results.

In order to calculate the mean moment in a changing field, we must determine the distribution function. Now in the equilibrium case the rotating groups will have the Maxwell-Boltzmann distribution so that the mean moments are easily determined in equilibrium. We think of both the fixed and the moving moment of the molecule as being divided into two components: the component of the fixed or moving moment in the direction of the axis of rotation is $\mu_{a'}$ or $\mu_{a''}$ and it is $\mu_{a'} + \mu_{a''} = \mu_a$, the components in the plane perpendicular to the axis of rotation are μ_b or μ_c. If we draw rays parallel to μ_a, μ_b, μ_c for each molecule from the centre of the unit sphere, then we can characterise the directions of these moments by the usual polar coordinates ϑ, ψ, which determine the direction of μ_a relative to the field strength, and by the angles of rotation φ and χ, which indicate the position of μ_b and μ_c, respectively, in the plane perpendicular to μ_a; φ and χ are measured from the plane ψ (Fig. 1.).

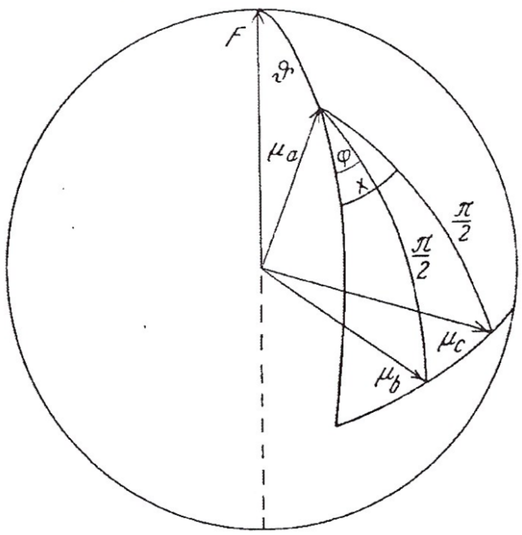

Fig. 1.

We can now determine the distribution function in the familiar manner of Debye [3]. In other words, we consider how the moments change their orientations in an infinitesimal time δt on the unit sphere. The number of molecules of moment μ_a which had at time t orientations lying between (ϑ, ψ) and $(\vartheta + d\vartheta, \psi + d\psi)$, μ_b between φ and $\varphi + d\varphi$, μ_c between χ and $\chi + d\chi$ is $f dV = f \sin\vartheta d\vartheta d\psi d\varphi d\chi$; and this number changes with time both due to the Brownian rotational movement of the molecules and also due to the imposed field. The first type of change (i.e. Brownian) in the time interval δt is

$$-f dV + \int f' dV' w dV,$$

where integration with respect to (the configuration space) volume element dV' yields $w dV$ the (element) of probability whereby a given moment system lying in the element dV' may be found at time $t+\delta t$ in dV. When $f' = f(\vartheta', \psi', \varphi', \chi', t)$ then via (Taylor) series expansion of the integrand in the above expression (Einstein's method) in powers of the increments

$$\vartheta' - \vartheta = \Delta_\vartheta, \quad \varphi' - \varphi = \Delta_\varphi, \quad \chi' - \chi = \Delta_\chi,$$

and truncation at the quadratic terms in the increments (note that f for reasons of rotational symmetry about the polar axis is independent of ψ and that w is a p.d.f. so that $\int w dV' = 1$), yields for the number of molecules at time δt in the volume element dV

$$\begin{aligned}\Delta N_1 =& dV \left[\overline{\Delta_\vartheta} \frac{\partial f}{\partial \vartheta} + \overline{\Delta_\varphi} \frac{\partial f}{\partial \varphi} + \overline{\Delta_\chi} \frac{\partial f}{\partial \chi} + \frac{1}{2} \overline{\Delta_\vartheta^2} \frac{\partial^2 f}{\partial \vartheta^2} + \frac{1}{2} \overline{\Delta_\varphi^2} \frac{\partial^2 f}{\partial \varphi^2} + \frac{1}{2} \overline{\Delta_\chi^2} \frac{\partial^2 f}{\partial \chi^2} \right. \\ & \left. + \overline{\Delta_\vartheta \Delta_\varphi} \frac{\partial^2 f}{\partial \vartheta \partial \varphi} + \overline{\Delta_\vartheta \Delta_\chi} \frac{\partial^2 f}{\partial \vartheta \partial \chi} + \overline{\Delta_\varphi \Delta_\chi} \frac{\partial^2 f}{\partial \varphi \partial \chi} \right]. \end{aligned} \tag{2}$$

The mean values $\overline{\Delta_\vartheta}, \overline{\Delta_\vartheta^2}, \overline{\Delta_\vartheta \Delta_\varphi}$ are defined via the (usual Einstein) formulas

$$\overline{\Delta_\vartheta} = \int \Delta_\vartheta w dV', \quad \overline{\Delta_\vartheta^2} = \int \Delta_\vartheta^2 w dV', \quad \overline{\Delta_\vartheta \Delta_\varphi} = \int \Delta_\vartheta \Delta_\varphi w dV'.$$

Next to determine the change in the number of molecules in the element dV in a time interval δt due to the imposed field F we decompose that field into the sum of 3 vectors F_a, F_b, F_c so that at each point in time

$$F_a = F \cos\vartheta, \quad F_b = -F \sin\vartheta \frac{\sin\chi}{\sin(\chi - \varphi)}, \quad F_c = F \sin\vartheta \frac{\sin\varphi}{\sin(\chi - \varphi)}. \tag{3}$$

then the effective torques acting on the molecule are

$$M_{ab} = \mu_a F_b - \mu_b F_a, \quad M_{ac} = \mu_a F_c - \mu_c F_a. \tag{4}$$

Now in the particular class of molecules treated the angle between μ_a and μ_b like that between μ_a and μ_c is unchanging (equals $\pi/2$) and since the torques have no components in the direction of the axis of rotation of the group, we can consider the rotation that these torques cause as the rotation of the whole molecule if we make the usual assumption that the angular velocity of the strain is proportional to the moments (in our case the resultant of M_{ab} and M_{ac}, denoted by M), the molecule will rotate during the time δt and the angle

$$\delta\alpha = \frac{M}{\rho} \delta t, \tag{5}$$

which is a single axis whose orientation lies along the direction of M. The drag coefficient (denoted by ρ) is strictly speaking strongly dependent on the (precise) location of the groups inside the molecule; however, we take the drag coefficient ρ as constant and following Stokes law as applied to the direction of rotation of the groups. As far as the angle $\delta\alpha$ is concerned we can with our chosen coordinates $(\vartheta, \psi, \varphi, \chi)$ resolve our M into three (contravariant) components: M_ψ is the component in the direction of the polar axis, M_ϑ is the component in the plane perpendicular to the polar axis and μ_a in the same plane and M_φ in the direction of the axis of rotation of the group, i.e. in the direction of μ_a, one then has for the components of the angles $\delta\alpha$

$$\delta\vartheta = \frac{M_\vartheta}{\rho}\delta t, \quad \delta\psi = \frac{M_\psi}{\rho}\delta t, \quad \delta\varphi = \delta\chi = \frac{M_\varphi}{\rho}\delta t. \tag{6}$$

We then find for the torque components following the usual rules of vectors, the result

$$\begin{aligned} M_\vartheta =& M_{ab}\cos\varphi + M_{ac}\cos\chi, \\ M_\psi =& \left(M_{ab}\sin\varphi + M_{ac}\sin\chi\right)\frac{1}{\sin\vartheta}, \\ M_\varphi =& -\left(M_{ab}\sin\varphi + M_{ac}\sin\chi\right)\cot\vartheta. \end{aligned} \tag{7}$$

It is still necessary to account for the remaining torques viz.,

$$\mu_b F_c \sin\left(\chi - \varphi\right), \quad \text{and} \quad -\mu_c F_b \sin\left(\chi - \varphi\right), \tag{8}$$

which each act in the direction of the axis of rotation of the group. Because of the assumed completely free rotation the first of these torques rotates the whole molecule with the exception of the rotatable group, in contrast the second only rotates the rotatable group itself. The friction constant during the first type of rotation we call ρ', that during the second type independent of the other, we call ρ''. We can then write the ensuing rotations during a time δt as

$$\begin{aligned} \delta\varphi =& \frac{\mu_b F_c \delta t}{\rho'}\sin\left(\chi - \varphi\right), \\ \delta\chi =& -\frac{\mu_c F_b \delta t}{\rho''}\sin\left(\chi - \varphi\right). \end{aligned} \tag{9}$$

Due to Eqs. (6) and (9) combined with Eqs. (3), (4), and (7), one can now characterise the rotation of molecules possessing a rotating group by

$$
\begin{aligned}
\delta\vartheta =& -\frac{F\delta t}{\rho}\left[\mu_a \sin\vartheta + \mu_b \cos\vartheta\cos\varphi + \mu_c \cos\vartheta\cos\chi\right],\\
\delta\psi =& -\frac{F\delta t}{\rho}\frac{\cos\vartheta}{\sin\vartheta}\left[\mu_b\sin\varphi + \mu_c\sin\chi\right],\\
\delta\varphi =& F\delta t\left[\frac{\cos^2\vartheta}{\rho\sin\vartheta}\left(\mu_b\sin\varphi+\mu_c\sin\chi\right)+\frac{\sin\vartheta}{\rho'}\mu_b\sin\varphi\right],\\
\delta\chi =& F\delta t\left[\frac{\cos^2\vartheta}{\rho\sin\vartheta}\left(\mu_b\sin\varphi+\mu_c\sin\chi\right)+\frac{\sin\vartheta}{\rho''}\mu_c\sin\chi\right].
\end{aligned}
\tag{10}
$$

Hence the effective increase in the number of molecules in the volume element $dV = \sin\vartheta d\vartheta d\psi d\varphi d\chi$ due to the field alone is

$$
\begin{aligned}
\Delta N_2 =& -\left[\frac{\partial}{\partial\vartheta}\left(f\sin\vartheta\delta\vartheta d\psi d\varphi d\chi\right)d\vartheta + \frac{\partial}{\partial\psi}\left(f d\vartheta\delta\psi d\varphi d\chi\right)d\psi\right.\\
&\left.+\frac{\partial}{\partial\varphi}\left(f\sin\vartheta d\vartheta d\psi\delta\varphi d\chi\right)d\varphi + \frac{\partial}{\partial\chi}\left(f\sin\vartheta d\vartheta d\psi d\varphi\delta\chi\right)d\chi\right]\\
=& -d\vartheta d\psi d\varphi d\chi\left[\frac{\partial}{\partial\vartheta}\left(f\sin\vartheta\delta\vartheta\right)+\frac{\partial}{\partial\psi}\left(f\delta\psi\right)+\frac{\partial}{\partial\varphi}\left(f\sin\vartheta\delta\varphi\right)\right.\\
&\left.+\frac{\partial}{\partial\chi}\left(f\sin\vartheta\delta\chi\right)\right].
\end{aligned}
\tag{11}
$$

On the other hand, the change in the total number of the molecules in the elemental volume dV with time is

$$\frac{\partial f}{\partial t}\delta t dV.$$

This relation combined with the total change $\Delta N = \Delta N_1 + \Delta N_2$ (see Eqs. (2) and (11)) yields the partial differential equation for f:

$$
\begin{aligned}
\frac{\partial f}{\partial t} =& \frac{\overline{\Delta_\vartheta}}{\delta t}\frac{\partial f}{\partial\vartheta}+\frac{\overline{\Delta_\varphi}}{\delta t}\frac{\partial f}{\partial\varphi}+\frac{\overline{\Delta_\chi}}{\delta t}\frac{\partial f}{\partial\chi}+\frac{\overline{\Delta_\vartheta^2}}{2\delta t}\frac{\partial^2 f}{\partial\vartheta^2}+\frac{\overline{\Delta_\varphi^2}}{2\delta t}\frac{\partial^2 f}{\partial\varphi^2}+\frac{\overline{\Delta_\chi^2}}{2\delta t}\frac{\partial^2 f}{\partial\chi^2}+\frac{\overline{\Delta_\vartheta\Delta_\varphi}}{\delta t}\frac{\partial^2 f}{\partial\vartheta\partial\varphi}\\
&+\frac{\overline{\Delta_\vartheta\Delta_\chi}}{\delta t}\frac{\partial^2 f}{\partial\vartheta\partial\chi}+\frac{\overline{\Delta_\varphi\Delta_\chi}}{\delta t}\frac{\partial^2 f}{\partial\varphi\partial\chi}+\frac{f}{\rho\sin\vartheta}\left\{\frac{\partial}{\partial\vartheta}\left[f\sin\vartheta\left(\mu_a\sin\vartheta+\mu_b\cos\vartheta\cos\varphi\right.\right.\right.\\
&\left.\left.+\mu_c\cos\vartheta\cos\chi\right)\right]-\frac{\partial}{\partial\varphi}\left[f\left[\cos^2\vartheta\left(\mu_b\sin\varphi+\mu_c\sin\chi\right)+\frac{\rho}{\rho'}\mu_b\sin^2\vartheta\sin\varphi\right]\right]\\
&\left.-\frac{\partial}{\partial\chi}\left[f\left[\cos^2\vartheta\left(\mu_b\sin\varphi+\mu_c\sin\chi\right)+\frac{\rho}{\rho''}\mu_c\sin^2\vartheta\sin\chi\right]\right]\right\}.
\end{aligned}
\tag{12}
$$

Here the term $\frac{\partial}{\partial\psi}\left(f\delta\psi\right)$ is absent since f like $\delta\psi$ is independent of ψ.

The constants $\frac{\overline{\Delta_\vartheta}}{\delta t}$, ... , $\frac{\overline{\Delta_\varphi\Delta_\chi}}{\delta t}$ are determined from the condition that at equilibrium $\left(\frac{\partial f}{\partial t}=0\right)$ the function $f = e^{-\frac{u}{kT}}$ (which the potential energy u leads to) must be a solution of Eq. (12) where

$$u = -F\left(\mu_a\cos\vartheta - \mu_b\sin\vartheta\cos\varphi - \mu_c\sin\vartheta\cos\chi\right), \tag{13}$$

so we have on substitution

$$f = e^{\frac{F}{kT}(\mu_a \cos\vartheta - \mu_b \sin\vartheta\cos\varphi - \mu_c \sin\vartheta\cos\chi)},$$

into Eq. (12) (with $\frac{\partial f}{\partial t} = 0$) the following explicit results

$$\begin{aligned}
\frac{\overline{\Delta_\vartheta}}{\delta t} &= \frac{kT}{\rho}\frac{\cos\vartheta}{\sin\vartheta}, \quad \frac{\overline{\Delta_\vartheta^2}}{2\delta t} = \frac{kT}{\rho}, \quad \frac{\overline{\Delta_\varphi^2}}{2\delta t} = \frac{kT}{\sin^2\vartheta}\left(\frac{\cos^2\vartheta}{\rho} + \frac{\sin^2\vartheta}{\rho'}\right),\\
\frac{\overline{\Delta_\chi^2}}{2\delta t} &= \frac{kT}{\sin^2\vartheta}\left(\frac{\cos^2\vartheta}{\rho} + \frac{\sin^2\vartheta}{\rho''}\right), \quad \frac{\overline{\Delta_\varphi\Delta_\chi}}{\delta t} = \frac{2kT}{\rho}\frac{\cos^2\vartheta}{\sin^2\vartheta},
\end{aligned} \tag{14}$$

with all the remaining averages equal to zero.

By substituting the values in Eq. (12) we arrive at the desired form of the differential equation (kinetic or Smoluchowski equation) whereby we can determine the (time dependent) distribution function. When we have all the above quantities, we see that by taking only terms of the first order in the field strength into account (linear response), that we can make the assumption (for the time dependent distribution)

$$f = 1 + x_a(t)\cos\vartheta - x_b(t)\sin\vartheta\cos\varphi - x_c(t)\sin\vartheta\cos\chi, \tag{15}$$

where the quantities $x_a(t)$, $x_b(t)$, $x_c(t)$ are functions of time only. Therefore we have the following differential equations for the $x_j(t)$ terms

$$\begin{aligned}
\frac{dx_a}{dt} &= -kT\frac{2}{\rho}\left(x_a - \frac{\mu_a F}{kT}\right),\\
\frac{dx_b}{dt} &= -kT\left(\frac{1}{\rho} + \frac{1}{\rho'}\right)\left(x_b - \frac{\mu_b F}{kT}\right),\\
\frac{dx_c}{dt} &= -kT\left(\frac{1}{\rho} + \frac{1}{\rho''}\right)\left(x_c - \frac{\mu_c F}{kT}\right),
\end{aligned} \tag{16}$$

with solutions for sinusoidal fields:

$$F = F_0 e^{i\omega t},$$

which can be written as

$$x_j = \frac{1}{1 + i\omega\tau_j}\frac{\mu_j F_0 e^{i\omega t}}{kT},$$

thus, the "relaxation times" can be explicitly given as

$$\frac{1}{\tau_a} = \frac{2kT}{\rho}, \quad \frac{1}{\tau_b} = kT\left(\frac{1}{\rho} + \frac{1}{\rho'}\right), \quad \frac{1}{\tau_c} = kT\left(\frac{1}{\rho} + \frac{1}{\rho''}\right). \tag{17}$$

Thus, we have the explicit solution for the time dependent distribution

$$f(\theta,\varphi,\chi,t) = 1+\frac{F_0 e^{i\omega t}}{kT}\left[\frac{\mu_a}{1+i\omega\tau_a}\cos\vartheta - \frac{\mu_b}{1+i\omega\tau_b}\sin\vartheta\cos\varphi - \frac{\mu_c}{1+i\omega\tau_c}\sin\vartheta\cos\chi\right], \tag{18}$$

whence we can calculate the mean moment according to the usual formula

$$\overline{m} = \frac{\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} f\left[\mu_a\cos\vartheta - \mu_b\sin\vartheta\cos\varphi - \mu_c\sin\vartheta\cos\chi\right]\sin\vartheta d\vartheta d\psi d\varphi d\chi}{\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} f\sin\vartheta d\vartheta d\psi d\varphi d\chi},$$

therefore

$$\overline{m} = \frac{F_0 e^{i\omega t}}{3kT}\left[\frac{{\mu_a}^2}{1+i\omega\tau_a} + \frac{{\mu_b}^2}{1+i\omega\tau_b} + \frac{{\mu_c}^2}{1+i\omega\tau_c}\right]. \tag{19}$$

These results can immediately be generalised to n rotating groups all with *parallel axes* (embedded) in the particular molecule under study. The calculation is the same, however, one must now specify for *each group* its own (particular) angle of rotation. If we denote by μ_a the sum of all the dipole moment components in the direction of the axis of rotation and further denote by $\mu_1, \ldots, \mu_n$ all the components of the moments rotating in the *plane of the rotation axis itself* we have the result

$$\overline{m} = \frac{F_0 e^{i\omega t}}{3kT}\left[\frac{{\mu_a}^2}{1+i\omega\tau_a} + \frac{{\mu_b}^2}{1+i\omega\tau_b} + \frac{{\mu_1}^2}{1+i\omega\tau_1} + \ldots + \frac{{\mu_n}^2}{1+i\omega\tau_n}\right], \tag{20}$$

with

$$\frac{1}{\tau_1} = kT\left(\frac{1}{\rho}+\frac{1}{\rho_1}\right), \ldots, \frac{1}{\tau_n} = kT\left(\frac{1}{\rho}+\frac{1}{\rho_n}\right). \tag{21}$$

Here we have denoted the friction coefficients of the various freely rotatable groups by $\rho_1, \ldots, \rho_n$; relations between τ_a, ρ, or between τ_b, ρ, ρ' apply unchanged (Eq. (17)).

In the static we can see from Eq. (20) that the mean moment has the form

$$\overline{m}_{stat} = \frac{F_0}{3kT}\left[{\mu_a}^2 + {\mu_b}^2 + {\mu_1}^2 + \ldots + {\mu_n}^2\right],$$

in agreement with the results of Zahn [1]. From the formula for the average moment one can calculate the dispersion and absorption indexes as a function of frequency. Those curves then exhibit several distinct maxima and their position and values in principle allow one to determine the constants $\tau_a, \ldots, \tau_n$. Let us treat for example the loss, we have for the imaginary part of the mean moment an expression of the form

$$\frac{\mu_a^2\omega^2\tau_a}{1+\omega^2\tau_a} + \ldots + \frac{\mu_n^2\omega^2\tau_n}{1+\omega^2\tau_n}.$$

Now at the usual measuring frequencies ($\omega^2\tau^2 \ll 1$) the losses should be proportional to

$$\omega^2 \left[\mu_a^2\tau_a + \mu_b^2\tau_b + ... + \mu_n^2\tau_n\right]. \tag{22}$$

However, (from Eqs. (17) and (21)) $\tau_b, \tau_1, ..., \tau_n$ are all smaller as compared to τ_a (ρ', $\rho_1, ...,$ ρ_n smaller than ρ) hence Eq. (22) is *smaller* than

$$\omega^2 \left[\mu_a^2 + \mu_b^2 + ... + \mu_n^2\right] \tau_a.$$

However since $\mu_a^2+\mu_b^2+...+\mu_n^2$ means the measurable dipole moment, this inequality states the losses should be smaller than those of a molecule which has the same dipole moment and is of the same size but does not possess a rotating group. In other words: if one calculates the molecular volume from the measured loss, this should be smaller than expected. Some experiments confirm this statement [4], in the quantitative side one must wait for further experimental confirmation.

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3. Magnetisation Relaxation Processes and Thermal Fluctuations

For the analysis of the magnetisation relaxation of fine single domain ferromagnetic nanoparticles, it is necessary to establish a comprehensive theory of thermal fluctuations and relaxation processes in nanomagnets for the accurate interpretation of experimental and computer simulation data via the use of rigorous mathematical models which have a foundation in the principles of non-equilibrium statistical mechanics. Fine single-domain ferromagnetic particles are known to exhibit unstable behaviour of the magnetisation due to thermal agitation, which results in superparamagnetism due effectively to each nanoparticle behaving as an enormous Langevin paramagnet of magnetic moment ($\sim 10^4 - 10^5$ Bohr magnetons μ_B). The magnetisation may spontaneously reverse its direction at temperatures above what is called the *blocking temperature* due to thermal fluctuations so that the stable magnetic behaviour that is characteristic of a ferromagnet is destroyed. Thus the initiation of thermal instability defined by a time-dependent magnetisation in the magnetic nanoparticles used has been of great consequence in magnetic recording as they are constantly being reduced in size in order to provide both increased signal-to-noise ratio and greater storage density. In addition to this, the aforementioned thermal instability has provided valuable insight into the subject of paleomagnetism, as the ability of igneous rock to keep a magnetic record hinges on the fact that the fine particles within the igneous rock have been able to preserve the direction of the earth's magnetic field from the epoch in which the temperature of the environment has fallen below the blocking temperature of the particles.

Louis Néel in 1949 [84, 85] codified his theory of magnetisation reversal over a potential barrier inside a nanoparticle through the implicit adaption of an *Ansatz* proposed by Debye through his book [3], in order to explain the dielectric relaxation of solids which upon melting will yield polar liquids. Debye (A.K.A. Debye's second model) has considered an ensemble of non-interacting polar molecules each of which have the same permanent dipole moment and situated for example each at the intersection points (sites) of a space lattice. It was further supposed by Debye that if a uniform field acts on a dipole, then it can orient itself in one of two *definite* directions only, either in the same direction as the field, or its opposite. This model is known as *discrete orientation* and has been further extended by Fröhlich in 1949 [56] and by Brown in 1956 [86]. This is in contrast to the more widely known *continuous* distribution of orientations model of non-interacting polar molecules representing a polar liquid also due to Debye (which is his first model). The first model which as we saw was initially based on a fixed-axis rotator version of Einstein's theory of Brownian motion [2] was later extended to rotation in space. In the discrete orientation model, in which the transition from one orientation to another occurs in a single big jump, as applied to polar dielectrics the essential difference between it and the free rotational diffusion one is that the latter (where the transition from one orientation at time t to another at $t + dt$ occurs by a succession of *small* jumps) predicts dispersion and absorption in the microwave region while typically the former roughly explains the dispersion and absorption in ice occurring at km wavelengths. Therefore a solid such as ice will behave as if it were a polar liquid with very high internal friction, and thus will have a very long relaxation time. This time turns out to be exponentially long as emphasised by Fröhlich due to the fact that the probability of the jumping of a dipole over a potential barrier is proportional to the appropriate Boltzmann factor $e^{-\Delta E}$. This factor results in Arrhenius behaviour of the escape rate $\Gamma = Ae^{-\Delta E}$, which is inversely proportional to the overbarrier relaxation time τ (note that ΔE is a dimensionless potential barrier and A is a prefactor).

A fundamentally similar result was also found for the longitudinal magnetisation relaxation of a single-domain ferromagnetic nanoparticle over an internal magnetocrystalline-anisotropy-Zeeman energy potential barrier by Néel [84,85]. This approach to the magnetisation reversal time mechanism, which is based on statistical mechanics, was started through his hypothesis that the reversal was governed via an activation process pertaining to escape over a barrier in the form of the discrete orientation model. The key difference however from standard reaction rate theory, since we treat a magnetisation *energy density potential*, is that the longest relaxation time of the magnetisation, now depending exponentially on the volume of the particle, can vary from *nanoseconds* to *geological epochs*. The ideas of Néel were later refined by Brown in 1963 [87]. He builds on his well expressed *Handbuch* article [86] on dielectrics, via setting the entire problem in the context of the general theory of stochastic processes. Thus he involved a form of Boltzmann's *Stosszahlansatz* [2] (of which the Brownian motion is a particular case) as was accomplished by Debye for dielectric relaxation. Brown's criticism of Néel's results for the reversal time of the magnetisation rests on two irrefutable facts:

1. The relaxing system is not treated explicitly as a gyromagnetic one.
2. It relies on the discrete orientation *Ansatz*.

Therefore despite the disturbance to the orientational Boltzmann distribution in a potential well due to the loss of magnetisation (i.e., representative points) at the barrier that distribution still prevails everywhere in accordance with transition state theory. The latter assumption is an inherent flaw of the discrete orientation *Ansatz* so that it is impossible to calculate accurately the escape rate and thus the relaxation time, *because the effect of the energy dissipation to the bath on the escape rate is completely ignored*. However, these problems were circumvented by Brown by formulating from the *magnetic Langevin equation*, i.e., the *Landau-Lifshitz-Gilbert equation* for the magnetisation evolution *as supplemented by stochastic terms*, the magnetic Fokker-Planck equation. This equation governs the probability density $W(\vartheta, \varphi, t)$ of the magnetic moment orientations on the unit sphere, where ϑ and φ are, respectively, the polar and azimuthal angles of the spherical polar coordinate system. Thus, he achieved the goals of both setting the magnetisation stochastic process within the framework of the general theory of the Brownian motion and *simultaneously* removing the difficulties associated with the discrete orientation *Ansatz* in effect similar to what Debye has achieved with his continuous distribution of orientations model with an external applied field. This was later utilised by Maier and Saupe with the addition of a mean field potential in the analysis of the dielectric relaxation of nematic liquid crystals [2].

Furthermore, Brown was able to identify the magnetisation reversal time with the inverse of the smallest non-vanishing eigenvalue of the magnetic Fokker-Planck equation which governs precession-aided rotational diffusion of the magnetic moment in the anisotropy-Zeeman energy potential thus for a given potential posing a Sturm-Liouville problem. The simplest uniaxial potential of the magneto-crystalline anisotropy-Zeeman energy was the example Brown used (which he intended only as an indicative example). As such in the longitudinal relaxation, the gyromagnetic terms are not explicitly involved because they immediately drop out from the Fokker-Plank equation. Therefore, in this effectively one-dimensional problem (through suitably adapting the Kramers theory [88] of escape of translating particles over potential barriers to classical macrospins) Brown found an asymptotic result which agrees with that of Néel [84, 85] as far as the exponential dependence of the magnetisation reversal time on the potential barrier height is concerned. As mentioned earlier, we seek the solution of the Fokker-Planck equation as a Fourier-Laplace series in the spherical harmonics $Y_{lm}(\vartheta, \varphi)$. These serve as an appropriate basis set for the evaluation of observables such as the magnetisation, and yield a multi-term differential-recurrence relation for the statistical moments. However, there is another procedure that we can follow which is completely equivalent. This involves taking the magnetic Langevin equation and rewriting it as a stochastic evolution equation for a spherical harmonic of arbitrary rank with the aid of the theory of angular momentum. The resulting stochastic recurrence relation is then averaged during an *infinitesimal time* (i.e., the *Ansatz* used by Einstein) over an ensemble of macrospins [2] which at some initial time all had the same orientation ϑ, φ. This procedure leads to the deterministic equation of motion of a spherical harmonic in terms of the sharp values ϑ and φ. However the latter are also random variables themselves. Thus we make a spatial average over their distribution to yield a time-dependent multi-term ordinary differential-recurrence relation. Upon so doing, the observables are then calculated via rapidly convergent matrix continued fractions [2].

Next, we shall briefly introduce the foundations of spin Brownian motion, as well as the kinds of relaxation processes we can observe in magnetic particles.

3.1 The Equations of Motion for Magnetic Moments and the Magnetic Properties of Solids

3.1.1 Magnetic Dipole Moment and the Larmor Equation

When analysing the magnetic properties of nanomagnets, it is important to understand the origin of the magnetic moment $\boldsymbol{\mu}$.

Currents in wires produce magnetic fields which take the form of concentric circles around the wire (i.e., the fields are solenoid vectors). The direction of the magnetic field will be perpendicular to the wire in a manner such that if you were to curl your fingers around the wire with your thumb pointed in the direction the current is travelling all with your right hand, the direction of the field is indicated by the direction of your curled fingers. But what about the magnetic field produced by a permanent magnet, be it a basic bar magnet or a single domain ferromagnetic particle etc., and what gives it the shape of that produced by a solenoid? In order to answer this question, we will need to consider the Bohr model of an atom, where we have electrons orbiting around the nucleus in a circle. In such a case, the orbiting electron appears similar to a current solenoidal loop. The existence of this current loop leads to the electron having an angular momentum $\mathbf{J}$. From this we can determine the magnetic moment $\boldsymbol{\mu}$ viz.,

$$\boldsymbol{\mu} = -\frac{\gamma \mathbf{J}}{\mu_0}, \tag{3.1}$$

where γ is the gyromagnetic ratio constant, where in this case it is associated with the electron spin, meaning that $\gamma = 2.2 \times 10^5 \mathrm{A}^{-1}\mathrm{ms}^{-1}$ and μ_0 is the permeability of free space $\mu_0 = 4\pi \times 10^{-7}$ $\mathrm{JA}^{-2}\mathrm{m}^{-1}$ in SI units ($4\pi \times 10^{-7}\mathrm{H/m}$).

Let us consider now what happens when this magnetic moment $\boldsymbol{\mu}$ is placed in a magnetic field $\mathbf{H}$. What we will observe is that it experiences a torque $\mathbf{K}$ expressed in vector form as

$$\mathbf{K} = \mu_0[\boldsymbol{\mu} \times \mathbf{H}]. \tag{3.2}$$

This torque will consequently lead to a rate of change of the angular momentum perpendicular to $\mathbf{J}$ viz.,

$$\frac{d\mathbf{J}}{dt} = \mathbf{K} = \mu_0[\boldsymbol{\mu} \times \mathbf{H}], \tag{3.3}$$

leading to $\boldsymbol{\mu}$ undergoing a precession about the direction of $\mathbf{H}$. Therefore

$$\frac{d\boldsymbol{\mu}}{dt} = \gamma[\mathbf{H} \times \boldsymbol{\mu}]. \tag{3.4}$$

This is equation is called the *Larmor equation* [89] and the angular frequency of the precession is called the *Larmor frequency* given by

$$\boldsymbol{\omega} = \gamma\mathbf{H}, \tag{3.5}$$

and as is demonstrated mathematically in Eq. (3.5), it is directly proportional to the applied magnetic field $\mathbf{H}$.

3.1.2 Magnetic Solids and their Properties

Up to this point, we have been studying magnetic moments in isolation, but what about solid materials with magnetic properties? We find that these can be classified as either *diamagnetic, paramagnetic*, or *ferromagnetic* depending on their response to an external applied magnetic field.

Diamagnetic materials [31, 34] are those substances which end up being weakly magnetised when subjected to an applied external magnetic field, in a direction opposite to the applied field. Some examples of diamagnetic materials include copper, gold, silver, lead, mercury, and water.

Paramagnetic materials [31, 34] are those which are weakly magnetised when subjected to an applied external magnetic field in the same direction as the applied field. In paramagnetic substances, the orbital and spin magnetic moments of an atom are oriented in a manner such that each atom has a permanent magnetic dipole moment. However, because of thermal motion (fluctuations), the direction of the magnetic moments of atoms have random orientations, leading to the net magnetic moment being zero. When subjected to an applied external magnetic field, each of the atomic magnets (permanent magnetic dipole moment of each atom) will tend to align in the direction of the field, thus leading to the paramagnetic substance having a net magnetic moment $\mu L(\xi)$, where $\xi = \mu H_0/kT$ and $L(\xi) = \coth\xi - \xi^{-1}$ is called the *Langevin function* [90] and the theory is a replica of the Debye treatment of the static electric polarization [49]. Some examples of paramagnetic substances include aluminium, platinum, chromium, tungsten and lithium.

Ferromagnetic materials are those substances which are strongly magnetised in an external magnetic field in the same direction as the external applied field and can retain its magnetic moment even upon removal of the external field. In domain theory a ferromagnetic substance consists of a large number of smaller regions called *domains.* A *domain* can be defined as an extremely small region containing a large number of atomic magnets which have magnetic axes aligned in the same direction due to a strong *exchange coupling*, leading to each domain having its own magnetic dipole moment. When a ferromagnetic substance is subjected to an applied external magnetic field, the permanent alignment of the domain due to a strong interaction (force) takes place, this force is called *exchange coupling* (*exchange interaction*). In the absence of an external magnetic field, the various domains will have random orientations, leading to the magnetic moment as a whole being zero. When the field is switched on, each domain experiences a torque, leading to some domains rapidly rotating and remaining aligned parallel to the direction of the field (a phenomenon called domain flipping). The concept of ferromagnetic materials consisting of these domains was first proposed in 1907 by Weiss [91] who was under the assumption that the regions coincided with the crystals the material was composed of. This was later disproven by Frenkel and Dorfman and by Heisenberg and Bloch [91], who realised that even a single crystal can consist of these magnetic domains. The exact nature of these domains was later identified by Landau and Lifshitz [91], whom found them to be in the form of *elementary layers.*

It should be noted that generally speaking, a particle of ferromagnetic material [92] below a certain critical size (which is usually 150 Å in radius) will constitute a *single-domain* particle [91], which means that it is in a state of uniform magnetisation for any applied field. The magnetic dipole moment of such a particle can be denoted by

$$\boldsymbol{\mu} = v\mathbf{M}, \tag{3.6}$$

where $\mathbf{M}$ is the magnetisation and v is the volume of the particle.

Furthermore, we find that in small ferromagnetic nanoparticles, there exists a form of magnetism called *superparamagnetism*, whereby the magnetic moment $\boldsymbol{\mu}$ is no longer that of a *single* atom, rather it is that of a *single-domain particle* of volume v which can be of the order of $10^4 - 10^5$ Bohr magnetons, so that the magnetic moments involved are very large in magnitude..

In addition to this, the single-domain particles will generally not be isotropic, but rather will give anisotropic contributions to their total energy associated with the external shape of the particle, imposed stress or the crystalline structure itself. This superparamagnetism, or thermal instability of the magnetisation tends to occur on the condition that the thermal energy kT (where k is Boltzmann's constant and T is the temperature) is enough to change the orientation of $\boldsymbol{\mu}$ of the entire particle in spite of the anisotropy potential. As such, the behaviour overall is similar to an ensemble of paramagnetic atoms, where there is no hysteresis, just saturation behaviour. Now a useful parameter for describing how much a material will become magnetised in an applied magnetic field is the *magnetic susceptibility*, which is a physical quantity that characterises the relation between the magnetic moment (magnetisation) of a substance and the applied external magnetic field which is dimensionless. The static magnetic susceptibility χ of diamagnetic and paramagnetic (superparamagnetic) substances, can be defined mathematically as

$$\mathbf{M} = \chi\mathbf{H}. \tag{3.7}$$

Note that in anisotropic solids, $\mathbf{M}$ and $\mathbf{H}$ are likely not to be parallel to one another, which means that the *magnetic susceptibility will vary with direction in the crystal.*

Notice that in diamagnetic materials, $\chi < 0$, while for paramagnetic materials $\chi > 0$ and ferromagnetic materials will have very large values for χ.

3.1.3 Magnetocrystalline Anisotropy

On the subject of magnetic anisotropy, it should be noted that most ferromagnetic solids are indeed magnetically anisotropic, meaning that it takes more energy to magnetise it in certain directions than in others. The main cause of this being the *spin-orbit interactions*, which stems from the orbital motion of the electrons coupling with the crystal electric field, thereby giving rise to the first order contributions to the magneto-crystalline anisotropy. The second order contribution will arise from the mutual interaction of the magnetic dipoles.

We find that there are certain crystal systems which exhibit a single axis of high symmetry, the anisotropy of which is labelled *uniaxial anisotropy* (see Figure 3.2). Generally speaking, the magnetocrystalline anisotropy energy is represented in powers of the direction cosines of the magnetisation (u_X, u_Y, u_Z) which are components of a unit vector $\mathbf{u}$ directed along $\mathbf{M}$. For uniaxial anisotropy, with the Z-axis taken to be the principal axis of the symmetry of the crystal, the free energy density of the magnetic particle V is

$$V = K(u_X^2 + u_Y^2) = K \sin^2 \vartheta, \tag{3.8}$$

where K is an anisotropy constant, with units of energy density and is dependent on the composition. If $K > 0$, then the directions of lowest energy are $u_Z = \pm 1 (\vartheta = 0$ and $\vartheta = \pi)$, i.e., the polar axis as seen in Figure 3.1. If the applied dc field $\mathbf{H}_0$ is assumed to be parallel to the polar axis, then the total free energy per unit volume is

$$V(\vartheta) = K \sin^2 \vartheta - \mu_0 M_S H_0 \cos \vartheta, \tag{3.9}$$

where M_S is the saturation magnetisation.

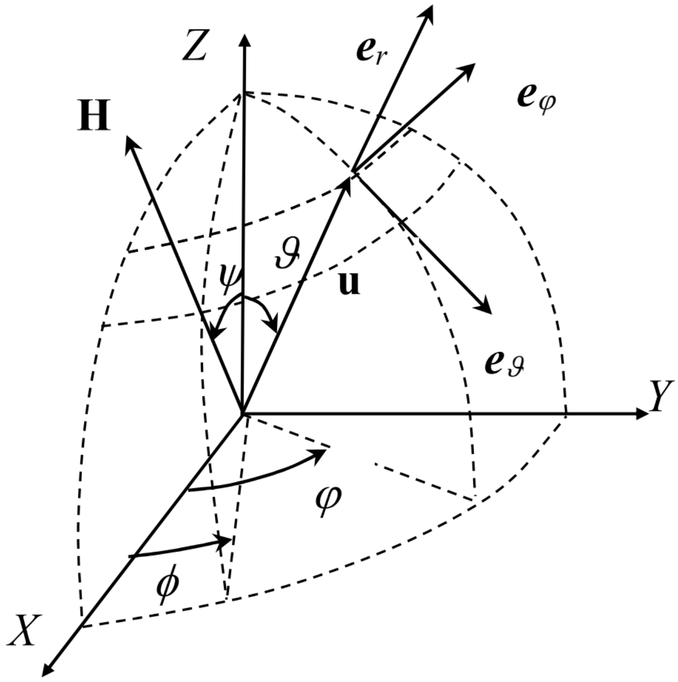

Figure 3.1: Spherical polar coordinate system. (aft. [34])

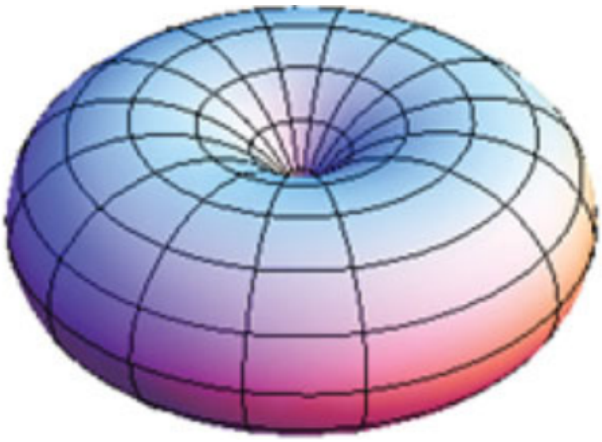

Figure 3.2: Uniaxial anisotropy potential given by Eq. (3.8). (aft. [93])

Every anisotropy potential $V(\vartheta)$ generates an effective magnetic field $\mathbf{H}$ which is proportional to the negative gradient of the free energy density V, viz.,

$$\mathbf{H} = -\frac{1}{\mu_0}\frac{\partial V}{\partial \mathbf{M}} \text{ or } \frac{\partial V}{\partial \mathbf{M}} = \mathbf{i}\frac{\partial V}{\partial M_X} + \mathbf{j}\frac{\partial V}{\partial M_Y} + \mathbf{k}\frac{\partial V}{\partial M_Z}. \tag{3.10}$$

The field $\mathbf{H}$ in the usual spherical coordinate basis $\{\mathbf{e}_r, \mathbf{e}_\vartheta, \mathbf{e}_\varphi\}$ is given by

$$\begin{aligned}\mathbf{H} &= -\frac{1}{\mu_0 M_S}\left(\frac{\partial V}{\partial \vartheta}\mathbf{e}_\vartheta + \frac{1}{\sin\vartheta}\frac{\partial V}{\partial \varphi}\mathbf{e}_\varphi\right)\\ &= -\frac{1}{\mu_0 M_S}\left(0, \frac{\partial V}{\partial \vartheta}, \frac{1}{\sin\vartheta}\frac{\partial V}{\partial \varphi}\right).\end{aligned} \tag{3.11}$$

3.1.4 Landau-Lifshitz and Gilbert Equations

The first dynamical model for the precessional motion of the magnetisation $\mathbf{M}$ of a single-domain ferromagnetic particle or macrospin was proposed by Landau and Lifshitz in 1935 [2, 34, 94]. They asserted that in the absence of damping, the magnetisation will simply precess about an effective magnetic field $\mathbf{H}$ according to the gyromagnetic equation [34]

$$\dot{\mathbf{u}} = \gamma[\mathbf{H} \times \mathbf{u}],\ \mathbf{H} = -\frac{1}{\mu_0 M_S}\frac{\partial V}{\partial \mathbf{u}}, \tag{3.12}$$

where

$$\mathbf{u} = \frac{\mathbf{M}}{M_S} = (\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta), \tag{3.13}$$

is a unit vector directed along $\mathbf{M}$ where we are proceeding under the assumption that the single-domain ferromagnetic particle is at its saturation magnetisation M_S so that only the orientation of $\mathbf{M}$ can change, V is the free energy density consisting of both an anisotropy potential and the Zeeman energy due to an external magnetic field, and $\partial/\partial\mathbf{u}$ is the gradient on the surface of a unit sphere expressed in spherical coordinates as

$$\frac{\partial}{\partial \mathbf{u}} = \frac{\partial}{\partial \vartheta}\mathbf{e}_\vartheta + \frac{1}{\sin\vartheta}\frac{\partial}{\partial \varphi}\mathbf{e}_\varphi. \tag{3.14}$$

Eq. (3.12) is simply the Larmor equation (Eq. (3.4)) for a single spin generalised to the coherent rotation of a macrospin. As a consequence of this, the evolution of the magnetisation as described by Eq. (3.12) has no energy loss to the surroundings through the motion of the magnetisation. What we will effectively observe is that $\mathbf{M}$ will follow paths of constant energy in what are called Stoner-Wohlfarth orbits [95,96] (See Figure 3.3 [34]), precessing *ad infinitum* in a well of the potential under the condition that the energy of the applied magnetic field is less than the barrier height.

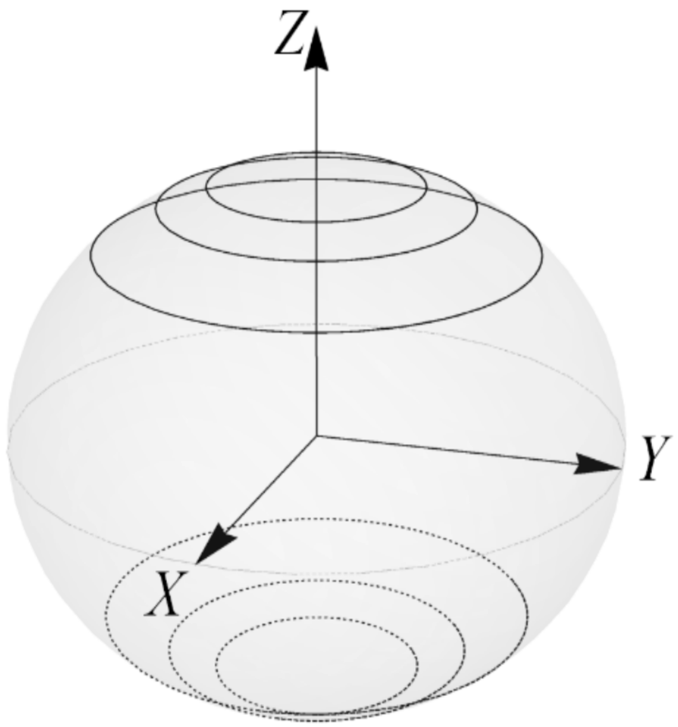

Figure 3.3: Stoner-Wohlfarth orbits which are encircling an energy minimum along the polar positive and negative Z-axis (solid lines) or crossing a potential barrier lying in the XY plane (dashed lines). (aft. [34])

It is at this point that Landau and Lifshitz [2, 34, 94] introduced a damping torque opposing the precession to model the effect of energy dissipation. Thus the gyromagnetic equation (Eq. (3.12)) becomes either the Landau-Lifshitz equation [34]

$$\dot{\mathbf{u}} = \gamma[\mathbf{H} \times \mathbf{u}] - \lambda[\mathbf{u} \times [\mathbf{u} \times \mathbf{H}]], \tag{3.15}$$

where λ is a dimensionless damping parameter, or the Landau-Lifshitz-Gilbert equation [34], which was proposed by Gilbert [97]

$$\dot{\mathbf{u}} = \gamma[\mathbf{H} \times \mathbf{u}] + \alpha[\mathbf{u} \times \dot{\mathbf{u}}], \tag{3.16}$$

where $\alpha > 0$ is the dimensionless damping constant which varies depending on the material, and which represents the effect of all the the microscopic degrees of freedom.

In both equations we find now that the energy of the system is no longer conserved, rather it is continuously being dissipated by the drag torque. **M** will now have a tendency to spiral towards the easy axis in a manner seen in Figure 3.4 [34]

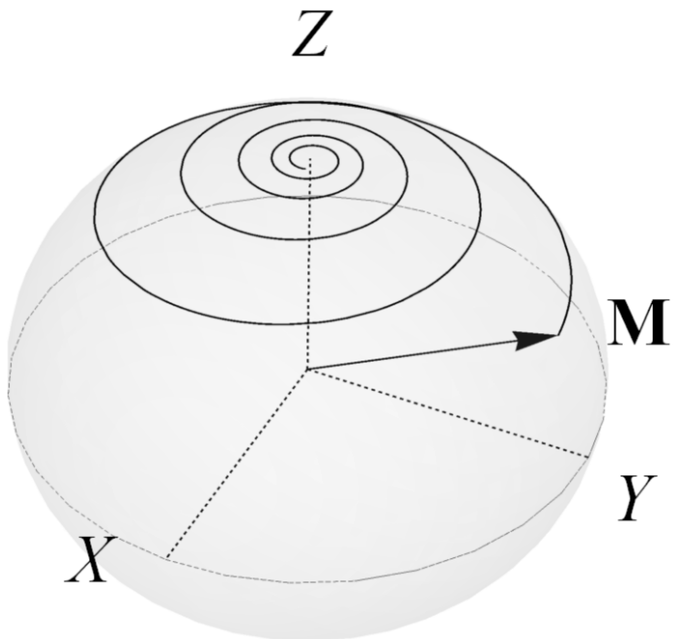

Figure 3.4: Collapse of a Stoner-Wohlfarth orbit until it becomes a singularity as is captured by the Landau-Lifshitz-Gilbert equation with $\gamma H_Z(1+\alpha^2)^{-1} = 1$. (aft. [34])

For our purpose, we will only be using the Landau-Lifshitz-Gilbert equation. The reasons for doing this are highlighted in a discussion by Coffey, Kalmykov and Titov in [34].

3.1.5 Néel Relaxation

We shall consider here the magnetic after-effect behaviour of single-domain particles, through understanding the conditions necessary for an assembly of said particles to achieve thermal equilibrium. For ferrofluids, this can be accomplished through the physical rotation of these particles in the liquid they are suspended in. The rate at which they reach equilibrium here is controlled by the viscosity of the carrying fluid/medium. The Debye theory of orientational relaxation [2] is suitable for the modelling of this mechanism, more so than for electric dipoles due to the relatively larger size of the magnetic particles, which leads to the magnetic particles more closely approximating idealised Brownian rotators.

This physical rotation of the particles however cannot take place in solids. Nevertheless it was speculated by Néel [84,85,98] in 1949 that provided a single-domain particle was *sufficiently small*, the *direction of magnetisation* is likely to undergo a form of Brownian motion, destroying its stable magnetic behaviour, under thermal fluctuations. The inertia of the particle plays no role into the relaxation of the magnetic moment since the magnetic moment is inside the particle, and the particle itself will not undergo physical rotation. The barrier due to the anisotropy-Zeeman energy prevents the magnet in question from moving from one magnetic state to another and must be overcome by the thermal energy kT as highlighted by Brown [99]. If the barrier is not too large (so that the probability per unit time of a jump over it is very small) or too small in comparison to the the thermal energy kT, then the specimen in question neither remains in a single stable state for a long time nor does it attain thermal equilibrium in a short time after a change in the field. Rather what happens is that it undergoes a change in magnetisation that lags behind the field instead of changing instantly. This phenomenon is referred to as the *Néel relaxation* (or *magnetic after-effect*) [2,34] and only occurs in ferromagnetic particles deemed sufficiently fine. To demonstrate the Néel mechanism [91], we shall follow an example from Section 1.4.1 of [34] and consider an assembly of aligned uniaxial particles which are subjected to a field $\mathbf{H}$, with a potential energy governed by Eq. (3.9). As such the particles are fully magnetised along the polar axis, which is the axis of symmetry. Once the field has been switched off for a sufficiently long time, the remanence will vanish as

$$M_r(t) = M_r(0)e^{-\frac{t}{\tau}}, \tag{3.17}$$

where τ is the reversal time of the magnetisation. This is the longest lived mode of the relaxation process. From transition state theory [100, 101], Néel [84, 85, 98] suggested that τ may be evaluated as [34]

$$\tau^{-1} = f_A e^{-\Delta E}, \tag{3.18}$$

where f_A is the frequency of the gyromagnetic precession [102] and $\Delta E = E(\vartheta_C) -$

$E(\vartheta_A)$ is the energy barrier (ϑ_C is the point located at top of the energy barrier and ϑ_A is the point situated at the bottom of the potential well) such that, through varying the volume or the temperature of the particles, τ can be made to vary from 10^{-9}s to millions of years. Brown [87] however criticised Néel's calculation of τ on two fronts

1. The system is not explicitly treated as a gyromagnetic one.
2. It relies on a discrete orientation approximation.

Furthermore the dependence of the prefactor on damping is ignored. Brown [87] proposed that these difficulties can be overcome through construction of the Fokker-Planck equation for the probability distribution function of magnetic moment orientations on the unit sphere from the appropriate Langevin equation for the evolution of the magnetisation $\mathbf{M}$. Then by adapting the Kramers theory of escape of particles over potential barriers to magnetisation of single domain ferromagnetic particles, he was able to find an approximate formula for τ in the high-barrier for the potential in Eq. (3.9) which aside from the prefactor f_A, agreed with Néel's formula.

3.2 Linear Response Theory as applied to Magnetic Nanoparticles

In Section 2.2 of the thesis, we have demonstrated the use of linear response theory [35] via its application to dielectric relaxation of a system of electric dipoles and how it can be used to obtain observables such as the complex polarisability of the electric dipoles. This can be done through solving the relevant matrix differential-recurrence relations. In the case of magnetic dipoles we can also use linear response theory to determine the relevant observables, such as the longitudinal and transverse components of the magnetisation $\mathbf{M}(t)$ and their characteristic times, the components of the complex magnetic susceptibility tensor $\hat{\chi}(\omega)$, the equilibrium correlation functions of the longitudinal and transverse components of the magnetisation etc. The longitudinal $\chi_{\|}(\omega)$ and transverse $\chi_{\perp}(\omega)$ components of the magnetic susceptibility of a magnetic nanoparticle are defined using linear response theory [35] as

$$\frac{\chi_k(\omega)}{\chi_k} = 1 - i\omega \int_0^{\infty} e^{-i\omega t} C_k(t)\, dt,\ (k = \|, \perp), \tag{3.19}$$

where $C_k(t)$ are the equilibrium correlation functions given by

$$C_k(t) = \frac{\langle M_k(0)\, M_k(t)\rangle_0 - \langle M_k(0)\rangle_0^2}{\langle M_k^2(0)\rangle_0 - \langle M_k(0)\rangle_0^2},\ (k = \|, \perp), \tag{3.20}$$

and

$$\chi_k = \frac{v}{kT}\left[\langle M_k^2(0)\rangle_0 - \langle M_k(0)\rangle_0^2\right],\ (k = \|, \perp), \tag{3.21}$$

are the components of the static magnetic susceptibility. The angular brackets denote the equilibrium ensemble average which is given as

$$\langle A\rangle_0 = \int_0^{2\pi}\int_0^{\pi} A(\vartheta, \varphi)\, W_0(\vartheta, \varphi) \sin\vartheta d\vartheta d\varphi, \tag{3.22}$$

where $W_0(\vartheta, \varphi) = Z^{-1} e^{-\frac{vV(\vartheta,\varphi)}{kT}}$ is the equilibrium Boltzmann distribution function and Z is the partition function. The Cartesian components of the magnetisation, labelled $M_X, M_Y,$ and M_Z, which are expressed as

$$\begin{aligned} M_X =& M_S \sin\vartheta \cos\varphi, \\ M_Y =& M_S \sin\vartheta \sin\varphi, \\ M_Z =& M_S \cos\vartheta, \end{aligned} \tag{3.23}$$

where here ϑ is the colatitude and φ is the longitude can be written in terms of spherical harmonics of rank 1 as

$$\begin{aligned} M_X =& M_S \sqrt{\frac{2\pi}{3}} \left[Y_{1-1}(\vartheta, \varphi) - Y_{11}(\vartheta, \varphi)\right], \\ M_Y =& i M_S \sqrt{\frac{2\pi}{3}} \left[Y_{1-1}(\vartheta, \varphi) + Y_{11}(\vartheta, \varphi)\right], \\ M_Z =& M_S \sqrt{\frac{4\pi}{3}} Y_{10}(\vartheta, \varphi). \end{aligned} \tag{3.24}$$

It should be noted that these components are not independent since

$$M_X^2 + M_Y^2 + M_Z^2 = M_S^2. \tag{3.25}$$

The time behaviour of the equilibrium correlation function $C_k(t)$ can be characterised with the introduction of the *integral relaxation time* τ_{int}^k viz.,

$$\tau_{\text{int}}^k = \int_0^\infty C_k(t)dt, \tag{3.26}$$

which is essentially the area under the normalised decay curve $C_k(t)$, and the *effective relaxation time* τ_{ef}^k which is given by

$$\tau_{\text{ef}}^k = -1/\dot{C}_k(0), \tag{3.27}$$

which is capable of providing precise information on the initial decay of $C_k(t)$. Furthermore, τ_{int}^k and τ_{ef}^k can be equivalently defined through the use of the eigenvalues (λ_j^k) of the Fokker-Planck operator because $C_k(t)$ may formally be written as an infinite series of decaying exponentials, viz.,

$$C_k(t) = \sum_j c_j^k e^{-\lambda_j^k t}, \tag{3.28}$$

such that from Eqs. (3.26) - (3.28) we get

$$\tau_{\text{int}}^k = \sum_j \frac{c_j^k}{\lambda_j^k}, \tag{3.29}$$

and

$$\tau_{\text{ef}}^k = \frac{1}{\sum_j \lambda_j^k c_j^k}. \tag{3.30}$$

These times will contain contributions from *all* the eigenvalues λ_j^k. Therefore generally in order to numerically evaluate $C_k(t)$, τ_{int}^k and τ_{ef}^k, we require knowledge of all the λ_j^k and c_j^k. We can also however evaluate τ_{ef}^k in terms of equilibrium averages from the exact analytic equations [103] given by

$$\tau_{\text{ef}}^{\parallel} = 2\tau_N \frac{\left\langle M_{\parallel}^2 \right\rangle_0 - \langle M_{\parallel} \rangle_0^2}{M_S^2 - \left\langle M_{\parallel}^2 \right\rangle_0}, \tag{3.31}$$

$$\tau_{\text{ef}}^{\perp} = 2\tau_N \frac{\langle M_{\perp}^2 \rangle_0}{2M_S^2 - \langle M_{\perp}^2 \rangle_0}. \tag{3.32}$$

As can be observed in Eq. (3.19), the behaviour of $\chi_k(\omega)$ in the frequency domain is determined completely by the time behaviour of $C_k(t)$. In addition to this, Eqs. (3.19) and (3.28) which define $C_k(t)$ allow for the formal writing of the dynamic susceptibility $\chi_k(\omega)$ as an infinite sum of Lorentzians given by

$$\frac{\chi_k(\omega)}{\chi_k} = \sum_j \frac{c_j^k}{1 + i\omega/\lambda_j^k}. \tag{3.33}$$

Consequently in both the low frequency $\omega \to 0$ and high frequency $\omega \to \infty$ limits we have from Eq. (3.33)

$$\frac{\chi_k(\omega)}{\chi_k} = \begin{cases} 1 - i\omega\tau_{\text{int}}^k + ..., & \omega \to 0, \\ -i/\omega\tau_{\text{ef}}^k + ..., & \omega \to \infty. \end{cases} \tag{3.34}$$

Consequently, the low and high-frequency behaviour of $\chi_k(\omega)$ are determined completely by the integral τ_{int}^k and effective τ_{ef}^k relaxation times respectively.

4. The Langevin and Fokker-Planck Equations and Methods of Solution

4.1 The Langevin Equation

The Langevin equation [2, 45, 104, 105] is a stochastic differential equation which describes the time evolution of a set of degrees of freedom, in our case Brownian motion obeying the dynamics of a Markov process.

If we were to consider a large particle of mass m (which we will call here a *Brownian particle*) suspended in a fluid, which itself consists of much smaller particles (atoms or molecules), then we end up in a situation where the Brownian particle will be subjected to a force from the collisions of the small particles with the Brownian particle. The force itself consists of two parts, the first part is a deterministic hydrodynamic drag force $F_{fr} = -\zeta v(t)$, where ζ is the friction coefficient and v is the velocity of the particle, which will resist the motion, and the second part is a rapidly fluctuating zero-mean force $\overline{F(t)} = 0$ due to the collisions of the smaller particles with the Brownian particle which tries to maintain the motion. The second force is characterised through a probabilistic description and exhibits the properties of *white noise*. Following Newton's second law of motion, the Langevin equation is thus [2, 45]

$$m\ddot{x} = -\zeta v(t) + F(t), \tag{4.1}$$

where it is assumed that the friction force $-\zeta v$ is governed by Stokes' law, which states that the frictional force decelerating a spherical particle of radius a moving in a one dimensional extension x is $-\zeta v = -6\pi\eta a v$, where η is the viscosity of the surrounding fluid and $v = \dot{x}$. Furthermore since the collisions are so rapid that they are practically instantaneous they can be expressed by the autocorrelation function [104]

$$\overline{F(t)F(t+\tau)} = 2\zeta kT\delta(\tau), \tag{4.2}$$

where $2\zeta kT$ is the *spectral density.* Now we have already seen that the autocorrelation function of the random variable $F(t)$ is defined as

$$\overline{F(t)F(t+\tau)} = \lim_{T'\to\infty} \frac{1}{T'} \int_{-\frac{T'}{2}}^{\frac{T'}{2}} F(t)F(t+\tau)dt, \tag{4.3}$$

that is the time average of a two-time product over an arbitrary range time T' which is allowed to become infinite [44]. A detailed description of how Langevin derived the formula for the mean squared displacement of a Brownian particle is provided in section 1.3 of [2].

4.2 The Langevin Equation for Magnetic Moments

The Landau-Lifshitz-Gilbert equation discussed earlier in the thesis ignores thermal fluctuations due to the nanomagnets being maintained at a finite temperature T. Upon their inclusion, the precessional motion would endure because the heat bath the nanomagnets are contained in would provide energy. As discussed, Néel [84, 85] initiated the idea of thermal fluctuations of the magnetisation, which was further developed by Brown [87, 99, 106] who framed it in the context of the general theory of stochastic processes.

In order to include thermal fluctuations Brown [87] in 1963 added a random isotropic noise magnetic field $\mathbf{h}$ to the Landau-Lifshitz-Gilbert equation seen in Eq. (3.16) which in direct contrast to the *dissipative field* acts as a *source of energy* to the system

$$\dot{\mathbf{u}} = \gamma\left[(\mathbf{H}+\mathbf{h})\times\mathbf{u}\right] + \alpha[\mathbf{u}\times\dot{\mathbf{u}}]. \tag{4.4}$$

This is called the *magnetic Langevin equation.* The random magnetic field is regarded as *spatially isotropic Gaussian white noise* so that

$$\overline{h_i(t_1)} = 0, \ \overline{h_i(t_1)h_j(t_2)} = 2D\delta_{ij}\delta(t_1 - t_2), \tag{4.5}$$

where D is the noise-strength constant given by

$$D = \frac{\alpha kT}{v\gamma\mu_0 M_S}, \tag{4.6}$$

is determined through imposing the Boltzmann equilibrium distribution of orientations [2, 87], δ_{ij} is Kronecker's delta and $i, j = 1, 2, 3$ represent the Cartesian axes of the laboratory coordinate system. The overbars denote statistical averages over a very large number of moments, which have all started with the same orientation (ϑ, φ) (We are using spherical coordinates as seen in Figure 3.1). The random field accounts for the thermal fluctuations of the magnetisation of an *individual* single-domain particle. Note that according to Eq. (4.4) the magnitude of the magnetisation vector $\mathbf{M}$ does not fluctuate. However, since the random torque which arises from the noise field *counteracts* the damping torque it can, if the temperature is high enough, *reverse* the direction of the precession. The time taken for the reversal of the direction of precession over the ansisotropy-Zeeman energy barrier is known (as we have seen) as the *superparamagnetic (magnetisation) relaxation time.* Eq. (4.4) is often used in the treatment of stochastic magnetisation dynamics.

4.3 The Fokker-Planck Equation

As discussed earlier, the Langevin equation [2,45,104,105] is a stochastic differential equation which we can use to describe the time evolution of a Brownian particle undergoing Brownian motion in a thermal bath (fluid) obeying the dynamics of a Markov process. In solving it we can obtain information on the particle's trajectory. However, since the Langevin equation is stochastic, we will get different trajectories upon repeating the calculations with the same initial conditions. In other words, since $F(t)$ varies from system to system in the ensemble, the velocity will also vary from system to system (i.e., the velocity is stochastic). Therefore it would be expedient to instead investigate for an ensemble of Brownian particles how many of them have velocities in the interval $(v, v + dv)$ at time t. Since v is a continuous variable, we seek the answer to this through a probability distribution function $W(v)$. Then the interval dv times $W(v)$ is the probability of finding the Brownian particle in the interval $(v, v + dv)$. This distribution function will be dependent on both the time t and the initial conditions. The deterministic equation for $W(v, t)$ us given by

$$\frac{\partial W}{\partial t} = \beta \frac{\partial \left(vW\right)}{\partial v} + \frac{\beta kT}{m} \frac{\partial^2 W}{\partial v^2}, \tag{4.7}$$

where $v = \dot{x}$.

Eq. (4.7) is the *Fokker-Planck* equation for the distribution function of a free particle in velocity space and it is one of the simplest forms of that equation. The Fokker-Planck equation is generally an equation for the time evolution of the probability distribution function of fluctuating macroscopic variables [45]. It is a specialised form of the Boltzmann integral equation [45, 107]. The general form of the Fokker-Planck equation for one variable x is given by [45]

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial x}(D^{(1)}(x)W) + \frac{\partial^2}{\partial x^2}(D^{(2)}(x)W), \tag{4.8}$$

where $D^{(1)}(x)$ is the drift coefficient, and $D^{(2)}(x)$ is the diffusion coefficient [2, 45], both of which are calculated from the Langevin equation in order to obtain the Fokker-Planck equation, under the condition that the driving stimulus is Gaussian white noise in the Langevin equation [2]. Eq. (4.8) may also be generalised to N variables $\boldsymbol{\xi} = \xi_1, ..., \xi_N$ viz. [45]

$$\frac{\partial W}{\partial t} = -\sum_{i=1}^{N} \frac{\partial}{\partial \xi_i} \left[\left(D_i{}^{(1)} W \right) + \sum_{i,j=1}^{N} \frac{\partial}{\partial \xi_j} \left(D_{ij}{}^{(2)} W \right) \right], \tag{4.9}$$

where $W(\boldsymbol{\xi}, t)$ is the probability distribution function for N macroscopic variables $\boldsymbol{\xi} = \xi_1, ..., \xi_N$, and the drift vector $D_i^{(1)}$ and diffusion tensor $D_{ij}^{(2)}$ are themselves generally dependent on the N macroscopic variables. We shall describe two forms of the Fokker-Planck equation in the following sub-section.

4.3.1 The Klein-Kramers and Smoluchowski equations

The Klein-Kramers [45, 104] and the Smoluchowski [45, 104] equation are both special forms of the Fokker-Planck equation. The Klein-Kramers equation is used for obtaining the distribution functions in both velocity and position space describing the Brownian motion of particles under the influence of an external force. In the case of a particle moving in a one dimensional $x \in \mathbb{R}$ it is given by

$$\frac{\partial W(x,v,t)}{\partial t} = \left[-\frac{\partial}{\partial x}v + \frac{\partial}{\partial v}\left(\beta v - \frac{E(x)}{m}\right) + \frac{\beta kT}{m}\frac{\partial^2}{\partial v^2}\right] W(x,v,t), \tag{4.10}$$

where $\beta = \zeta/m$ is the friction coefficient per unit mass, m is the mass of the particle, T is the temperature of the fluid in question, k is Boltzmann's constant, and $E(x) = -mf'(x)$ is the external force where $mf(x)$ is the potential.

The system of stochastic differential equations in the phase space (x, v) corresponding to Eq. (4.10) is given by

$$\left.\begin{aligned} \dot{x} =& \ v, \\ \dot{v} =& -\beta v + \tfrac{E(x)}{m} + \tfrac{F(t)}{m}, \\ \langle F(t')F(t)\rangle =& \ 2\zeta kT\delta(t-t'). \end{aligned}\right\} \tag{4.11}$$

which can be written as the Langevin equation

$$m\ddot{x} + m\beta\dot{x} = E(x) + F(t). \tag{4.12}$$

Suppose then that the friction constant β is large, then in Eq. (4.12), we can neglect $m\ddot{x}$ as its value in this situation is negligible. We will end up with the Langevin equation

$$m\beta\dot{x} = E(x) + mF(t), \tag{4.13}$$

whose corresponding Fokker-Planck equation is given by

$$\frac{\partial W(x,t)}{\partial t} = \frac{1}{m\beta}\left[-\frac{\partial}{\partial x}E(x) + kT\frac{\partial^2}{\partial x^2}\right] W(x,t), \tag{4.14}$$

where now we have an equation of motion for the distribution function in just position space. This is called the Smoluchowski equation, which assumes that the velocity distribution has reached statistical equilibrium (i.e., It has the Maxwellian distribution). It was first given in 1905 by Einstein for the special case where $E = 0$ [104]. A detailed account of Smoluchowski's derivation of his equation is given by Mazo [108]. For the purpose of the thesis, the Smoluchowski equation will be utilised to discuss the Budó model in the non-inertial case.

4.4 Derivation of the Fokker-Planck Equation from the Langevin Equation

As discussed earlier, in order to obtain the Fokker-Planck equation from the Langevin equation, we need to evaluate the drift and diffusion coefficients from the Langevin equation. Here we will indicate the general form of the derivation process as shown by Risken [45] for a single stochastic variable $\xi(t)$ (for more information see Sections 1.9 and 1.10 of [2]). Recall that the general Langevin equation with one stochastic variable $\xi(t)$ is given by

$$\dot{\xi}(t) = h\left(\xi(t), t\right) + g\left(\xi(t), t\right) F(t), \tag{4.15}$$

and remark that the general form of the *multi-variable Fokker-Planck* equation is given by [45]

$$\frac{\partial W}{\partial t} = -\sum_{i=1}^{N} \frac{\partial}{\partial \xi_i}\left[\left(D_i{}^{(1)}W\right) + \sum_{i,j=1}^{N} \frac{\partial}{\partial \xi_j}\left(D_{ij}{}^{(2)}W\right)\right], \tag{4.16}$$

where the drift coefficients $D_i^{(1)}$ are given by

$$D_i^{(1)} = \lim_{\Delta t \to 0} \frac{\overline{\left[\xi_i(t+\Delta t) - x_i\right]}}{\Delta t}, \tag{4.17}$$

and the diffusion coefficients $D_{ij}^{(2)}$ are given by

$$D_{ij}^{(2)} = \lim_{\Delta t \to 0} \frac{\overline{\left[\xi_i(t+\Delta t) - x_i\right]\left[\xi_j(t+\Delta t) - x_j\right]}}{2\Delta t}. \tag{4.18}$$

In both the drift and diffusion coefficients, x_i are the state variables for initially sharp values at time t. It should be noted that we have made use of Isserlis's theorem [2, 107, 109] and Eq. (4.2) as well as the fact that the fluctuating force is zero-mean $\overline{F(t)} = 0$ in the Langevin equation as discussed earlier. It should be noted that the drift and diffusion coefficients are themselves the first two terms of the *Kramers-Moyal expansion* [45]. As an example we evaluate the drift and diffusion coefficients from the 1D equation (Eq. (4.15)), we start by following the procedure of Risken [2, 45] and treating Eq. (4.15) as an integral equation

$$\xi\left(t+\Delta t\right)=\xi\left(t\right)+\int_{t}^{t+\Delta t}\dot{\xi}\left(t'\right)dt'. \tag{4.19}$$

Substituting Eq. (4.15) into Eq. (4.19) we get

$$\xi\left(t+\Delta t\right)-x=\int_{t}^{t+\Delta t}\left[h\left(\xi\left(t'\right),t'\right)+g\left(\xi\left(t'\right),t'\right)F\left(t'\right)\right]dt', \tag{4.20}$$

where x is a sharp value of ξ at an initial time t.

Then we expand $h\left(\xi\left(t\right),t\right)$ and $g\left(\xi\left(t\right),t\right)$ as a Taylor series about the sharp value x,

$$\begin{aligned} h\left(\xi\left(t'\right),t'\right)=&h\left(x,t'\right)+\left(\xi\left(t'\right)-x\right)\frac{\partial}{\partial x}h\left(x,t'\right)+\ \ldots\ , \\ g\left(\xi\left(t'\right),t'\right)=&g\left(x,t'\right)+\left(\xi\left(t'\right)-x\right)\frac{\partial}{\partial x}g\left(x,t'\right)+\ \ldots\ . \end{aligned} \tag{4.21}$$

Iterating for $(\xi(t')-x)$ in Eq. (4.20) yields [45]

$$\begin{aligned} \xi\left(t+\Delta t\right)-x=&\int_{t}^{t+\Delta t}h\left(x,t'\right)dt'+\int_{t}^{t+\Delta t}\int_{t}^{t'}h\left(x,t''\right)\frac{\partial h\left(x,t'\right)}{\partial x}dt''dt' \\ &+\int_{t}^{t+\Delta t}\int_{t}^{t'}g\left(x,t''\right)\frac{\partial h\left(x,t'\right)}{\partial x}F\left(t''\right)dt''dt'+\int_{t}^{t+\Delta t}g\left(x,t'\right)F\left(t'\right)dt' \\ &+\int_{t}^{t+\Delta t}\int_{t}^{t'}h\left(x,t''\right)\frac{\partial g\left(x,t'\right)}{\partial x}F\left(t'\right)dt''dt' \\ &+\int_{t}^{t+\Delta t}\int_{t}^{t'}g\left(x,t''\right)\frac{\partial g\left(x,t'\right)}{\partial x}F\left(t''\right)F\left(t'\right)dt''dt'+\ldots\ , \end{aligned} \tag{4.22}$$

Eq. (4.22) is then simplified mindful of the definition Eq. (4.17). In so doing, we find that the terms in Eq. (4.22) containing $F(t')$ or $F(t'')$ will vanish due to the aforementioned fact that $\overline{F(t)} = 0$. Furthermore, the second term in Eq. (4.22) can be ignored as it is of the order $(\Delta t)^2$. However, the term containing $F(t')F(t'')$ can be rewritten using Eq. (4.2) and the delta function property

$$\int_a^b \delta\left(b - x\right) f\left(x\right) dx = \frac{1}{2} f\left(b\right), \tag{4.23}$$

so that

$$2D \int_t^{t'} g\left(x, t''\right) \delta\left(t' - t''\right) dt'' = D g\left(x, t'\right). \tag{4.24}$$

where $D = \zeta k T$.

Thus we get (for the drift coefficient) [45]

$$D^{(1)} = \lim_{\Delta t \to 0} \frac{\overline{\xi\left(t + \Delta t\right) - x}}{\Delta t} = h\left(x, t\right) + D g\left(x, t\right) \frac{\partial}{\partial x} g\left(x, t\right), \tag{4.25}$$

so that the last term on the right hand side is called the noise-induced drift and Eq. (4.25) may also be considered as an evolution equation for the sharp value x and so forms the basis of the Langevin method of treating the problem. It should be noted that due to Isserlis's theorem [2, 107, 109] all the higher order terms in Eq. (4.22) vanish in the limit of an infinitesimally small Δt. In a similar manner we can substitute Eq. (4.22) into Eq. (4.18) to get

$$\begin{aligned}
\left[\xi\left(t + \Delta t\right) - x\right]^2 = & \int_t^{t+\Delta t} \int_t^{t+\Delta t} h\left(x, t'\right) h\left(x, t''\right) dt' dt'' \\
& + 2 \int_t^{t+\Delta t} h\left(x, t'\right) dt' \int_t^{t+\Delta t} g\left(x, t'\right) dt' \\
& + \int_t^{t+\Delta t} \int_t^{t+\Delta t} g\left(x, t'\right) g\left(x, t''\right) F\left(t'\right) F\left(t''\right) dt' dt'' + \ldots .
\end{aligned} \tag{4.26}$$

So again the terms which have contributions of the order $(\Delta t)^2$ in Eq. (4.26) will vanish and again due to Isserlis's theorem [2, 107, 109] all the higher order terms will vanish. Thus we get

$$\begin{aligned}
\left[\xi\left(t + \Delta t\right) - x\right]^2 = & 2D \int_t^{t+\Delta t} \int_t^{t+\Delta t} g\left(x, t'\right) g\left(x, t''\right) \delta\left(t' - t''\right) dt' dt'' + O(\Delta t)^2 \\
= & 2D g^2\left(x, t + \Theta_1 \Delta t\right) \Delta t + O(\Delta t)^2,
\end{aligned} \tag{4.27}$$

where $(0 \leq \Theta_1 \leq 1)$. Thus upon substituting Eq. (4.27) into Eq. (4.18) we get for the diffusion coefficient [45]

$$D^{(2)} = \lim_{\Delta t \to 0} \frac{\overline{[\xi (t + \Delta t) - x]^2}}{2\Delta t} = Dg^2 (x, t) . \tag{4.28}$$

Thus from our deterministic drift and noise-induced drift Dgg' (Eq. (4.25)) and diffusion (Eq. (4.28)) coefficients we have the corresponding Fokker-Planck equation for $W(x, t)$

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial x} \left(h + Dg\frac{\partial g}{\partial x} \right) W + D\frac{\partial^2}{\partial x^2}(g^2 W). \tag{4.29}$$

We shall apply a similar methodology later to obtain the Smoluchowski equation [2, 45] from the non-inertial Langevin equation [2].

4.5 Obtaining the Differential-Recurrence Relation from the Fokker-Planck Equation

We have discussed earlier in the thesis the use of linear response theory to determine the time behaviour of statistical averages from the Langevin equation or the Fokker-Planck equation in order to obtain the linear response of a system to a weak applied stimulus. This was done using as example dielectric relaxation, where we are interested in the response to a small applied electric field. This is irrespective of whether we are studying the response to a field being switched on at some time $t = 0$, or the opposite case where the field was applied at $t = -\infty$ and is then suddenly switched off at time $t = 0$. In general, the method of calculating the average properties of a dynamical system (e.g., mean-square displacement, velocity correlation function, etc.) used is that once the Fokker-Planck equation (in phase space) is constructed from the Langevin equation for the random variables representing for example the position x and velocity v of a Brownian particle (or for the Smoluchowski equation, just the position), the distribution function is then expanded into a product of a set of orthogonal functions in the position, and/or an orthogonal set in the velocities. The coefficients of this (generalised Fourier series) correspond directly to the averages of the dynamical quantities which one wishes to calculate. This procedure leads to a set of differential-recurrence relations for the coefficients of the generalised Fourier series governing the time behaviour of the averages of the desired dynamical quantities (observables) in question. To demonstrate this we shall first derive the differential-recurrence relation for the Smoluchowski equation for an earlier paper by Coffey et al. published in 1993 [110]. This paper demonstrates "how exact formulas for the longitudinal and transverse dielectric correlation times and complex polarisability tensor, of a single axis rotator with two equivalent sites may be found. This is accomplished by writing the Laplace transforms of the dipole autocorrelation functions as three term recurrence relations and solving them in terms of continued fractions."

The Smoluchowski equation for the angular displacement φ of the rotator is

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial \varphi}\left(\frac{W}{\zeta}\frac{\partial V}{\partial \varphi}\right) + \frac{1}{\tau}\frac{\partial^2 W}{\partial \varphi^2}, \tag{4.30}$$

where $W(\varphi, t)$ is the probability density of orientations of a dipole on the unit circle, τ_D is the Debye relaxation time for a fixed axis rotator given by $\tau_D = \zeta/kT$, ζ is the viscous drag coefficient of the rotator. The potential $V(\varphi)$ is given by

$$V(\varphi) = U\sin^2\varphi - \mu E\cos\varphi, \tag{4.31}$$

where U is the potential barrier between the sites and $\boldsymbol{\mu}$ is the dipole moment of the rotator.

We seek the after-effect solution of the equation (where E is removed at $t = 0$). Since the solution of Eq. (4.30) must be periodic in φ, it can be assumed that it has the form of the Fourier series

$$W(\varphi, t) = \sum_{p=-\infty}^{\infty} a_p(t)e^{ip\varphi}. \tag{4.32}$$

Substituting Eq. (4.32) into Eq. (4.30) we get

$$\sum_{p=-\infty}^{\infty} \dot{a}_p(t)e^{ip\varphi} = \frac{\sigma}{\tau}\sum_{p=-\infty}^{\infty} a_p(t)((p+2)e^{i(p+2)\varphi} - (p-2)e^{i(p-2)\varphi}) - \frac{p^2}{\tau}\sum_{p=-\infty}^{\infty} a_p(t)e^{ip\varphi}. \tag{4.33}$$

What we need to do now in order to break down the summation to obtain the differential-recurrence relation is to take advantage of the orthogonality property of circular functions

$$\frac{1}{2\pi}\int_0^{2\pi} e^{-iq\varphi}e^{iq'\varphi}d\varphi = \frac{1}{2\pi}\int_0^{2\pi} e^{i(q'-q)\varphi}d\varphi = \delta_{qq'}. \tag{4.34}$$

To do this we shall multiply both sides of Eq. (4.33) by $e^{-iq\varphi}$ and then evaluate the integrals through exploiting the orthogonality property to get

$$\begin{aligned}\sum_{p=-\infty}^{\infty}\int_0^{2\pi}\dot{a}_p(t)e^{i(p-q)\varphi}d\varphi =& \frac{\sigma}{\tau}\sum_{p=-\infty}^{\infty}\int_0^{2\pi}a_p(t)((p+2)e^{i(p+2-q)\varphi}-(p-2)e^{i(p-2-q)\varphi})d\varphi\\ &-\frac{p^2}{\tau}\sum_{p=-\infty}^{\infty}\int_0^{2\pi}a_p(t)e^{i(p-q)\varphi}d\varphi.\end{aligned} \tag{4.35}$$

Using the orthogonality property of complex exponentials (see Eq. (4.34)) Eq. (4.35) becomes

$$\sum_{p=-\infty}^{\infty}\dot{a}_p(t)\delta_{pq} = \frac{\sigma}{\tau}\sum_{p=-\infty}^{\infty}a_p(t)((p+2)\delta_{p-2q}-(p-2))\delta_{p+2q}-\frac{p^2}{\tau}a_p(t)\delta_{pq}, \tag{4.36}$$

which by orthogonality leads to the final answer for the differential-recurrence relation

$$\dot{a}_p(t) = \frac{\sigma p}{\tau}(a_{p-2}(t)-a_{p+2}(t))-\frac{p^2}{\tau}a_p(t). \tag{4.37}$$

The solution of the differential recurrence-relation seen in Eq. (4.37) yields the correlation times in terms of modified Bessel functions of the first kind as detailed in [110]. Notice that a differential-recurrence relation is nearly always encountered in separating the variables in a diffusion equation rather than just simply a differential equation.

4.6 Solving Differential-Recurrence Relations via Continued Fractions

As we have seen, the solution of either the Langevin equation or the Fokker-Planck equation can be reduced to the solution of an infinite hierarchy of equations for the moments which describe the dynamics of the system in question. These equations can consist of three term or higher order differential-recurrence relations, and so the behaviour of any selected average is coupled to that of all the others. The solutions to these differential-recurrence relations can be found through the use of continued fractions [2, 34, 45], where for a scalar three-term recurrence relation, ordinary continued fractions can be used. If however the Langevin or Fokker-Planck equation cannot be reduced to a scalar three-term differential-recurrence relation, then one can convert a multi-term recurrence relation to a matrix three-term recurrence relation. This can then be formally solved in terms of matrix continued fractions [2, 34, 45, 111]. To demonstrate this procedure, we shall refer to section 2.7 of the book "The Langevin Equation: With Applications to Stochastic Problems in Physics, Chemistry and Electrical Engineering" [2].

Using Risken's notation [2, 45], we can generally write the three-term matrix differential-recurrence relation as

$$\tau_\varepsilon \frac{d}{dt}\mathbf{C}_p(t) = \mathbf{Q}_p^- \mathbf{C}_{p-1}(t) + \mathbf{Q}_p \mathbf{C}_p(t) + \mathbf{Q}_p^+ \mathbf{C}_{p+1}(t), \ (p \geq 1), \tag{4.38}$$

where τ_ε is a characteristic relaxation time, $\mathbf{C}_p(t)$ are column vectors formed from statistical moments with $\mathbf{C}_0(t) = \mathbf{0}$ and $\mathbf{Q}_p^\pm$, $\mathbf{Q}_p$ are time independent non-commutative matrices. Taking the Laplace transform of Eq. (4.38), we get

$$\mathbf{Q}_p^- \tilde{\mathbf{C}}_{p-1}(s) + (\mathbf{Q}_p - s\tau_\varepsilon \mathbf{I})\tilde{\mathbf{C}}_p(s) + \mathbf{Q}_p^+ \tilde{\mathbf{C}}_{p+1}(s) = -\tau_\varepsilon \mathbf{C}_p(0), \tag{4.39}$$

where $\mathbf{I}$ is the identity matrix, and

$$\mathbf{C}_p(s) = \int_0^\infty \mathbf{C}_p(t) e^{-st} dt. \tag{4.40}$$

The desired solution of Eq. (4.39) takes on the form of the sum of a complementary solution plus a particular integral just like a linear differential equation as

$$\tilde{\mathbf{C}}_p(s) = \mathbf{S}_p(s)\tilde{\mathbf{C}}_{p-1}(s) + \mathbf{R}_p(s), \tag{4.41}$$

where the matrix $\mathbf{S}_p(s)$ is given by

$$\mathbf{S}_p(s) = \left[s\tau_\varepsilon \mathbf{I} - \mathbf{Q}_p - \mathbf{Q}_p^+ \mathbf{S}_{p+1}(s)\right]^{-1} \mathbf{Q}_p^-, \tag{4.42}$$

which represents an infinite matrix continued fraction. Substituting Eq. (4.41) into Eq. (4.39) yields the following result for $\mathbf{R}_p(s)$ the particular solution

$$[s\tau_\varepsilon \mathbf{I} - \mathbf{Q}_p - \mathbf{Q}_p^+ \mathbf{S}_{p+1}(s)]\mathbf{R}_p(s) - \mathbf{Q}_p^+ \mathbf{R}_{p+1}(s) = \tau_\varepsilon \mathbf{C}_p(0), \tag{4.43}$$

therefore we have

$$\mathbf{R}_p(s) = \mathbf{\Delta}_p(s) \left[\tau_\varepsilon \mathbf{C}_p(0) + \mathbf{Q}_p^+ \mathbf{R}_{p+1}(s)\right], \tag{4.44}$$

where $\mathbf{\Delta}_p(s)$ is the matrix continued fraction given by

$$\mathbf{\Delta}_p(s) = \left[s\tau_\varepsilon \mathbf{I} - \mathbf{Q}_p - \mathbf{Q}_p^+ \mathbf{\Delta}_{p+1}(s)\mathbf{Q}_{p+1}^-\right]^{-1}. \tag{4.45}$$

Through iteration, we can solve for Eq. (4.44) to get

$$\mathbf{R}_p(s) = \tau_\varepsilon \mathbf{\Delta}_p(s) \left[\mathbf{C}_p(0) + \sum_{n=1}^{\infty} \prod_{k=1}^{n} \mathbf{Q}_{p+k-1}^+ \mathbf{\Delta}_{p+k}(s)\mathbf{C}_{p+n}(0)\right], \tag{4.46}$$

which can be substituted into Eq. (4.41) to get the formal complete solution [111]

$$\tilde{\mathbf{C}}_p(s) = \mathbf{S}_p(s)\tilde{\mathbf{C}}_{p-1}(s) + \tau_\varepsilon \mathbf{\Delta}_p(s) \left[\mathbf{C}_p(0) + \sum_{n=1}^{\infty} \prod_{k=1}^{n} \mathbf{Q}_{p+k-1}^+ \mathbf{\Delta}_{p+k}(s)\mathbf{C}_{p+n}(0)\right], \tag{4.47}$$

which is the complete solution of Eq. (4.39) rendered in algebraic form as a calculable sum of products of matrix continued fractions in the s domain. For $\tilde{\mathbf{C}}_1(s)$, the *exact* *solution* is given by

$$\tilde{\mathbf{C}}_1(s) = \tau_\varepsilon \mathbf{\Delta}_1(s) \left[\mathbf{C}_1(0) + \sum_{n=1}^{\infty} \prod_{k=1}^{n} \mathbf{Q}_k^+ \mathbf{\Delta}_{k+1}(s) \mathbf{C}_{n+1}(0) \right], \tag{4.48}$$

The initial condition vectors $\mathbf{C}_p(0)$ can be expressed in terms of equilibrium (stationary in the general case) averages. These averages will be solutions of the time independent vector recurrence relation

$$\mathbf{Q}_p^- \mathbf{C}_{p-1}^0 + \mathbf{Q}_p \mathbf{C}_p^0 + \mathbf{Q}_p^+ \mathbf{C}_{p+1}^0 = \mathbf{0}, \tag{4.49}$$

where the column vector $\mathbf{C}_p^0$ is formed from equilibrium (stationary) averages. Since Eq. (4.49) is tri-diagonal, it is possible to express $\mathbf{C}_p^0$ in terms of the matrix continued fraction $\mathbf{S}_p(0)$, which is obtained from letting $s = 0$ in Eq. (4.42). Considering Eq. (4.49) for $p = 1$ we have

$$\mathbf{Q}_1^- \mathbf{C}_0^0 + \mathbf{Q}_1 \mathbf{C}_1^0 + \mathbf{Q}_1^+ \mathbf{C}_2^0 = \left[\mathbf{Q}_1^- + \mathbf{Q}_1 \mathbf{S}_1(0) + \mathbf{Q}_1^+ \mathbf{S}_2(0) \mathbf{S}_1(0) \right] \mathbf{C}_0^0 = \mathbf{0}, \tag{4.50}$$

where $\mathbf{C}_0^0$ is given by

$$\mathbf{C}_0^0 = \begin{pmatrix} C_0^1 \\ \vdots \\ C_0^P \end{pmatrix}. \tag{4.51}$$

We may always choose a particular element of $\mathbf{C}_0^0$ (e.g. $C_0^P = 1$) because of the normalisation condition. This leads to Eq. (4.50) representing a set of *inhomogeneous* linear equations. Therefore $C_0^1, C_0^2, ..., C_0^P$ can be determined. The other vectors $\mathbf{C}_p^0$ are obtained viz.,

$$\mathbf{C}_p^0 = \mathbf{S}_p(0) \mathbf{S}_{p-1}(0) ... \mathbf{S}_1(0) \mathbf{C}_0^0. \tag{4.52}$$

5. Generalization to Anomalous Diffusion of Budó's Treatment of Polar Molecules containing Interacting Rotating Groups

5.1 Fractional Smoluchowski Equation for Non-Interacting Molecules containing Polar Rotating Groups

In Budó's dynamical treatment [12,16] of hindered rotation a typical rotating polar molecule of a non-interacting assembly contains two interacting groups, 1 and 2 of equal size having a common rotational axis (see Figure 5.1) about which the entire molecule can rotate. The dipole moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ of the embedded groups are also supposed perpendicular to the molecular axis z. We specify the orientation of each group (denoted by the subscript $j = 1, 2$) by a set of three Eulerian angles (Figure 5.1a), namely $(\theta, \varphi, \psi_j)$, which are always functions of time because of the physical rotation of the molecule due to the external field and Brownian torques. The Eulerian angles θ and φ determine the orientation of the common molecular axis z and coincide for both groups, while the angle ψ_j determines the angular position of $\boldsymbol{\mu}_j$ in the plane perpendicular to the z-axis (Figure 5.1b).

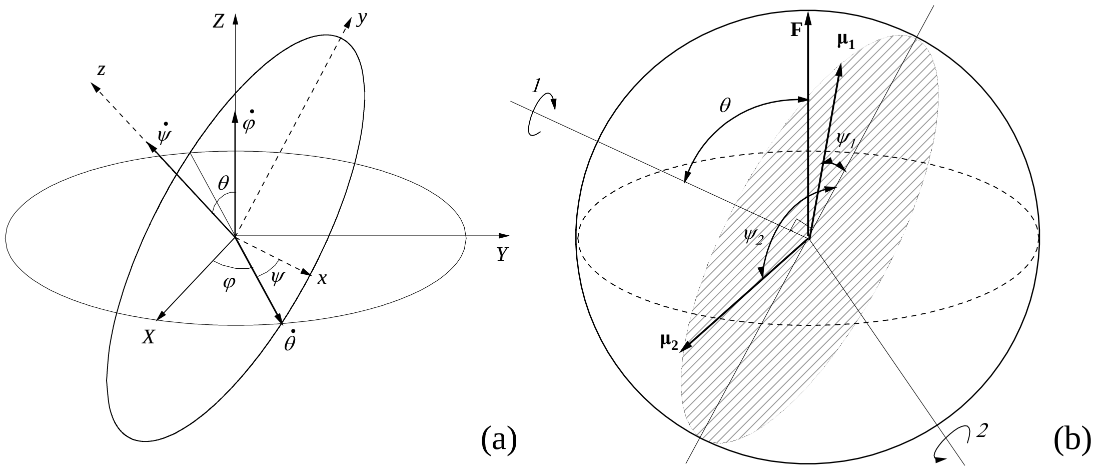

Figure 5.1: Geometry of the task; (a) Eulerian angles (aft. [58]); (b) the molecule consisting of two interacting groups. Notation follows that of L.D. Landau and E. M. Lifshitz, Mechanics, Volume 1 of Course of Theoretical Physics, 3rd Ed., Pergamon, 1976, p. 110, Figure 47. (aft. [58])

Clearly the mutual potential energy of the groups giving rise to the hindered rotation is then a function of the angular difference $\psi_1 - \psi_2$ only. We consider [19], following Budó [16], cosine coupling, and consequently the interaction potential is [16, 112]

$$V(\psi_1 - \psi_2) = -V_0 \cos(\psi_1 - \psi_2). \tag{5.1}$$

The torque exerted by the dipole $\boldsymbol{\mu}_2$ on $\boldsymbol{\mu}_1$, is then $-V'(\psi_1 - \psi_2)$, where the prime means differentiation with respect to the argument of V. The system of coupled non-inertial Langevin equations (involving multiplicative noise) of motion of the polar groups in a dc field $\mathbf{F}$ applied in the Z direction of the space-fixed system appropriate to the Budó model [16] are (as shown in Appendix 5.B)

$$\dot{\theta} = -\sum_{i=1,2}\left[\frac{\mu_j F}{\xi}\cos\theta\cos\psi_i - \sqrt{\frac{kT}{2\xi}}\left(\cos\psi_i\Lambda_x^{(i)} - \sin\psi_i\Lambda_y^{(i)}\right)\right], \tag{5.2}$$

$$\begin{aligned}\dot{\psi}_j &= \cot\theta\sum_{i=1,2}\left[\frac{\mu_i F}{\xi}\cos\theta\sin\psi_i - \sqrt{\frac{kT}{2\xi}}\left(\sin\psi_i\Lambda_x^{(i)} + \cos\psi_i\Lambda_y^{(i)}\right)\right] \\ &\quad + \frac{F\mu_j}{\xi_z}\sin\theta\sin\psi_j + (-1)^j\frac{V'(\psi_1-\psi_2)}{\xi_z} + \sqrt{\frac{kT}{\xi_z}}\Lambda_z^{(j)},\end{aligned} \tag{5.3}$$

where k is Boltzmann's constant, T is the temperature, $\xi_x = \xi_y = \xi$ are the drag coefficients for rotations about axis 2 (v. Figure 5.1b) while ξ_z is that for rotations about axis 1. The projection of $\boldsymbol{\mu}_j$ on $\mathbf{F}$ does not depend on the Eulerian angle φ owing to the circular symmetry, while the entire molecule rotates about the direction of $\mathbf{F}$. Thus, the equation of motion of φ is not needed. In Eqs. (5.2) and (5.3) the white noise torques $\Lambda_k^{(j)}$ are supposed to be centred Gaussian random variables with correlation functions [2]

$$\left\langle \Lambda_k^{(j)}(t)\Lambda_{k'}^{(j)}(t') \right\rangle = 2\delta_{kk'}\delta(t-t'), \quad k,k' = x,y,z, \tag{5.4}$$

where $\delta_{kk'}$ is Kronecker's delta and $\delta(t)$ is the Dirac delta function. Notice that Budó originally treated his model [15] via the appropriate Smoluchowski equation, which he determined without explicitly mentioning the Langevin equations (5.2) and (5.3) at all, by suitably adapting the method of Debye for rotation in space as described in Chapter V of his book *Polar Molecules* [3]. The Budó model of course ignores inertial effects and thus is invalid at far-infrared or THz frequencies.

The general method of derivation of the Smoluchowski (Fokker-Planck) equation in terms of the hydrodynamical derivative of the probability density $f(\boldsymbol{\Omega},t)$ in the configuration space of orientations $\boldsymbol{\Omega}$ ($\boldsymbol{\Omega}$ denotes the set of state variables, i.e., $\{\theta,\psi_1,\psi_2\}$) for normal diffusion from the corresponding Langevin equations [2] (v. Appendix 5.B) yields that evolution equation in the standard form [2] of a Boltzmann equation

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \hat{\mathrm{L}}f = \mathrm{St}(f). \tag{5.5}$$

Here the deterministic operator is defined by (see Appendix 5.C) [2, 15, 16]

$$\begin{aligned}\hat{\mathrm{L}}f =& \Bigg\{ \frac{F}{\xi}\Bigg[(\mu_1\sin\psi_1 + \mu_2\sin\psi_2)\frac{\cos^2\theta}{\sin\theta}\left(\frac{\partial}{\partial\psi_1}+\frac{\partial}{\partial\psi_2}\right) \\ &+ \left(\left(1+\frac{\xi}{\xi_z}\right)\sin\theta - \cos\theta\frac{\partial}{\partial\theta}\right)\sum_{i=1,2}\mu_i\cos\psi_i + \frac{\xi}{\xi_z}\sin\theta\sum_{i=1,2}\mu_i\sin\psi_i\frac{\partial}{\partial\psi_i}\Bigg] \\ &- \frac{V'(\psi_1-\psi_2)}{\xi_z}\left(\frac{\partial}{\partial\psi_1}-\frac{\partial}{\partial\psi_2}\right) - 2\frac{V''(\psi_1-\psi_2)}{\xi_z}\Bigg\} f,\end{aligned} \tag{5.6}$$

while the collision kernel is

$$\mathrm{St}(f) = \frac{kT}{\xi}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + 2\mathrm{cot}^2\theta\frac{\partial^2}{\partial\psi_1\psi_2} + \left(\mathrm{cot}^2\theta + \frac{\xi}{\xi_z}\right)\sum_{i=1,2}\frac{\partial^2}{\partial{\psi_i}^2}\right]f. \quad (5.7)$$

To determine the fractional Smoluchowski equation from the general form Eq. (5.5) we again use as in the entirely different problem of inertial effects in the itinerant oscillator model as treated in Ref. [20] a method of Barkai and Silbey [113]. This originally entailed writing a fractional Klein-Kramers equation in phase space (q, p) for the evolution of the joint probability density function of the positions q and momenta p of a translating particle from the normal Klein-Kramers equation. However, we can also apply this method to the problem at hand. Therefore in order to achieve this in our configuration space $\mathbf{\Omega}$ of orientations we simply introduce the fractional operator ${}_0D_t^{1-\alpha}$ in the right-hand side of Eq. (5.5), so that this equation becomes [2, 20] the fractional diffusion equation [19]

$$\frac{\partial f}{\partial t} + \hat{\mathrm{L}}f = \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\mathrm{St}\,(f)\,. \quad (5.8)$$

The fractional operator ${}_0D_t^{1-\alpha} \equiv \frac{\partial}{\partial t}\,{}_0D_t^{-\alpha}$ in Eq. (5.8) is defined via the convolution (the Riemann-Liouville definition) [79–82]

$${}_0D_t^{-\alpha}f(\,\mathbf{\Omega}, t) = \frac{1}{\Gamma(\alpha)}\int_0^t \frac{f(\mathbf{\Omega}\,, t')dt'}{(t-t')^{1-\alpha}}, \quad (5.9)$$

$\Gamma(\alpha)$ denoting the gamma function [83]. In selecting the fractional Smoluchowski equation for the time evolution of the probability density function in configuration space in this way we should mention that alternative forms of that equation exist and have been reviewed by Friedrich and coworkers [114–116]. However, the Barkai and Silbey version, which we have already used [2, 20] appears the most suitable for the explanation of the dielectric susceptibility at microwave frequencies [2]. The reason is that including inertial effects in their equation as applied to the original Debye model of non-interacting rotating dipoles then correctly describes the THz behaviour of the absorption coefficient in so far as optical transparency is regained at those frequencies. Clearly, the fractional derivative is in itself just another *Stosszahlansatz* for the Boltzmann equation for the single particle distribution function of which Eqs. (5.5) and (5.8) are essentially particular configuration space forms. We now assert (in essence following Barkai and Silbey who imposed the Maxwell-Boltzmann distribution as the stationary solution of their fractional Klein-Kramers equation) that the stationary solution of the fractional Smoluchowski equation is the Boltzmann distribution, which must prevail on physical grounds. Hence we require that the operator ${}_0D_t^{1-\alpha}$ in Eq. (5.8) must not act on the deterministic terms in the convective derivative $\dot{f}$ so that the conventional form [2] of a Boltzmann equation with Brownian motion *Stosszahlansatz* as modified by ${}_0D_t^{1-\alpha}$ is preserved. Here we recall the work of Heymans and Podlubny [117] concerning the choice of initial conditions on physical grounds. In a normal diffusion process, $\alpha = 1$. If $\alpha > 1$, the phenomenon is called super-diffusion. If $\alpha < 1$, the particle undergoes sub-diffusion.

5.2 Statistical Moments and Response Functions

To use linear response theory, we suppose as usual that a weak external dc field $\mathbf{F}$, having been applied to the system in the infinite past ($t \to -\infty$), is suddenly switched off at time $t = 0$, meaning that we study the relaxation of a typical molecule with embedded groups, starting from an initial equilibrium state at $t = 0$ with Boltzmann distribution given by

$$f_F(\mathbf{\Omega}) = Z_F^{-1} e^{\frac{(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2)\cdot\mathbf{F}}{kT} + \sigma_V \cos(\psi_1-\psi_2)}, \tag{5.10}$$

to another equilibrium state as $t \to \infty$ with new Boltzmann distribution

$$f_0(\mathbf{\Omega}) = f_{F=0}(\mathbf{\Omega}) = Z_0^{-1} e^{\sigma_V \cos(\psi_1-\psi_2)}, \tag{5.11}$$

where $\sigma_V = V_0/kT$ is the dimensionless interaction parameter. The dynamics of the molecule immediately following the removal of $\mathbf{F}$ may then be described by the normalised relaxation function (see Appendix 5.D) [8, 29]

$$C(t) = \frac{\mu_1 c_1(t) + \mu_2 c_2(t)}{\mu_1 c_1(0) + \mu_2 c_2(0)} = \frac{c_1(t) + \kappa c_2(t)}{c_1(0) + \kappa c_2(0)}, \; t > 0, \tag{5.12}$$

where $\mu_2 = \kappa\mu_1$ so that κ is the dipole moment ratio and from inspection of Figure 5.1b we have defined individual response (after-effect) functions

$$c_i(t) = \langle \sin\theta \cos\psi_i \rangle (t). \tag{5.13}$$

Here $i = 1, 2$, the angular brackets $\langle A \rangle (t)$ represent the time-dependent ensemble averages associated with the relaxation of an observable A while $\langle A \rangle_0$ represents the equilibrium ensemble averages, namely

$$\langle A \rangle_0 = \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} A(\theta, \psi_1, \psi_2) f_0(\theta, \psi_1, \psi_2) \sin\theta d\theta d\psi_1 d\psi_2. \tag{5.14}$$

In the linear approximation in $\mathbf{F}$, which requires that the external field parameters $\sigma_i = \mu_i F/(kT) << 1$, the initial conditions for the after effect-functions $c_1(t)$ and $c_2(t)$ are

$$c_i(0) \approx \sigma_i \left\langle \sin^2\theta \cos^2\psi_i \right\rangle_0 + \sigma_{3-i} \left\langle \sin^2\theta \cos\psi_1 \cos\psi_2 \right\rangle_0. \tag{5.15}$$

The complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ can then be determined from the usual formula of linear response theory [18, 29]

$$\frac{\chi(\omega)}{\chi} = 1 - i\omega \int_0^{\infty} C(t) e^{-i\omega t} dt, \tag{5.16}$$

where $\chi = \chi'(0) = [\mu_1 c_1(0) + \mu_2 c_2(0)] / F$ is the static susceptibility and the normalized relaxation function $C(t)$ is given by Eq. (5.12).

To simplify the fractional diffusion equation Eq. (5.8) we now follow Budó and introduce the new variables [19] (see Appendix 5.E)

$$\nu = \frac{(\psi_1 + \psi_2)}{2}, \; \eta = \frac{(\psi_1 - \psi_2)}{2}. \tag{5.17}$$

Thus, we have the equation describing the relaxation process for $t > 0$ ($\mathbf{F} = 0$)

rendered as [19]

$$
\begin{aligned}
2\tau\frac{\partial f}{\partial t} = & \left\{ \frac{\tau}{\tau_z}\sigma_V \left[\sin 2\eta \frac{\partial}{\partial \eta} + 2\cos 2\eta\right] \right. \\
& \left. + \tau^{1-\alpha}\, {}_0D_t^{1-\alpha}\left[\Delta_{\theta,\nu} + \left(\frac{\tau}{2\tau_z} - 1\right)\frac{\partial^2}{\partial \nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial \eta^2}\right]\right\} f, \qquad (5.18)
\end{aligned}
$$

where $\Delta_{\theta,\nu}$ is the angular part of the Laplacian written in the spherical coordinates θ and ν, $\tau = \xi/(2kT)$ is the Debye relaxation time for rotations about the x and y axes and $\tau_z = \xi_z/(2kT)$ is the Debye relaxation time for rotation about the z axis.

The form of the fractional Smoluchowski equation (5.18) suggests seeking its solution as a Fourier-Laplace series [8] rather than reducing it to a Sturm-Liouville like eigenvalue problem as done by Budó [16] for normal diffusion because this procedure ultimately leads to the solution for $\chi(\omega)$ as a scalar continued fraction which is easily computed, thus

$$
f(\theta, \nu, \eta, t) = \frac{1}{2\pi}\sum_{l,p,q} f_{pq}^l(t) Y_{lp}^*(\theta, \nu) e^{-iq\eta}. \qquad (5.19)
$$

The Fourier amplitudes $f_{pq}^l(t)$ are the statistical moments defined by

$$
f_{pq}^l(t) = \int Y_{lp}(\theta, \nu) e^{iq\eta} f(\theta, \nu, \eta, t) d\Omega' = \left\langle Y_{lp}(\theta, \nu) e^{iq\eta} \right\rangle (t), \qquad (5.20)
$$

where $d\Omega' = \sin\theta d\theta d\nu d\eta$, $Y_{lp}(\theta, \nu)$ are the spherical harmonics, $l = 0, 1, 2, ...$, $p = 0, \pm 1, ..., \pm l$ and $q = 0, \pm 2, \pm 4, ...$ for even p and $q = \pm 1, \pm 3, ...$ for odd p.

By substituting Eq. (5.19) into Eq. (5.8), we then have the differential-recurrence equations for the $f_{pq}^l(t)$ in the following three-index (pql) form [19] (see Appendix 5.F)

$$
\begin{aligned}
2\tau\frac{d}{dt} f_{pq}^l(t) = & \left\{ \frac{\tau\sigma_V}{2\tau_z} q \left[f_{pq-2}^l(t) - f_{pq+2}^l(t)\right] \right. \\
& \left. - \tau^{1-\alpha}\, {}_0D_t^{1-\alpha}\left[l(l+1) + p^2\left(\frac{\tau}{2\tau_z} - 1\right) + q^2\frac{\tau}{2\tau_z}\right] f_{pq}^l(t)\right\}, \qquad (5.21)
\end{aligned}
$$

which as it stands leads to a three-term matrix differential recurrence relation [2].

5.3 Continued Fraction Solution of the Fractional Smoluchowski Equation

The definition of the response function as given by Eq. (5.13) indicates however that only the Fourier amplitudes f^{1}_{-1q} are needed in order to calculate $C(t)$. Therefore, to facilitate this, we introduce new functions defined by (cf. Eqs. (5.19) and (5.20))

$$a^c_q(t) = \langle Y_{1-1} \cos q\eta \rangle (t), \;\; a^s_q(t) = \langle Y_{1-1} \sin q\eta \rangle (t). \tag{5.22}$$

Their time behaviour is then described by an equation following directly from Eq. (5.21), namely [19] (see Appendix 5.G)

$$2\tau \frac{d}{dt} a^J_{2q-1}(t) = Q^-_{2q-1} a^J_{2q-3}(t) + Q^+_{2q-1} a^J_{2q+1}(t) + \tau^{1-\alpha}\, {}_0D^{1-\alpha}_t Q_{2q-1} a^J_{2q-1}(t), \tag{5.23}$$

where $J = c, s,\;\; q = 1, 2, 3, ...,\; a^c_{-1}(t) = a^c_1(t),\; a^s_{-1}(t) = -a^s_1(t)$, and

$$Q_{2q-1} = -1 - \gamma \left(1 + (2q-1)^2\right),\; Q^{\pm}_{2q-1} = \mp \sigma_V \gamma (2q-1), \tag{5.24}$$

and $\gamma = \tau/(2\tau_z)$ is a ratio of Debye times. However, the new set of Eqs. (5.23) simply constitutes a single index (q) three-term differential-recurrence equation so that the calculation of $a^J_q(t)$ is relatively simple (because its solution may then be expressed as a scalar continued fraction unlike that of the three-index differential recurrence relation obtaining when $\mathbf{F} \neq 0$ leading to three-term matrix fractions).

On taking the Laplace transform of Eq. (5.23), we then have an algebraic three-term recurrence equation in the frequency domain, viz.,

$$(1-\delta_{q1})\, Q^-_{2q-1} \tilde{a}^J_{2q-3}(s) + \left(\bar{Q}_{2q-1}(s) + b^J \delta_{q1}\right) \tilde{a}^J_{2q-1}(s) + Q^+_{2q-1} \tilde{a}^J_{2q+1}(s) = -2\tau a^J_{2q-1}(0), \tag{5.25}$$

where $b^c = \gamma\sigma_V$, $b^s = -\gamma\sigma_V$,

$$\bar{Q}_q(s) = (\tau s)^{1-\alpha} Q_q - 2\tau s, \tag{5.26}$$

and

$$\tilde{a}_q^J(s) = \int_0^\infty a_q^J(t)e^{-st}dt. \tag{5.27}$$

The initial values are determined from Eqs. (5.10) and (5.22) yielding the closed form as follows (see Appendix 5.I):

$$\begin{aligned} a_q^c(0) =& Z_F^{-1} \int Y_{1-1}(\theta,\nu)\cos q\eta\, e^{(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2)\mathbf{F}/kT+\sigma_V\cos 2\eta}d\Omega' \\ =& \frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi}I_0(\sigma_V)}\left(I_{(q+1)/2}(\sigma_V)+I_{(q-1)/2}(\sigma_V)\right), \end{aligned} \tag{5.28}$$

and

$$\begin{aligned} a_q^s(0) =& Z_F^{-1} \int Y_{1-1}(\theta,\nu)\sin q\eta\, e^{(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2)\mathbf{F}/kT+\sigma_V\cos 2\eta}d\Omega' \\ =& \frac{i\sigma_1(\kappa-1)}{4\sqrt{6\pi}I_0(\sigma_V)}\left(I_{(q+1)/2}(\sigma_V)-I_{(q-1)/2}(\sigma_V)\right), \end{aligned} \tag{5.29}$$

where the $I_m(\sigma_V)$ are the modified Bessel functions of the first kind of order m [83].

By invoking the familiar continued-fraction method for solving scalar three-term recurrence relations [2], we have the explicit solution for the desired spectrum $\tilde{a}_1^J(s)$ in the form of a scalar continued fraction, viz., (see Appendix 5.J)

$$\tilde{a}_1^J(s) = 2\tau\frac{a_1^J(0)+Q_1^+\Delta_3(s)\left(a_3^J(0)+Q_3^+\Delta_5(s)\left(a_5^J(0)+...\right)\right)}{-\bar{Q}_1(s)+s_J\gamma\sigma_V-Q_1^+\Delta_3(s)Q_3^-}, \tag{5.30}$$

where $s_c = -1$ and $s_s = 1$. The recurring quantity $\Delta_n(s)$ (corresponding to the complementary solution) is calculated by taking successive convergents from its continued-fraction definition viz.,

$$\Delta_{2n-1}(s) = \left[-\bar{Q}_{2n-1}(s)-Q_{2n-1}^+\Delta_{2n+1}(s)Q_{2n+1}^-\right]^{-1}. \tag{5.31}$$

Having determined $\tilde{a}_1^J(s)$, we have the spectrum of the relaxation function $C(t)$ from Eq. (5.12)

$$\tilde{C}(i\omega) = \frac{\tilde{c}_1(i\omega)+\kappa\tilde{c}_2(i\omega)}{c_1(0)+\kappa c_2(0)}. \tag{5.32}$$

The response functions $\tilde{c}_i(i\omega)$ are expressed in terms of one-sided Fourier transforms of $a_1^J(t)$ as (see Appendix 5.K)

$$\tilde{c}_j(\omega) = \sqrt{\frac{2\pi}{3}}\left(\tilde{a}_1^c(\omega) + \tilde{a}_1^{c*}(-\omega) + (-1)^j i\left(\tilde{a}_1^s(\omega) - \tilde{a}_1^{s*}(-\omega)\right)\right), \tag{5.33}$$

where the initial conditions are rendered in the closed form (see Appendix 5.L)

$$\begin{aligned} c_j(0) =& \sqrt{\frac{2\pi}{3}}\left(a_1^c(0) + a_1^{c*}(0) + (-1)^j i\left(a_1^s(0) - a_1^{s*}(0)\right)\right) \\ =& \frac{\sigma_1}{3}\frac{I_{j-1}(\sigma_V) + \kappa I_{2-j}(\sigma_V)}{I_0(\sigma_V)}. \end{aligned} \tag{5.34}$$

Eqs. (5.30) - (5.34) taken in combination yield the solution for the linear response. Notice that they also apply to the normal diffusion, entirely avoiding the Sturm-Liouville problem encountered by Budó.

Appendices - Details of the various calculations

5.A Langevin Equations for a Single Dipole

The equation of motion for a rigid body in the non-inertial case is

$$\boldsymbol{\xi}\boldsymbol{\omega}(t) = [\boldsymbol{\mu}(t) \times \mathbf{F}(t)] + \boldsymbol{\Gamma}(t), \tag{5.35}$$

where $\boldsymbol{\Gamma}(t) = (\Gamma_x(t), \Gamma_y(t), \Gamma_z(t))^{\mathrm{T}}$ is the Gaussian white noise torque arising from the heat bath and is represented by a Wiener process, the angular velocity $\boldsymbol{\omega}(t) = (\omega_x(t), \omega_y(t), \omega_z(t))^{\mathrm{T}}$, $[\boldsymbol{\mu}(t) \times \mathbf{F}(t)]$ is the deterministic external torque arising from $\mathbf{F}(t)$, $\boldsymbol{\xi}\boldsymbol{\omega}(t)$ is the frictional torque and

$$\boldsymbol{\xi} = \left\{\begin{array}{ccc} \xi_x & 0 & 0 \\ 0 & \xi_y & 0 \\ 0 & 0 & \xi_z \end{array}\right\}, \tag{5.36}$$

is the tensor of the friction coefficients, which is diagonal in molecular fixed axes.

Consider a dipole $\boldsymbol{\mu}$ with the following components referred to the *molecular* *fixed* axes

$$\boldsymbol{\mu} = (0,\ \mu,\ 0)\,. \tag{5.37}$$

The electric field $\mathbf{F}(t)$ can be expressed as

$$\mathbf{F}\,(t) = F\sin\theta\sin\psi\,\mathbf{i} + F\sin\theta\cos\psi\,\mathbf{j} + F\cos\theta\,\mathbf{k}, \tag{5.38}$$

where $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the unit vectors in the directions of the molecular axes x, y, z respectively. The cross product $\boldsymbol{\mu}\,(t) \times \mathbf{F}\,(t)$ is given by

$$[\boldsymbol{\mu}\,(t) \times \mathbf{F}\,(t)] = \mu F\cos\theta\,\mathbf{i} + 0\,\mathbf{j} - \mu F\sin\theta\sin\psi\,\mathbf{k}. \tag{5.39}$$

From the equation of motion in Eq. (5.35), we get

$$\xi_x\omega_x = \mu F\cos\theta + \Gamma_x, \tag{5.40}$$

$$\xi_y\omega_y = \Gamma_y, \tag{5.41}$$

$$\xi_z\omega_z = -\,\mu F\sin\theta\sin\psi + \Gamma_z. \tag{5.42}$$

The Eulerian angles θ, φ, ψ are shown in Figure 5.2. These angles connect molecular fixed axes xyz with laboratory fixed axes XYZ. The angular velocities $\omega_x,\ \omega_y,\ \omega_z$ can now be expressed in terms of these angles and their time derivatives [58].

$$\omega_x = \dot\varphi\sin\theta\sin\psi + \dot\theta\cos\psi, \tag{5.43}$$

$$\omega_y = \dot\varphi\sin\theta\cos\psi - \dot\theta\sin\psi, \tag{5.44}$$

$$\omega_z = \dot\varphi\cos\theta + \dot\psi. \tag{5.45}$$

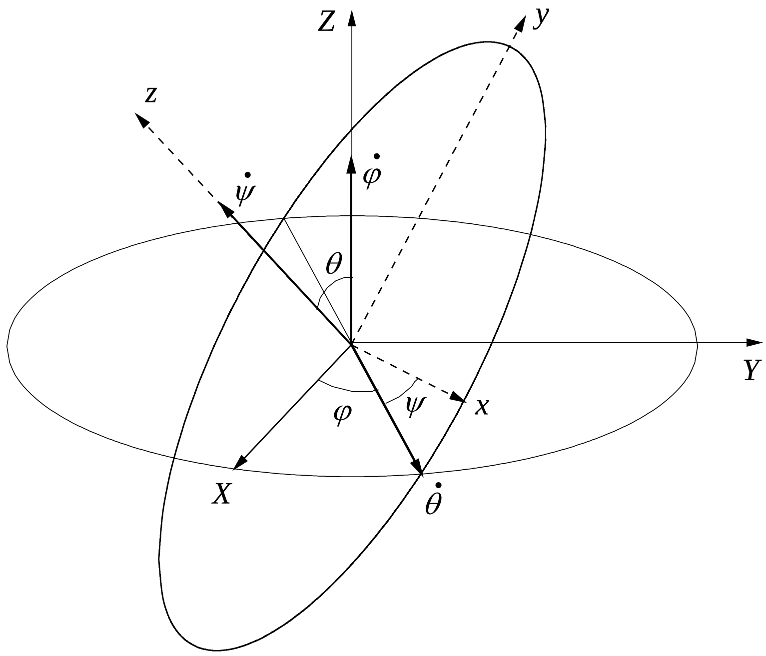

Figure 5.2: Eulerian angles. (aft. [118])

The Gaussian noise torques Γ_i are given by [2]

$$\Gamma_i = \sqrt{kT\xi_i}\Lambda_i \;, \quad i = x, y, z, \tag{5.46}$$

$$\xi = \xi_x = \xi_y, \tag{5.47}$$

where Λ_i are centred Gaussian random variables with correlation functions [2]

$$\left\langle \Lambda_k^{(j)}(t)\Lambda_{k'}^{(j)}(t') \right\rangle = 2\delta_{kk'}\delta(t - t'), \quad k, k' = x, y, z, \tag{5.48}$$

where $\delta_{kk'}$ is Kronecker's delta and $\delta(t)$ is the Dirac delta function.

Substituting Eq. (5.46) into Eqs. (5.40) - (5.42), we obtain

$$\xi\omega_x = \mu F \cos\theta + \sqrt{kT\xi}\Lambda_x, \tag{5.49}$$

$$\xi\omega_y = \sqrt{kT\xi}\Lambda_y, \tag{5.50}$$

$$\xi_z\omega_z = -\mu F \sin\theta \sin\psi + \sqrt{kT\xi_z}\Lambda_z. \tag{5.51}$$

From Eqs. (5.43) - (5.45), and Eqs. (5.49) - (5.51) we have

$$\begin{aligned}\dot{\varphi}\sin\theta\sin\psi+\dot{\theta}\cos\psi &= \frac{\mu F}{\xi}\cos\theta+\sqrt{\frac{kT}{\xi}}\Lambda_x, &(5.52)\\ \dot{\varphi}\sin\theta\cos\psi-\dot{\theta}\sin\psi &= \sqrt{\frac{kT}{\xi}}\Lambda_y, &(5.53)\\ \dot{\varphi}\cos\theta+\dot{\psi} &= -\frac{\mu F}{\xi_z}\sin\theta\sin\psi+\sqrt{\frac{kT}{\xi_z}}\Lambda_z. &(5.54)\end{aligned}$$

To obtain an expression for $\dot{\theta}$, we shall multiply Eq. (5.53) by $\sin\psi$ then subtract it from Eq. (5.52) multiplied by $\cos\psi$ to get

$$\dot{\theta}=\frac{\mu F}{\xi}\cos\theta\cos\psi+\sqrt{\frac{kT}{\xi}}\left(\Lambda_x\cos\psi-\Lambda_y\sin\psi\right). \tag{5.55}$$

To obtain an expression for $\dot{\varphi}$ we shall multiply Eq. (5.52) by $\sin\psi$ then add it to Eq. (5.53) multiplied by $\cos\psi$ to get

$$\dot{\varphi}=\frac{\mu F}{\xi}\frac{\cos\theta}{\sin\theta}\sin\psi+\sqrt{\frac{kT}{\xi}}\frac{1}{\sin\theta}\left(\Lambda_x\sin\psi+\Lambda_y\cos\psi\right). \tag{5.56}$$

To obtain an expression for $\dot{\psi}$, we substitute Eq. (5.56) into Eq. (5.54) to get

$$\begin{aligned}\dot{\psi}= &-\frac{\mu F}{\xi_z}\sin\theta\sin\psi\\ &+\sqrt{\frac{kT}{\xi_z}}\Lambda_z-\frac{\mu F}{\xi}\frac{\cos^2\theta}{\sin\theta}\sin\psi-\sqrt{\frac{kT}{\xi}}\frac{\cos\theta}{\sin\theta}\left(\Lambda_x\sin\psi+\Lambda_y\cos\psi\right). \qquad (5.57)\end{aligned}$$

So for a single dipole, we have the Langevin equations

$$\dot{\theta} = \frac{\mu F}{\xi}\cos\theta\cos\psi + \sqrt{\frac{kT}{\xi}}\left(\Lambda_x\cos\psi - \Lambda_y\sin\psi\right), \tag{5.58}$$

$$\dot{\varphi} = \frac{\mu F}{\xi}\frac{\cos\theta}{\sin\theta}\sin\psi + \sqrt{\frac{kT}{\xi}}\frac{1}{\sin\theta}\left(\Lambda_x\sin\psi + \Lambda_y\cos\psi\right), \tag{5.59}$$

$$\dot{\psi} = -\frac{\mu F}{\xi_z}\sin\theta\sin\psi + \sqrt{\frac{kT}{\xi_z}}\Lambda_z - \dot{\varphi}\cos\theta. \tag{5.60}$$

5.B Langevin Equations for Two Interacting Dipoles

We wish to obtain the Langevin equation for two dipoles μ_1 and μ_2, these can be expressed from Eqs. (5.58) - Eqs. (5.60) as

$$\dot{\theta} = \sum_{i=1,2}\left[\frac{\mu_i F}{\xi}\cos\theta\cos\psi_i + \sqrt{\frac{kT}{2\xi}}\left(\cos\psi_i\Lambda_x^{(i)} - \sin\psi_i\Lambda_y^{(i)}\right)\right], \tag{5.61}$$

$$\dot{\varphi} = \sum_{i=1,2}\left[\frac{\mu_i F}{\xi}\frac{\cos\theta}{\sin\theta}\sin\psi_i + \sqrt{\frac{kT}{2\xi}}\frac{1}{\sin\theta}\left(\sin\psi_i\Lambda_x^{(i)} + \cos\psi_i\Lambda_y^{(i)}\right)\right], \tag{5.62}$$

$$\begin{aligned}\dot{\psi}_j =& -\frac{\mu_j F}{\xi_z}\sin\theta\sin\psi_j + \sqrt{\frac{kT}{\xi_z}}\Lambda_z^{(j)} \\ &+ \sum_{i=1,2}\left[-\frac{\mu_i F}{\xi}\cot\theta\cos\theta\sin\psi_i - \sqrt{\frac{kT}{2\xi}}\cot\theta\left(\sin\psi_i\Lambda_x^{(i)} + \cos\psi_i\Lambda_y^{(i)}\right)\right],\end{aligned} \tag{5.63}$$

where $\Lambda_k^{(j)}$, $k = x, y, z$ are centred Gaussian random variables with correlation functions [2]

$$\left\langle \Lambda_k^{(j)}(t)\Lambda_{k'}^{(j)}(t')\right\rangle = 2\delta_{kk'}\delta(t-t'), \quad k, k' = x, y, z. \tag{5.64}$$

We now introduce the effect of interaction between the dipoles μ_1 and μ_2. Let $V(\psi_1 - \psi_2)$ denote the mutual potential energy of the two groups. The moment of force exerted by the dipole μ_2 on μ_1 is then $-V'(\psi_1 - \psi_2)$. The contribution of the intra-molecular forces in $\dot{\psi}_1$ is given by $-V'(\psi_1 - \psi_2)/\xi_z$ and similarly in $\dot{\psi}_2$ by $V'(\psi_1 - \psi_2)/\xi_z$ (see Budó 1949 [16], page 687), as such since both μ_1 and μ_2 rotate about the z-axis on the same plane, Eq. (5.63) can now be written as

$$\begin{aligned}\dot{\psi}_1 =& -\frac{\mu_1 F}{\xi_z}\sin\theta\sin\psi_1 + \sqrt{\frac{kT}{\xi_z}}\Lambda_z^{(1)} - \frac{V'(\psi_1-\psi_2)}{\xi_z} \\ &+ \sum_{i=1,2}\left[-\frac{\mu_i F}{\xi}\cot\theta\cos\theta\sin\psi_i - \sqrt{\frac{kT}{2\xi}}\cot\theta\left(\sin\psi_i\Lambda_x^{(i)} + \cos\psi_j\Lambda_y^{(i)}\right)\right], \end{aligned} \tag{5.65}$$

$$\begin{aligned}\dot{\psi}_2 =& -\frac{\mu_2 F}{\xi_z}\sin\theta\sin\psi_2 + \sqrt{\frac{kT}{\xi_z}}\Lambda_z^{(2)} + \frac{V'(\psi_1-\psi_2)}{\xi_z} \\ &+ \sum_{i=1,2}\left[-\frac{\mu_i F}{\xi}\cot\theta\cos\theta\sin\psi_i - \sqrt{\frac{kT}{2\xi}}\cot\theta\left(\sin\psi_i\Lambda_x^{(i)} + \cos\psi_i\Lambda_y^{(i)}\right)\right]. \end{aligned} \tag{5.66}$$

5.C Derivation of the Smoluchowski Equation from the system of Langevin Equations

For N stochastic variables $\mathbf{x} = \{x_1, ..., x_N\}$ the general form of the Langevin equation involves multiplicative noise terms and is

$$\dot{x}_i = h_i(\mathbf{x}, t) + g_{ij}(\mathbf{x}, t)\Lambda_j(t), \tag{5.67}$$

$$\langle \Lambda_i(t)\Lambda_j(t')\rangle = 2\delta_{ij}\delta(t-t'), \tag{5.68}$$

while the corresponding Smoluchowski equation for the *distribution function* $W(\mathbf{x}, t)$ in turn has the general form

$$\frac{d}{dt}W(\mathbf{x},t) = \frac{\partial}{\partial t}W(\mathbf{x},t) + \hat{\mathrm{L}}W(\mathbf{x},t) = \mathrm{St}\left\{W(\mathbf{x},t)\right\}, \tag{5.69}$$

where

$$\hat{\mathrm{L}}W(\mathbf{x},t) = \frac{\partial}{\partial x_i}h_i(\mathbf{x},t)W(\mathbf{x},t), \tag{5.70}$$

represents the deterministic drift part of the Smoluchowski equation while

$$\mathrm{St}(W(\mathbf{x},t)) = \left(-\frac{\partial}{\partial x_i}\left[D_i(\mathbf{x},t) - h_i(\mathbf{x},t)\right] + \frac{\partial^2}{\partial x_i x_j} D_{ij}(\mathbf{x},t)\right) W(\mathbf{x},t), \qquad (5.71)$$

is the collision kernel, corresponding to the free Brownian motion. From Eq. (5.70) onwards, Einstein's summation convention is used. Here D_i and D_{ij} are the drift and the diffusion coefficients, respectively. These coefficients can be obtained from the general form of the Langevin equation in Eq. (5.67) as [2]

$$D_i(\mathbf{x},t) = h_i(\mathbf{x},t) + g_{kj}(\mathbf{x},t)\frac{\partial}{\partial x_k} g_{ij}(\mathbf{x},t), \qquad (5.72)$$

which as usual is the sum of the *deterministic* and *noise induced drift* and

$$D_{ij}(\mathbf{x},t) = g_{ik}(\mathbf{x},t) g_{jk}(\mathbf{x},t). \qquad (5.73)$$

We wish to derive the corresponding Smoluchowski equation for the distribution function $W(\mathbf{\Omega},t)$ from the Langevin equations (involving multiplicative noise) of motion of the polar groups in a dc field $\mathbf{F}$ applied in the Z-direction of the space-fixed system seen in Eqs. (5.61) - (5.63) and Eqs. (5.65) and (5.66). First we seek to determine the $h_i(\mathbf{\Omega},t)$ and $g_{kj}(\mathbf{\Omega},t)$ functions by comparing the *general* form of the Langevin equation in Eq. (5.67) to the aforementioned Langevin equations

$$\dot{\theta} = h_\theta + g_{\theta x_1}\Lambda_x^{(1)} + g_{\theta y_1}\Lambda_y^{(1)} + g_{\theta z_1}\Lambda_z^{(1)} + g_{\theta x_2}\Lambda_x^{(2)} + g_{\theta y_2}\Lambda_y^{(2)} + g_{\theta z_2}\Lambda_z^{(2)}, \qquad (5.74)$$

$$\dot{\psi}_1 = h_{\psi_1} + g_{\psi_1 x_1}\Lambda_x^{(1)} + g_{\psi_1 y_1}\Lambda_y^{(1)} + g_{\psi_1 z_1}\Lambda_z^{(1)} + g_{\psi_1 x_2}\Lambda_x^{(2)} + g_{\psi_1 y_2}\Lambda_y^{(2)} + g_{\psi_1 z_2}\Lambda_z^{(2)}, \qquad (5.75)$$

$$\dot{\psi}_2 = h_{\psi_2} + g_{\psi_2 x_1}\Lambda_x^{(1)} + g_{\psi_2 y_1}\Lambda_y^{(1)} + g_{\psi_2 z_1}\Lambda_z^{(1)} + g_{\psi_2 x_2}\Lambda_x^{(2)} + g_{\psi_2 y_2}\Lambda_y^{(2)} + g_{\psi_2 z_2}\Lambda_z^{(2)}, \qquad (5.76)$$

$$\dot{\varphi} = h_\varphi + g_{\varphi x_1}\Lambda_x^{(1)} + g_{\varphi y_1}\Lambda_y^{(1)} + g_{\varphi z_1}\Lambda_z^{(1)} + g_{\varphi x_2}\Lambda_x^{(2)} + g_{\varphi y_2}\Lambda_y^{(2)} + g_{\varphi z_2}\Lambda_z^{(2)}. \qquad (5.77)$$

By comparing Eqs. (5.74) - (5.77) to Eqs. (5.61), (5.62), (5.65) and (5.66) we get for the *deterministic* drift components

$$h_\theta = \frac{F}{\xi} \cos\theta(\mu_1 \cos\psi_1 + \mu_2 \cos\psi_2), \tag{5.78}$$

$$h_\varphi = -\frac{F}{\xi} \frac{\cos\theta}{\sin\theta}(\mu_1 \sin\psi_1 + \mu_2 \sin\psi_2), \tag{5.79}$$

$$h_{\psi_1} = -\frac{F}{\xi} \frac{\cos^2\theta}{\sin\theta}(\mu_1 \sin\psi_1 + \mu_2 \sin\psi_2) - \frac{F}{\xi_z}\mu_1 \sin\theta \sin\psi_1 - \frac{V'(\psi_1 - \psi_2)}{\xi_z}, \tag{5.80}$$

$$h_{\psi_2} = -\frac{F}{\xi} \frac{\cos^2\theta}{\sin\theta}(\mu_1 \sin\psi_1 + \mu_2 \sin\psi_2) - \frac{F}{\xi_z}\mu_2 \sin\theta \sin\psi_2 + \frac{V'(\psi_1 - \psi_2)}{\xi_z}, \tag{5.81}$$

while the functions needed to calculate the noise induced drift etc. are

$$g_{\theta x_1} = \sqrt{\frac{kT}{2\xi}} \cos\psi_1, \qquad g_{\theta x_2} = \sqrt{\frac{kT}{2\xi}} \cos\psi_2, \tag{5.82}$$

$$g_{\theta y_1} = -\sqrt{\frac{kT}{2\xi}} \sin\psi_1, \qquad g_{\theta y_2} = -\sqrt{\frac{kT}{2\xi}} \sin\psi_2, \tag{5.83}$$

$$g_{\varphi x_1} = \sqrt{\frac{kT}{2\xi}} \frac{\sin\psi_1}{\sin\theta}, \qquad g_{\varphi x_2} = \sqrt{\frac{kT}{2\xi}} \frac{\sin\psi_2}{\sin\theta}, \tag{5.84}$$

$$g_{\varphi y_1} = \sqrt{\frac{kT}{2\xi}} \frac{\cos\psi_1}{\sin\theta}, \qquad g_{\varphi y_2} = \sqrt{\frac{kT}{2\xi}} \frac{\cos\psi_2}{\sin\theta}, \tag{5.85}$$

$$g_{\psi_1 x_1} = g_{\psi_2 x_1} = -\sqrt{\frac{kT}{2\xi}} \sin\psi_1 \cot\theta, \quad g_{\psi_1 x_2} = g_{\psi_2 x_2} = -\sqrt{\frac{kT}{2\xi}} \sin\psi_2 \cot\theta, \tag{5.86}$$

$$g_{\psi_1 y_1} = g_{\psi_2 y_1} = -\sqrt{\frac{kT}{2\xi}} \cos\psi_1 \cot\theta, \quad g_{\psi_1 y_2} = g_{\psi_2 y_2} = -\sqrt{\frac{kT}{2\xi}} \cos\psi_2 \cot\theta, \tag{5.87}$$

$$g_{\psi_1 z_1} = \sqrt{\frac{kT}{\xi_z}}, \quad g_{\psi_2 z_2} = \sqrt{\frac{kT}{\xi_z}}. \tag{5.88}$$

We can now determine the drift D_i and diffusion D_{ij} coefficients as

$$\begin{aligned}
D_\theta =& h_\theta + g_{\theta x_1}\frac{\partial}{\partial\theta}g_{\theta x_1} + g_{\varphi x_1}\frac{\partial}{\partial\varphi}g_{\theta x_1} + g_{\psi_1 x_1}\frac{\partial}{\partial\psi_1}g_{\theta x_1} + g_{\psi_2 x_1}\frac{\partial}{\partial\psi_2}g_{\theta x_1} \\
&+ g_{\theta x_2}\frac{\partial}{\partial\theta}g_{\theta x_2} + g_{\varphi x_2}\frac{\partial}{\partial\varphi}g_{\theta x_2} + g_{\psi_1 x_2}\frac{\partial}{\partial\psi_1}g_{\theta x_2} + g_{\psi_2 x_2}\frac{\partial}{\partial\psi_2}g_{\theta x_2} \\
&+ g_{\theta y_1}\frac{\partial}{\partial\theta}g_{\theta y_1} + g_{\varphi y_1}\frac{\partial}{\partial\varphi}g_{\theta y_1} + g_{\psi_1 y_1}\frac{\partial}{\partial\psi_1}g_{\theta y_1} + g_{\psi_2 y_1}\frac{\partial}{\partial\psi_2}g_{\theta y_1} \\
&+ g_{\theta y_2}\frac{\partial}{\partial\theta}g_{\theta y_2} + g_{\varphi y_2}\frac{\partial}{\partial\varphi}g_{\theta y_2} + g_{\psi_1 y_2}\frac{\partial}{\partial\psi_1}g_{\theta y_2} + g_{\psi_2 y_2}\frac{\partial}{\partial\psi_2}g_{\theta y_2} \\
=& h_\theta + \frac{kT}{2\xi}\cot\theta\left(\left(\sin^2\psi_1 + \cos^2\psi_1\right) + \left(\sin^2\psi_2 + \cos^2\psi_2\right)\right) \\
=& h_\theta + \frac{kT}{\xi}\cot\theta,
\end{aligned} \tag{5.89}$$

$$\begin{aligned}
D_\varphi =& h_\varphi + g_{\theta x_1}\frac{\partial}{\partial\theta}g_{\varphi x_1} + g_{\varphi x_1}\frac{\partial}{\partial\varphi}g_{\varphi x_1} + g_{\psi_1 x_1}\frac{\partial}{\partial\psi_1}g_{\varphi x_1} + g_{\psi_2 x_1}\frac{\partial}{\partial\psi_2}g_{\varphi x_1} \\
&+ g_{\theta x_2}\frac{\partial}{\partial\theta}g_{\varphi x_2} + g_{\varphi x_2}\frac{\partial}{\partial\varphi}g_{\varphi x_2} + g_{\psi_1 x_2}\frac{\partial}{\partial\psi_1}g_{\varphi x_2} + g_{\psi_2 x_2}\frac{\partial}{\partial\psi_2}g_{\varphi x_2} \\
&+ g_{\theta y_1}\frac{\partial}{\partial\theta}g_{\varphi y_1} + g_{\varphi y_1}\frac{\partial}{\partial\varphi}g_{\varphi y_1} + g_{\psi_1 y_1}\frac{\partial}{\partial\psi_1}g_{\varphi y_1} + g_{\psi_2 y_1}\frac{\partial}{\partial\psi_2}g_{\varphi y_1} \\
&+ g_{\theta y_2}\frac{\partial}{\partial\theta}g_{\varphi y_2} + g_{\varphi y_2}\frac{\partial}{\partial\varphi}g_{\varphi y_2} + g_{\psi_1 y_2}\frac{\partial}{\partial\psi_1}g_{\varphi y_2} + g_{\psi_2 y_2}\frac{\partial}{\partial\psi_2}g_{\varphi y_2} \\
=& h_\varphi - \frac{kT}{2\xi}\frac{\cos\psi_1\sin\psi_1\cot\theta}{\sin\theta} - \frac{kT}{2\xi}\frac{\sin\psi_1\cos\psi_1\cot\theta}{\sin\theta} \\
&- \frac{kT}{2\xi}\frac{\cos\psi_2\sin\psi_2\cot\theta}{\sin\theta} - \frac{kT}{2\xi}\frac{\sin\psi_2\cos\psi_2\cot\theta}{\sin\theta} \\
&+ \frac{kT}{2\xi}\frac{\sin\psi_1\cos\psi_1\cot\theta}{\sin\theta} + \frac{kT}{2\xi}\frac{\cos\psi_1\sin\psi_1\cos\psi_1\cot\theta}{\sin\theta} \\
&+ \frac{kT}{2\xi}\frac{\sin\psi_2\cos\psi_2\cot\theta}{\sin\theta} + \frac{kT}{2\xi}\frac{\cos\psi_2\sin\psi_2\cot\theta}{\sin\theta} \\
=& h_\varphi,
\end{aligned} \tag{5.90}$$

$$
\begin{aligned}
D_{\psi_1} =& h_{\psi_1} + g_{\theta x_1}\frac{\partial}{\partial\theta}g_{\psi_1 x_1} + g_{\varphi x_1}\frac{\partial}{\partial\varphi}g_{\psi_1 x_1} + g_{\psi_1 x_1}\frac{\partial}{\partial\psi_1}g_{\psi_1 x_1} + g_{\psi_2 x_1}\frac{\partial}{\partial\psi_2}g_{\psi_1 x_1} \\
&+ g_{\theta x_2}\frac{\partial}{\partial\theta}g_{\psi_1 x_2} + g_{\varphi x_2}\frac{\partial}{\partial\varphi}g_{\psi_1 x_2} + g_{\psi_1 x_2}\frac{\partial}{\partial\psi_1}g_{\psi_1 x_2} + g_{\psi_2 x_2}\frac{\partial}{\partial\psi_2}g_{\psi_1 x_2} \\
&+ g_{\theta y_1}\frac{\partial}{\partial\theta}g_{\psi_1 y_1} + g_{\varphi y_1}\frac{\partial}{\partial\varphi}g_{\psi_1 y_1} + g_{\psi_1 y_1}\frac{\partial}{\partial\psi_1}g_{\psi_1 y_1} + g_{\psi_2 y_1}\frac{\partial}{\partial\psi_2}g_{\psi_1 y_1} \\
&+ g_{\theta y_2}\frac{\partial}{\partial\theta}g_{\psi_1 y_2} + g_{\varphi y_2}\frac{\partial}{\partial\varphi}g_{\psi_1 y_2} + g_{\psi_1 y_2}\frac{\partial}{\partial\psi_1}g_{\psi_1 y_2} + g_{\psi_2 y_2}\frac{\partial}{\partial\psi_2}g_{\psi_1 y_2} \\
&+ g_{\theta z_1}\frac{\partial}{\partial\theta}g_{\psi_1 z_1} + g_{\varphi z_1}\frac{\partial}{\partial\varphi}g_{\psi_1 z_1} + g_{\psi_1 z_1}\frac{\partial}{\partial\psi_1}g_{\psi_1 z_1} + g_{\psi_2 z_1}\frac{\partial}{\partial\psi_2}g_{\psi_1 z_1} \\
&+ g_{\theta z_2}\frac{\partial}{\partial\theta}g_{\psi_1 z_2} + g_{\varphi z_2}\frac{\partial}{\partial\varphi}g_{\psi_1 z_2} + g_{\psi_1 z_2}\frac{\partial}{\partial\psi_1}g_{\psi_1 z_2} + g_{\psi_2 z_2}\frac{\partial}{\partial\psi_2}g_{\psi_1 z_2} \\
=& h_{\psi_1} + \frac{kT}{2\xi}\sin\psi_1\cos\psi_1\left(1+\cot^2\theta\right) + \frac{kT}{2\xi}\sin\psi_1\cos\psi_1\cot^2\theta \\
&+ \frac{kT}{2\xi}\sin\psi_2\cos\psi_2\left(1+\cot^2\theta\right) + \frac{kT}{2\xi}\sin\psi_2\cos\psi_2\cot^2\theta \\
&- \frac{kT}{2\xi}\sin\psi_1\cos\psi_1\left(1+\cot^2\theta\right) - \frac{kT}{2\xi}\sin\psi_1\cos\psi_1\cot^2\theta \\
&- \frac{kT}{2\xi}\sin\psi_2\cos\psi_2\left(1+\cot^2\theta\right) - \frac{kT}{2\xi}\sin\psi_2\cos\psi_2\cot^2\theta \\
=& h_{\psi_1},
\end{aligned}
\tag{5.91}
$$

$$
\begin{aligned}
D_{\psi_2} =& h_{\psi_2} + g_{\theta x_1}\frac{\partial}{\partial\theta}g_{\psi_2 x_1} + g_{\varphi x_1}\frac{\partial}{\partial\varphi}g_{\psi_2 x_1} + g_{\psi_1 x_1}\frac{\partial}{\partial\psi_1}g_{\psi_2 x_1} + g_{\psi_2 x_1}\frac{\partial}{\partial\psi_2}g_{\psi_2 x_1} \\
&+ g_{\theta x_2}\frac{\partial}{\partial\theta}g_{\psi_2 x_2} + g_{\varphi x_2}\frac{\partial}{\partial\varphi}g_{\psi_2 x_2} + g_{\psi_1 x_2}\frac{\partial}{\partial\psi_1}g_{\psi_2 x_2} + g_{\psi_2 x_2}\frac{\partial}{\partial\psi_2}g_{\psi_2 x_2} \\
&+ g_{\theta y_1}\frac{\partial}{\partial\theta}g_{\psi_2 y_1} + g_{\varphi y_1}\frac{\partial}{\partial\varphi}g_{\psi_2 y_1} + g_{\psi_1 y_1}\frac{\partial}{\partial\psi_1}g_{\psi_2 y_1} + g_{\psi_2 y_1}\frac{\partial}{\partial\psi_2}g_{\psi_2 y_1} \\
&+ g_{\theta y_2}\frac{\partial}{\partial\theta}g_{\psi_2 y_2} + g_{\varphi y_2}\frac{\partial}{\partial\varphi}g_{\psi_2 y_2} + g_{\psi_1 y_2}\frac{\partial}{\partial\psi_1}g_{\psi_2 y_2} + g_{\psi_2 y_2}\frac{\partial}{\partial\psi_2}g_{\psi_2 y_2} \\
&+ g_{\theta z_1}\frac{\partial}{\partial\theta}g_{\psi_2 z_1} + g_{\varphi z_1}\frac{\partial}{\partial\varphi}g_{\psi_2 z_1} + g_{\psi_1 z_1}\frac{\partial}{\partial\psi_1}g_{\psi_2 z_1} + g_{\psi_2 z_1}\frac{\partial}{\partial\psi_2}g_{\psi_2 z_1} \\
&+ g_{\theta z_2}\frac{\partial}{\partial\theta}g_{\psi_2 z_2} + g_{\varphi z_2}\frac{\partial}{\partial\varphi}g_{\psi_2 z_2} + g_{\psi_1 z_2}\frac{\partial}{\partial\psi_1}g_{\psi_2 z_2} + g_{\psi_2 z_2}\frac{\partial}{\partial\psi_2}g_{\psi_2 z_2} \\
=& h_{\psi_2},
\end{aligned}
\tag{5.92}
$$

$$
\begin{aligned}
D_{\theta\theta} =& g_{\theta x_1}g_{\theta x_1} + g_{\theta x_2}g_{\theta x_2} + g_{\theta y_1}g_{\theta y_1} + g_{\theta y_2}g_{\theta y_2} + g_{\theta z_1}g_{\theta z_1} + g_{\theta z_2}g_{\theta z_2} \\
=& \frac{kT}{2\xi}\left(\left(\sin^2\psi_1 + \cos^2\psi_1\right) + \left(\sin^2\psi_2 + \cos^2\psi_2\right)\right) \\
=& \frac{kT}{\xi},
\end{aligned}
\tag{5.93}
$$

$$
\begin{aligned}
D_{\varphi\varphi} =& g_{\varphi x_1}g_{\varphi x_1} + g_{\varphi x_2}g_{\varphi x_2} + g_{\varphi y_1}g_{\varphi y_1} + g_{\varphi y_2}g_{\varphi y_2} + g_{\varphi z_1}g_{\varphi z_1} + g_{\varphi z_2}g_{\varphi z_2} \\
=& \frac{kT}{2\xi}\frac{1}{\sin^2\theta}\left[\sin^2\psi_1 + \cos^2\psi_1 + \sin^2\psi_2 + \cos^2\psi_2\right] \\
=& \frac{kT}{\xi}\frac{1}{\sin^2\theta},
\end{aligned}
\tag{5.94}
$$

$$
\begin{aligned}
D_{\psi_1\psi_1} =& g_{\psi_1 x_1}g_{\psi_1 x_1} + g_{\psi_1 x_2}g_{\psi_1 x_2} + g_{\psi_1 y_1}g_{\psi_1 y_1} + g_{\psi_1 y_2}g_{\psi_1 y_2} + g_{\psi_1 z_1}g_{\psi_1 z_1} + g_{\psi_1 z_2}g_{\psi_1 z_2} \\
=& kT\left(\frac{\left(\sin^2\psi_1 + \cos^2\psi_1\right)\cot^2\theta}{2\xi} + \frac{\left(\sin^2\psi_2 + \cos^2\psi_2\right)\cot^2\theta}{2\xi} + \frac{1}{\xi_z}\right) \\
=& kT\left(\frac{\cot^2\theta}{\xi} + \frac{1}{\xi_z}\right),
\end{aligned}
\tag{5.95}
$$

$$
\begin{aligned}
D_{\psi_2\psi_2} =& g_{\psi_2 x_1}g_{\psi_2 x_1} + g_{\psi_2 x_2}g_{\psi_2 x_2} + g_{\psi_2 y_1}g_{\psi_2 y_1} + g_{\psi_2 y_2}g_{\psi_2 y_2} + g_{\psi_2 z_1}g_{\psi_2 z_1} + g_{\psi_2 z_2}g_{\psi_2 z_2} \\
=& kT\left(\frac{\cot^2\theta}{\xi} + \frac{1}{\xi_z}\right),
\end{aligned}
\tag{5.96}
$$

$$
\begin{aligned}
D_{\theta\psi_1} =& D_{\psi_1\theta} = g_{\theta x_1} g_{\psi_1 x_1} + g_{\theta x_2} g_{\psi_1 x_2} + g_{\theta y_1} g_{\psi_1 y_1} + g_{\theta y_2} g_{\psi_1 y_2} + g_{\theta z_1} g_{\psi_1 z_1} + g_{\theta z_2} g_{\psi_1 z_2} \\
=& -\frac{kT}{2\xi}\sin\psi_1\cos\psi_1\cot\theta - \frac{kT}{2\xi}\sin\psi_2\cos\psi_2\cot\theta \\
& + \frac{kT}{2\xi}\sin\psi_1\cos\psi_1\cot\theta + \frac{kT}{2\xi}\sin\psi_2\cos\psi_2\cot\theta \\
=& 0, \qquad (5.97)
\end{aligned}
$$

$$
\begin{aligned}
D_{\theta\psi_2} =& D_{\psi_2\theta} = g_{\theta x_1} g_{\psi_2 x_1} + g_{\theta x_2} g_{\psi_2 x_2} + g_{\theta y_1} g_{\psi_2 y_1} + g_{\theta y_2} g_{\psi_2 y_2} + g_{\theta z_1} g_{\psi_2 z_1} + g_{\theta z_2} g_{\psi_2 z_2} \\
=& 0, \qquad (5.98)
\end{aligned}
$$

$$
\begin{aligned}
D_{\psi_1\psi_2} =& D_{\psi_2\psi_1} = g_{\psi_1 x_1} g_{\psi_2 x_1} + g_{\psi_1 x_2} g_{\psi_2 x_2} + g_{\psi_1 y_1} g_{\psi_2 y_1} + g_{\psi_1 y_2} g_{\psi_2 y_2} + g_{\psi_1 z_1} g_{\psi_2 z_1} + g_{\psi_1 z_2} g_{\psi_2 z_2} \\
=& \frac{kT}{2\xi}\cot^2\theta\left(\left(\sin^2\psi_1 + \cos^2\psi_1\right) + \left(\sin^2\psi_2 + \cos^2\psi_2\right)\right) \\
=& \frac{kT}{\xi}\cot^2\theta. \qquad (5.99)
\end{aligned}
$$

Now that all the relevant terms have been evaluated the next step is to obtain the deterministic drift part $\hat{\mathrm{L}}W(\mathbf{\Omega}, t)$ and the collision kernel $\mathrm{St}(W(\mathbf{\Omega}, t))$. The distribution function $W(\theta, \psi_1, \psi_2, t)$ may be written as $W(\theta, \psi_1, \psi_2, t) = f(\theta, \psi_1, \psi_2, t)\sin\theta$. We start with the deterministic drift part $\hat{\mathrm{L}}W(\mathbf{\Omega}, t)$:

$$
\begin{aligned}
\hat{\mathrm{L}}W(\mathbf{\Omega}, t) =& \frac{\partial}{\partial x_i} h_i(\mathbf{\Omega}, t) W(\mathbf{\Omega}, t) \\
=& \left[\frac{\partial}{\partial\theta} h_\theta(\mathbf{\Omega}, t) + \frac{\partial}{\partial\varphi} h_\varphi(\mathbf{\Omega}, t) + \frac{\partial}{\partial\psi_1} h_{\psi_1}(\mathbf{\Omega}, t) + \frac{\partial}{\partial\psi_2} h_{\psi_2}(\mathbf{\Omega}, t)\right] W(\mathbf{\Omega}, t). \qquad (5.100)
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow \hat{\mathrm{L}}\,(f\sin\theta) = \Bigg[&\frac{\partial}{\partial\theta}\left\{\frac{F}{\xi}\cos\theta(\mu_1\cos\psi_1+\mu_2\cos\psi_2)\right\} \\
&+\frac{\partial}{\partial\varphi}\left\{\frac{F\cos\theta}{\xi\sin\theta}(\mu_1\sin\psi_1+\mu_2\sin\psi_2)\right\} \\
&+\frac{\partial}{\partial\psi_1}\left\{-\frac{F}{\xi}\,\frac{\cos^2\theta}{\sin\theta}(\mu_1\sin\psi_1+\mu_2\sin\psi_2)\right. \\
&\left.-\frac{F}{\xi_z}\mu_1\sin\theta\sin\psi_1-\frac{V'(\psi_1-\psi_2)}{\xi_z}\right\} \\
&+\frac{\partial}{\partial\psi_2}\left\{-\frac{F}{\xi}\,\frac{\cos^2\theta}{\sin\theta}(\mu_1\sin\psi_1+\mu_2\sin\psi_2)\right. \\
&\left.-\frac{F}{\xi_z}\mu_2\sin\theta\sin\psi_2+\frac{V'(\psi_1-\psi_2)}{\xi_z}\right\}\Bigg]\,f\sin\theta. \qquad (5.101)
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow \hat{\mathrm{L}}\,(f\sin\theta) = \sin\theta\Bigg[&-\frac{F}{\xi}\sin\theta\,(\mu_1\cos\psi_1+\mu_2\cos\psi_2) \\
&+\frac{F}{\xi}\cos\theta\,(\mu_1\cos\psi_1+\mu_2\cos\psi_2)\,\frac{\partial}{\partial\theta} \\
&+\frac{F}{\xi}\frac{\cos^2\theta}{\sin\theta}\,(\mu_1\cos\psi_1+\mu_2\cos\psi_2) \\
&-\frac{F}{\xi}\frac{\cos^2\theta}{\sin\theta}\,(\mu_1\cos\psi_1)-\frac{F}{\xi_z}\mu_1\sin\theta\cos\psi_1-\frac{V''(\psi_1-\psi_2)}{\xi_z} \\
&+\left\{-\frac{F}{\xi}\,\frac{\cos^2\theta}{\sin\theta}(\mu_1\sin\psi_1+\mu_2\sin\psi_2)\right. \\
&\left.-\frac{F}{\xi_z}\mu_1\sin\theta\sin\psi_1-\frac{V'(\psi_1-\psi_2)}{\xi_z}\right\}\frac{\partial}{\partial\psi_1} \\
&-\frac{F}{\xi}\frac{\cos^2\theta}{\sin\theta}\,(\mu_2\cos\psi_2)-\frac{F}{\xi_z}\mu_2\sin\theta\cos\psi_2-\frac{V''(\psi_1-\psi_2)}{\xi_z} \\
&+\left\{-\frac{F}{\xi}\,\frac{\cos^2\theta}{\sin\theta}(\mu_1\sin\psi_1+\mu_2\sin\psi_2)\right. \\
&\left.-\frac{F}{\xi_z}\mu_2\sin\theta\sin\psi_2+\frac{V'(\psi_1-\psi_2)}{\xi_z}\right\}\frac{\partial}{\partial\psi_2}\Bigg]\,f. \qquad (5.102)
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow \hat{\mathrm{L}}\,(f\sin\theta) = \sin\theta\Bigg\{&-\frac{F}{\xi}\left[\left(\left(1+\frac{\xi}{\xi_z}\right)\sin\theta-\cos\theta\frac{\partial}{\partial\theta}\right)(\mu_1\cos\psi_1+\mu_2\cos\psi_2)\right. \\
&+(\mu_1\sin\psi_1+\mu_2\sin\psi_2)\frac{\cos^2\theta}{\sin\theta}\left(\frac{\partial}{\partial\psi_1}+\frac{\partial}{\partial\psi_2}\right) \\
&+\frac{\xi}{\xi_z}\sin\theta\left(\mu_1\sin\psi_1\frac{\partial}{\partial\psi_1}+\mu_2\sin\psi_2\frac{\partial}{\partial\psi_2}\right) \\
&-2\frac{V''(\psi_1-\psi_2)}{\xi_z}-\frac{V'(\psi_1-\psi_2)}{\xi_z}\left(\frac{\partial}{\partial\psi_1}-\frac{\partial}{\partial\psi_2}\right)\Bigg\}\,f. \qquad (5.103)
\end{aligned}
$$

Next, we will evaluate the collision kernel $\mathrm{St}(W(\mathbf{\Omega}, t))$:

$$\mathrm{St}(W(\mathbf{\Omega}, t)) = \left(-\frac{\partial}{\partial x_i}\left[D_i(\mathbf{\Omega}, t) - h_i(\mathbf{\Omega}, t)\right] + \frac{\partial^2}{\partial x_i x_j} D_{ij}(\mathbf{\Omega}, t)\right) W(\mathbf{\Omega}, t). \tag{5.104}$$

$$\begin{aligned}
\Rightarrow \mathrm{St}(\mathrm{f}\sin\theta) = \Bigg\{ & -\frac{\partial}{\partial\theta}\left[D_\theta - h_\theta\right] + \frac{\partial^2}{\partial\theta^2} D_{\theta\theta} + \frac{\partial^2}{\partial\theta\partial\varphi}\overset{=0}{D_{\theta\varphi}} + \frac{\partial^2}{\partial\theta\partial\psi_1}\overset{=0}{D_{\theta\psi_1}} + \frac{\partial^2}{\partial\theta\partial\psi_2}\overset{=0}{D_{\theta\psi_2}} \\
& - \frac{\partial}{\partial\varphi}\overset{=0}{\left[D_\varphi - h_\varphi\right]} + \frac{\partial^2}{\partial\varphi^2}\overset{=0}{D_{\varphi\varphi}} + \frac{\partial^2}{\partial\varphi\partial\theta}\overset{=0}{D_{\varphi\theta}} + \frac{\partial^2}{\partial\varphi\partial\theta}\overset{=0}{D_{\varphi\psi_1}} + \frac{\partial^2}{\partial\varphi\partial\psi_2}\overset{=0}{D_{\varphi\psi_2}} \\
& - \frac{\partial}{\partial\psi_1}\overset{=0}{\left[D_{\psi_1} - h_{\psi_1}\right]} + \frac{\partial^2}{\partial{\psi_1}^2} D_{\psi_1\psi_1} + \frac{\partial^2}{\partial\psi_1\partial\theta}\overset{=0}{D_{\psi_1\theta}} + \frac{\partial^2}{\partial\psi_1\partial\psi_2} D_{\psi_1\psi_2} \\
& - \frac{\partial}{\partial\psi_2}\overset{=0}{\left[D_{\psi_2} - h_{\psi_2}\right]} + \frac{\partial^2}{\partial{\psi_2}^2} D_{\psi_2\psi_2} + \frac{\partial^2}{\partial\psi_2\partial\theta}\overset{=0}{D_{\psi_2\theta}} + \frac{\partial^2}{\partial\psi_2\partial\psi_1} D_{\psi_2\psi_1} \Bigg\} f\sin\theta
\end{aligned}$$

$$\begin{aligned}
= & -\frac{\partial}{\partial\theta}\left(\frac{kT}{\xi}\cot\theta\right) f\sin\theta + \frac{\partial^2}{\partial\theta^2}\left(\frac{kT}{\xi}\right) f\sin\theta \\
& + \frac{\partial^2}{\partial{\psi_1}^2}\left(\frac{kT}{\xi}\cot^2\theta + \frac{kT}{\xi_z}\right) f\sin\theta \\
& + \frac{\partial^2}{\partial\psi_1\partial\psi_2}\left(\frac{kT}{\xi}\cot^2\theta\right) f\sin\theta \\
& + \frac{\partial^2}{\partial{\psi_2}^2}\left(\frac{kT}{\xi}\cot^2\theta + \frac{kT}{\xi_z}\right) f\sin\theta \\
& + \frac{\partial^2}{\partial\psi_2\partial\psi_1}\left(\frac{kT}{\xi}\cot^2\theta\right) f\sin\theta \\
= & \frac{kT}{\xi}\sin\theta\Bigg[1 - \cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + 2\cot\theta\frac{\partial}{\partial\theta} - 1 \\
& + \frac{\partial^2}{\partial{\psi_1}^2}\left(\cot^2\theta + \frac{\xi}{\xi_z}\right) \\
& + \frac{\partial^2}{\partial\psi_1\partial\psi_2}\left(\cot^2\theta\right) + \frac{\partial^2}{\partial{\psi_2}^2}\left(\cot^2\theta + \frac{\xi}{\xi_z}\right) + \frac{\partial^2}{\partial\psi_2\partial\psi_1}\left(\cot^2\theta\right)\Bigg] f \\
= & \frac{kT}{\xi}\sin\theta\Bigg[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + 2\cot^2\theta\frac{\partial^2}{\partial\psi_1\partial\psi_2} \\
& + \left(\cot^2\theta + \frac{\xi}{\xi_z}\right)\left(\frac{\partial^2}{\partial{\psi_1}^2} + \frac{\partial^2}{\partial{\psi_2}^2}\right)\Bigg] f.
\end{aligned} \tag{5.105}$$

Substituting $W(\theta, \psi_1, \psi_2, t) = f(\theta, \psi_1, \psi_2, t)\sin\theta$ into Eq. (5.69) we have

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \hat{\mathrm{L}} f = \mathrm{St}(f), \tag{5.106}$$

where the deterministic operator is defined by

$$
\begin{aligned}
\hat{\mathrm{L}}f = \Bigg\{ & -\frac{F}{\xi}\Bigg[(\mu_1 \sin\psi_1 + \mu_2 \sin\psi_2)\frac{\cos^2\theta}{\sin\theta}\left(\frac{\partial}{\partial\psi_1}+\frac{\partial}{\partial\psi_2}\right) \\
& + \left(\left(1+\frac{\xi}{\xi_z}\right)\sin\theta - \cos\theta\frac{\partial}{\partial\theta}\right)\sum_{i=1,2}\mu_i\cos\psi_i \\
& + \frac{\xi}{\xi_z}\sin\theta\sum_{i=1,2}\mu_i\sin\psi_i\frac{\partial}{\partial\psi_i}\Bigg] \\
& - \frac{V'(\psi_1-\psi_2)}{\xi_z}\left(\frac{\partial}{\partial\psi_1}-\frac{\partial}{\partial\psi_2}\right) - 2\frac{V''(\psi_1-\psi_2)}{\xi_z}\Bigg\} f,
\end{aligned}
\tag{5.107}
$$

while the collision kernel is defined by

$$
\begin{aligned}
\mathrm{St}(f) = & \frac{kT}{\xi}\Bigg[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + 2\cot^2\theta\frac{\partial^2}{\partial\psi_1\psi_2} \\
& + \left(\cot^2\theta + \frac{\xi}{\xi_z}\right)\left(\frac{\partial^2}{\partial{\psi_1}^2}+\frac{\partial^2}{\partial{\psi_2}^2}\right)\Bigg] f.
\end{aligned}
\tag{5.108}
$$

5.D Linear Response Theory and Initial Values

To use linear response theory, we suppose that a weak external dc field $\mathbf{F}$, having been applied to the system in the infinite past $t \to -\infty$, is suddenly switched off at time $t = 0$ meaning that we study the relaxation of a typical molecule with embedded groups, starting from an initial equilibrium state at $t = 0$ with a Boltzmann distribution

$$
f_F(\mathbf{\Omega}) = Z_F^{-1} e^{(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2)\cdot\mathbf{F}/kT + \sigma_V\cos(\psi_1-\psi_2)}, \tag{5.109}
$$

to another equilibrium state as $t \to \infty$ with a new Boltzmann distribution

$$
f_0(\mathbf{\Omega}) = f_{F=0}(\mathbf{\Omega}) = Z_0^{-1} e^{\sigma_V\cos(\psi_1-\psi_2)}, \tag{5.110}
$$

where $\sigma_V = V_0/kT$ is the dimensionless interaction parameter. $\mathbf{F} = F\,\mathbf{i}_Z$ where $\mathbf{i}_Z$ is the unit vector in the direction of the positive (fixed) Z-axis. The component of $(\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2)$ in the direction of $\mathbf{F}$ is $(\mu_1 \sin\theta\cos\psi_1 + \mu_2\sin\theta\cos\psi_2)\,\mathbf{i}_Z$. The time-dependent ensemble average of $(\mu_1 \sin\theta\cos\psi_1 + \mu_2 \sin\theta\cos\psi_2)$ is

$$\begin{aligned}\left\langle \mu_1 \sin\theta\cos\psi_1 + \mu_2 \sin\theta\cos\psi_2\right\rangle (t) =& \left\langle \mu_1 \sin\theta\cos\psi_1\right\rangle (t) + \left\langle \mu_2 \sin\theta\cos\psi_2\right\rangle (t) \\ =& \mu_1 c_1 (t) + \mu_2 c_2 (t) ,\end{aligned} \tag{5.111}$$

where

$$c_i (t) = \left\langle \sin\theta\cos\psi_i\right\rangle (t) ,\ i = 1, 2. \tag{5.112}$$

Eq. (5.109) can now be written as

$$\begin{aligned}f_F(\mathbf{\Omega}) =& Z_F^{-1} e^{(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2)\cdot\mathbf{F}/kT+\sigma_V \cos(\psi_1-\psi_2)} \\ =& Z_F^{-1} e^{(\boldsymbol{\mu}_1+\boldsymbol{\mu}_2)\cdot\mathbf{F}/kT} e^{\sigma_V \cos(\psi_1-\psi_2)} \\ =& Z_F^{-1} e^{(\mu_1 \sin\theta\cos\psi_1+\mu_2 \sin\theta\cos\psi_2)F/kT} e^{\sigma_V \cos(\psi_1-\psi_2)} \\ =& Z_F^{-1} e^{(\sigma_1 \sin\theta\cos\psi_1+\sigma_2 \sin\theta\cos\psi_2)} e^{\sigma_V \cos(\psi_1-\psi_2)},\end{aligned} \tag{5.113}$$

where $\sigma_i = \mu_i F/kT$. Note that $(\sigma_1 \sin\theta\cos\psi_1 + \sigma_2 \sin\theta\cos\psi_2) \ll 1$ since we assume that the external field parameters $\sigma_i \ll 1$. Thus, we can approximate $e^{(\sigma_1 \sin\theta\cos\psi_1+\sigma_2 \sin\theta\cos\psi_2)}$ using the Taylor series expansion as

$$e^{(\sigma_1 \sin\theta\cos\psi_1+\sigma_2 \sin\theta\cos\psi_2)} \approx 1 + (\sigma_1 \sin\theta\cos\psi_1 + \sigma_2 \sin\theta\cos\psi_2) . \tag{5.114}$$

Substituting Eq. (5.114) into Eq. (5.113) we obtain

$$f_F(\mathbf{\Omega}) \approx Z_F^{-1} \left[1 + (\sigma_1 \sin\theta\cos\psi_1 + \sigma_2 \sin\theta\cos\psi_2)\right] e^{\sigma_V \cos(\psi_1-\psi_2)}. \tag{5.115}$$

We now wish to calculate the initial values of the after effect-functions $c_1(t)$ and $c_2(t)$ viz.,

$$c_i(0) \approx \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} (\sin\theta\cos\psi_i)\, f_F(\mathbf{\Omega}) \sin\theta d\theta d\psi_1 d\psi_2. \tag{5.116}$$

Substituting Eq. (5.115) into Eq. (5.116) we obtain

$$\begin{aligned}
c_i(0) \approx& \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} (\sin\theta \cos\psi_i)[1 + \sigma_1 \sin\theta \cos\psi_1 \\
&+ \sigma_2 \sin\theta \cos\psi_2] e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \\
=& \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} (\sin\theta \cos\psi_i)\, e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \\
&+ \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \left(\sigma_1 \sin^2\theta \cos\psi_i \cos\psi_1\right) e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \\
&+ \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \left(\sigma_2 \sin^2\theta \cos\psi_i \cos\psi_2\right) e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2.
\end{aligned} \tag{5.117}$$

Eq. (5.117) for $i = 1, 2$ may be written as

$$\begin{aligned}
c_i(0) \approx& \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} (\sin\theta \cos\psi_i)\, e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \\
&+ \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \left(\sigma_i \sin^2\theta \cos^2\psi_i\right) e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \\
&+ \frac{1}{Z_F} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \left(\sigma_{3-i} \sin^2\theta \cos\psi_1 \cos\psi_2\right) e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2.
\end{aligned} \tag{5.118}$$

Eq. (5.118) may be written as

$$\begin{aligned}
c_i(0) \approx& \frac{Z_0}{Z_F} \left[\int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} (\sin\theta \cos\psi_i)\, \frac{1}{Z_0} e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \right] \\
&+ \frac{Z_0}{Z_F} \left[\int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \left(\sigma_i \sin^2\theta \cos^2\psi_i\right) \frac{1}{Z_0} e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \right] \\
&+ \frac{Z_0}{Z_F} \left[\int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \left(\sigma_{3-i} \sin^2\theta \cos\psi_1 \cos\psi_2\right) \frac{1}{Z_0} e^{\sigma_V \cos(\psi_1 - \psi_2)} \sin\theta d\theta d\psi_1 d\psi_2 \right].
\end{aligned} \tag{5.119}$$

Now using Eq. (5.110) we can rewrite Eq. (5.119) as

$$c_i(0) \approx \frac{Z_0}{Z_F}\left[\langle\sin\theta\cos\psi_i\rangle_0 + \sigma_i\left\langle\sin^2\theta\cos^2\psi_i\right\rangle_0 + \sigma_{3-i}\left\langle\sin^2\theta\cos\psi_1\cos\psi_2\right\rangle_0\right]. \tag{5.120}$$

$$\Rightarrow c_i(0) \approx \frac{Z_0}{Z_F}\left[\sigma_i\left\langle\sin^2\theta\cos^2\psi_i\right\rangle_0 + \sigma_{3-i}\left\langle\sin^2\theta\cos\psi_1\cos\psi_2\right\rangle_0\right], \tag{5.121}$$

since $\langle\sin\theta\cos\psi_i\rangle_0 = 0$.

Note that by definition

$$Z_0 = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} e^{\sigma_V\cos(\psi_1-\psi_2)}\sin\theta d\theta d\psi_1 d\psi_2, \tag{5.122}$$

and

$$\begin{aligned} Z_F &= \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} e^{(\sigma_1\sin\theta\cos\psi_1+\sigma_2\sin\theta\cos\psi_2)}e^{\sigma_V\cos(\psi_1-\psi_2)}\sin\theta d\theta d\psi_1 d\psi_2 \\ &\approx \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\left[1 + (\sigma_1\sin\theta\cos\psi_1 + \sigma_2\sin\theta\cos\psi_2)\right]e^{\sigma_V\cos(\psi_1-\psi_2)}\sin\theta d\theta d\psi_1 d\psi_2. \end{aligned} \tag{5.123}$$

$$\begin{aligned} \Rightarrow Z_F \approx& \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} e^{\sigma_V\cos(\psi_1-\psi_2)}\sin\theta d\theta d\psi_1 d\psi_2 \\ &+ Z_0\left[\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}(\sigma_1\sin\theta\cos\psi_1 + \sigma_2\sin\theta\cos\psi_2)\frac{1}{Z_0}e^{\sigma_V\cos(\psi_1-\psi_2)}\sin\theta d\theta d\psi_1 d\psi_2\right]. \end{aligned} \tag{5.124}$$

$$\Rightarrow Z_F \approx Z_0 + Z_0\left[\sigma_1\langle\sin\theta\cos\psi_1\rangle_0 + \sigma_2\langle\sin\theta\cos\psi_2\rangle_0\right]. \tag{5.125}$$

Since $\langle\sin\theta\cos\psi_i\rangle_0 = 0,\ i = 1, 2,$ we get

$$Z_F \approx Z_0. \tag{5.126}$$

From Eqs. (5.121) and (5.126) we have

$$c_i(0) \approx \sigma_i \left\langle \sin^2\theta \cos^2\psi_i \right\rangle_0 + \sigma_{3-i} \left\langle \sin^2\theta \cos\psi_1 \cos\psi_2 \right\rangle_0 . \tag{5.127}$$

Let $\mathbf{m}\,(t)$ denote the instantaneous dipole moment of a body that is in the direction of $\mathbf{F}$. The constant field $\mathbf{F}$ has been operative for a very long time and is switched off at time $t = 0$. The relation between $\mathbf{m}\,(t)$ and $\mathbf{F}$ is then given by

$$\mathbf{m}\,(t) = \mathbf{F} b\,(t)\,,\ t \geq 0, \tag{5.128}$$

where the function $b(t)$ is called the after-effect function. Normalising Eq. (5.128) for $t = 0$ we get

$$\frac{\mathbf{m}\,(t)}{\mathbf{m}\,(0)} = \frac{\mathbf{F} b\,(t)}{\mathbf{F} b\,(0)} = \frac{b\,(t)}{b\,(0)}\ t \geq 0. \tag{5.129}$$

The normalised relaxation function $C(t)$ is given by

$$C(t) = \frac{\mu_1 c_1(t) + \mu_2 c_2(t)}{\mu_1 c_1(0) + \mu_2 c_2(0)} = \frac{c_1(t) + \kappa c_2(t)}{c_1(0) + \kappa c_2(0)} = \frac{b\,(t)}{b\,(0)}\ t \geq 0, \tag{5.130}$$

where $\mu_2 = \kappa \mu_1$.

Let $\alpha(\omega)$ and $\chi(\omega)$ denote the complex polarisability and the complex susceptibility of the body respectively. We have [2]

$$\frac{\alpha\,(\omega)}{\alpha\,(0)} = 1 - i\omega \int_0^\infty C\,(t)\, e^{-i\omega t} dt, \tag{5.131}$$

where the normalised relaxation function $C(t)$ is given by Eq. (5.130). As we are neglecting electrical interaction between the dipolar molecules we get

$$\frac{\chi\,(\omega)}{\chi} = \frac{\alpha\,(\omega)}{\alpha\,(0)}, \tag{5.132}$$

where $\chi = \chi(0)$ is the static susceptibility. Substituting Eq. (5.132) into Eq. (5.131) we get

$$\frac{\chi\,(\omega)}{\chi} = 1 - i\omega \int_0^\infty C\,(t)\, e^{-i\omega t} dt. \tag{5.133}$$

5.E Substitution of the Symmetric Variables in the Smoluchowski Equation

Recall that the deterministic operator is defined by

$$\begin{aligned}
\hat{\mathrm{L}}f = \Bigg\{ & -\frac{F}{\xi}\Bigg[(\mu_1 \sin\psi_1 + \mu_2 \sin\psi_2)\frac{\cos^2\theta}{\sin\theta}\left(\frac{\partial}{\partial\psi_1} + \frac{\partial}{\partial\psi_2}\right) \\
& + \left(\left(1 + \frac{\xi}{\xi_z}\right)\sin\theta - \cos\theta\frac{\partial}{\partial\theta}\right)\sum_{i=1,2}\mu_i \cos\psi_i \\
& + \frac{\xi}{\xi_z}\sin\theta\sum_{i=1,2}\mu_i \sin\psi_i \frac{\partial}{\partial\psi_i}\Bigg] \\
& - \frac{V'(\psi_1 - \psi_2)}{\xi_z}\left(\frac{\partial}{\partial\psi_1} - \frac{\partial}{\partial\psi_2}\right) - 2\frac{V''(\psi_1 - \psi_2)}{\xi_z}\Bigg\} f. \qquad (5.134)
\end{aligned}$$

Setting $F = 0$ in Eq. (5.134) we have,

$$\hat{\mathrm{L}}f = \left\{-\frac{V'(\psi_1 - \psi_2)}{\xi_z}\left(\frac{\partial}{\partial\psi_1} - \frac{\partial}{\partial\psi_2}\right) - 2\frac{V''(\psi_1 - \psi_2)}{\xi_z}\right\} f. \qquad (5.135)$$

The interaction potential $V(\psi_1 - \psi_2)$ is given by

$$V(\psi_1 - \psi_2) = -V_0 \cos(\psi_1 - \psi_2), \qquad (5.136)$$

and its derivatives with respect to $(\psi_1 - \psi_2)$ are

$$V'(\psi_1 - \psi_2) = V_0 \sin(\psi_1 - \psi_2), \qquad (5.137)$$

$$V''(\psi_1 - \psi_2) = V_0 \cos(\psi_1 - \psi_2). \qquad (5.138)$$

Substituting Eqs. (5.137) and (5.138) into Eq. (5.135) we have

$$\hat{\mathrm{L}}f = \left\{-\frac{V_0 \sin(\psi_1 - \psi_2)}{\xi_z}\left(\frac{\partial}{\partial\psi_1} - \frac{\partial}{\partial\psi_2}\right) - 2\frac{V_0 \cos(\psi_1 - \psi_2)}{\xi_z}\right\} f. \qquad (5.139)$$

With $F = 0$, the collision kernel $\mathrm{St}(f)$ is given by

$$\mathrm{St}(f) = \frac{kT}{\xi}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + 2\cot^2\theta\frac{\partial^2}{\partial\psi_1\psi_2} + \left(\cot^2\theta + \frac{\xi}{\xi_z}\right)\sum_{j=1,2}\frac{\partial^2}{\partial{\psi_j}^2}\right] f. \qquad (5.140)$$

The fractional diffusion equation is given by

$$\frac{d}{dt}f(\mathbf{\Omega},t) = \frac{\partial}{\partial t}f(\mathbf{\Omega},t) + \hat{\mathrm{L}}f(\mathbf{\Omega},t) = \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\mathrm{St}\left\{f(\mathbf{\Omega},t)\right\}, \tag{5.141}$$

which can be rewritten as

$$\frac{\partial}{\partial t}f(\mathbf{\Omega},t) = -\hat{\mathrm{L}}f(\mathbf{\Omega},t) + \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\mathrm{St}\left\{f(\mathbf{\Omega},t)\right\}, \tag{5.142}$$

where the fractional operator, ${}_0D_t^{1-\alpha} = \frac{\partial}{\partial t}{}_0D_t^{-\alpha}$ in Eq. (5.142) is defined via the convolution

$${}_0D_t^{-\alpha}f(\,\mathbf{\Omega},t) = \frac{1}{\Gamma(\alpha)}\int_0^t \frac{f(\mathbf{\Omega}\,,t')dt'}{(t-t')^{1-\alpha}}. \tag{5.143}$$

To simplify Eq. (5.142) we now introduce the new variables

$$\nu = \frac{(\psi_1+\psi_2)}{2}, \quad \eta = \frac{(\psi_1-\psi_2)}{2}. \tag{5.144}$$

Using the chain rule, we obtain

$$\begin{aligned}\frac{\partial f}{\partial \psi_1} =& \frac{\partial f}{\partial \nu}\frac{\partial \nu}{\partial \psi_1} + \frac{\partial f}{\partial \eta}\frac{\partial \eta}{\partial \psi_1} \\ =& \frac{1}{2}\frac{\partial f}{\partial \nu} + \frac{1}{2}\frac{\partial f}{\partial \eta},\end{aligned} \tag{5.145}$$

$$\begin{aligned}\frac{\partial f}{\partial \psi_2} =& \frac{\partial f}{\partial \nu}\frac{\partial \nu}{\partial \psi_2} + \frac{\partial f}{\partial \eta}\frac{\partial \eta}{\partial \psi_2} \\ =& \frac{1}{2}\frac{\partial f}{\partial \nu} - \frac{1}{2}\frac{\partial f}{\partial \eta},\end{aligned} \tag{5.146}$$

$$\frac{\partial f}{\partial \psi_1} - \frac{\partial f}{\partial \psi_2} = \frac{\partial f}{\partial \eta}, \tag{5.147}$$

$$\begin{aligned}\frac{\partial^2 f}{\partial \psi_1^2} =& \frac{\partial}{\partial \psi_1}\left[\frac{1}{2}\frac{\partial f}{\partial \nu} + \frac{1}{2}\frac{\partial f}{\partial \eta}\right] \\ =& \frac{1}{4}\left[\frac{\partial^2}{\partial \nu^2} + 2\frac{\partial^2}{\partial \nu \partial \eta} + \frac{\partial^2}{\partial \eta^2}\right] f,\end{aligned} \tag{5.148}$$

$$\begin{aligned}\frac{\partial^2 f}{\partial \psi_2^2} =& \frac{\partial}{\partial \psi_2}\left[\frac{1}{2}\frac{\partial f}{\partial \nu} - \frac{1}{2}\frac{\partial f}{\partial \eta}\right] \\ =& \frac{1}{4}\left[\frac{\partial^2}{\partial \nu^2} - 2\frac{\partial^2}{\partial \nu \partial \eta} + \frac{\partial^2}{\partial \eta^2}\right] f,\end{aligned} \tag{5.149}$$

$$\begin{aligned}\frac{\partial^2 f}{\partial \psi_1^2} + \frac{\partial^2 f}{\partial \psi_2^2} =& \left(\frac{1}{4}\frac{\partial^2 f}{\partial \nu^2} + \frac{1}{2}\frac{\partial^2 f}{\partial \nu \partial \eta} + \frac{1}{4}\frac{\partial^2 f}{\partial \eta^2}\right) + \left(\frac{1}{4}\frac{\partial^2 f}{\partial \nu^2} - \frac{1}{2}\frac{\partial^2 f}{\partial \nu \partial \eta} + \frac{1}{4}\frac{\partial^2 f}{\partial \eta^2}\right) \\ =& \frac{1}{2}\left(\frac{\partial^2}{\partial \nu^2} + \frac{\partial^2}{\partial \eta^2}\right) f,\end{aligned} \tag{5.150}$$

$$\begin{aligned}\frac{\partial^2 f}{\partial \psi_1 \partial \psi_2} =& \frac{\partial}{\partial \psi_1}\left(\frac{\partial f}{\partial \psi_2}\right) \\ =& \frac{1}{4}\left(\frac{\partial^2}{\partial \nu^2} - \frac{\partial^2}{\partial \eta^2}\right) f.\end{aligned} \tag{5.151}$$

Substituting Eqs. (5.145) - (5.151) into Eqs. (5.139) and (5.140) we obtain

$$\hat{\mathrm{L}}f = \left\{ -\frac{V_0 \sin 2\eta}{\xi_z}\frac{\partial}{\partial \eta} - 2\frac{V_0 \cos 2\eta}{\xi_z} \right\} f \,, \tag{5.152}$$

and

$$\begin{aligned} \mathrm{St}(f) =& \frac{kT}{\xi}\left[\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{2}{4}\cot^2\theta \left(\frac{\partial^2}{\partial \nu^2} - \frac{\partial^2}{\partial \eta^2} \right) \right. \\ & \left. + \frac{1}{2}\left(\cot^2\theta + \frac{\xi}{\xi_z} \right)\left(\frac{\partial^2}{\partial \nu^2} + \frac{\partial^2}{\partial \eta^2} \right) \right] f \\ =& \frac{kT}{\xi}\left[\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \cot^2\theta \frac{\partial^2}{\partial \nu^2} + \frac{\xi}{2\xi_z}\left(\frac{\partial^2}{\partial \nu^2} + \frac{\partial^2}{\partial \eta^2} \right) \right] f. \end{aligned} \tag{5.153}$$

Recalling that $\tau = \xi/(2kT)$ is the Debye relaxation time for rotations about the x and y axes and $\tau_z = \xi_z/(2kT)$ is the Debye relaxation time for rotations about the z-axis, we have

$$\begin{aligned} \frac{\tau}{2\tau_z} =& \frac{\frac{\xi}{2kT}}{2\left(\frac{\xi_z}{2kT}\right)} \\ =& \frac{\xi}{2\xi_z}. \end{aligned} \tag{5.154}$$

Using Eqs. (5.152) - (5.154) we can rewrite Eq. (5.141) as

$$\begin{aligned} & \frac{\partial}{\partial t}f - \left\{ \frac{V_0 \sin 2\eta}{\xi_z}\frac{\partial}{\partial \eta} + 2\frac{V_0 \cos 2\eta}{\xi_z} \right\} f \\ =& \tau^{1-\alpha}\, {}_0D_t^{1-\alpha} \left\{ \frac{kT}{\xi}\left[\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \cot^2\theta \frac{\partial^2}{\partial \nu^2} + \frac{\tau}{2\tau_z}\left(\frac{\partial^2}{\partial \nu^2} + \frac{\partial^2}{\partial \eta^2} \right) \right] f \right\}. \end{aligned} \tag{5.155}$$

$$\begin{aligned} \Rightarrow \frac{\partial}{\partial t}f = & \left\{ \frac{V_0}{\xi_z}\left[\sin 2\eta \frac{\partial}{\partial \eta} + 2\cos 2\eta \right] \right. \\ & \left. + \tau^{1-\alpha}\left(\frac{kT}{\xi}\right) {}_0D_t^{1-\alpha}\left[\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \cot^2\theta \frac{\partial^2}{\partial \nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial \nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial \eta^2} \right] \right\} f. \end{aligned} \tag{5.156}$$

Multiplying both sides of Eq. (5.156) by $\xi/(kT) = 2\tau$ we obtain

$$2\tau\frac{\partial}{\partial t}f = \Bigg\{\left(\frac{V_0}{kT}\right)\left(\frac{\xi}{\xi_z}\right)\left[\sin 2\eta\frac{\partial}{\partial\eta} + 2\cos 2\eta\right] + \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\Bigg\} f. \tag{5.157}$$

Noting that $\sigma_V = V_0/kT$ and $\xi/\xi_z = \tau/\tau_z$ we may write Eq. (5.157) as

$$\begin{aligned}2\tau\frac{\partial}{\partial t}f &= \Bigg\{\frac{\tau}{\tau_z}\,\sigma_V\left[\sin 2\eta\frac{\partial}{\partial\eta} + 2\cos 2\eta\right] \\ &\quad + \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\Bigg\} f \\ &= \Bigg\{\frac{\tau}{\tau_z}\,\sigma_V\left[\sin 2\eta\frac{\partial}{\partial\eta} + 2\cos 2\eta\right] \\ &\quad + \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \left(1+\cot^2\theta\right)\frac{\partial^2}{\partial\nu^2} + \left(\frac{\tau}{2\tau_z} - 1\right)\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\Bigg\} f.\end{aligned} \tag{5.158}$$

Consider the Laplace operator ∇^2 or Δ written in spherical coordinates

$$\Delta f = \frac{1}{r^2}\frac{\partial^2}{\partial r^2}(rf) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\nu^2}. \tag{5.159}$$

Note that

$$1+\cot^2\theta = 1 + \frac{\cos^2\theta}{\sin^2\theta} = \frac{\sin^2\theta + \cos^2\theta}{\sin^2\theta} = \frac{1}{\sin^2\theta}. \tag{5.160}$$

With $r = 1$, the angular part of the Laplacian, $\Delta_{\theta,\nu}$, is given by

$$\begin{aligned}\Delta_{\theta,\nu} f &= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\nu^2} \\ &= \frac{1}{\sin\theta}\left[\cos\theta\frac{\partial f}{\partial\theta} + \sin\theta\frac{\partial^2 f}{\partial\theta^2}\right] + \left(1+\cot^2\theta\right)\frac{\partial^2 f}{\partial\nu^2} \\ &= \cot\theta\frac{\partial f}{\partial\theta} + \frac{\partial^2 f}{\partial\theta^2} + \left(1+\cot^2\theta\right)\frac{\partial^2 f}{\partial\nu^2} \\ &= \left[\cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \left(1+\cot^2\theta\right)\frac{\partial^2}{\partial\nu^2}\right] f.\end{aligned} \tag{5.161}$$

Using Eq. (5.161) we can rewrite Eq. (5.158) as

$$2\tau\frac{\partial}{\partial t}f = \left\{\frac{\tau}{\tau_z}\,\sigma_V\left[\sin 2\eta\frac{\partial}{\partial\eta} + 2\cos 2\eta\right]\right.$$
$$\left. + \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\Delta_{\theta,\nu} + \left(\frac{\tau}{2\tau_z} - 1\right)\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\right\}f. \quad (5.162)$$

5.F Derivation of the Differential-Recurrence Relation

Recall that the Smoluchowski equation describing the relaxation process at time $t > 0$ ($\mathbf{F} = 0$) is

$$2\tau\frac{\partial}{\partial t}f = \left\{\frac{\sigma\tau}{\tau_z}\left[\sin 2\eta\frac{\partial}{\partial\eta} + 2\cos 2\eta\right]\right.$$
$$\left. + \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\Delta_{\theta,\nu} + \left(\frac{\tau}{2\tau_z} - 1\right)\frac{\partial^2}{\partial\nu^2} + \frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\right\}f, \quad (5.163)$$

where $\Delta_{\theta,\nu}$ is the angular part of Laplacian written in terms of θ and ν, $\tau = \xi/(2kT)$ is the Debye relaxation time with respect to rotations about the x and y axes and $\tau_z = \xi_z/(2kT)$ is the Debye relaxation time with respect to rotations about the z-axis.

We seek the solution of the Smoluchowski equation (5.163) as a Fourier-Laplace series

$$f(\theta,\nu,\eta,t) = \sum_{l,p,q} f^l_{pq}(t)Y^*_{lp}(\theta,\nu)e^{-iq\eta}, \quad (5.164)$$

where the Fourier amplitudes $f^l_{pq}(t)$ are the statistical moments defined by

$$f^l_{pq}(t) = \int Y_{lp}(\theta,\nu)e^{iq\eta}f\,d\Omega' = \left\langle Y_{lp}(\theta,\nu)e^{iq\eta}\right\rangle(t), \quad (5.165)$$

where $d\Omega' = \sin\theta d\theta d\nu d\eta$, $Y_{lp}(\theta,\nu)$ are spherical harmonics, with $l = 0, 1, 2, ...$, $p = 0, \pm 1, ..., \pm l$ and $q = 0, \pm 2, \pm 4, ...$ for even values of p and $q = \pm 1, \pm 3, ...$ for odd values of p.

To obtain the differential-recurrence equation, we start by substituting Eq.

(5.164) into Eq. (5.163) to get

$$2\tau\frac{\partial}{\partial t}\left[\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right] = \frac{\sigma\tau}{\tau_z}\left[\sin 2\eta\frac{\partial}{\partial\eta}+2\cos 2\eta\right]\left[\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right]$$
$$+\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\Delta_{\theta,\nu}+\left(\frac{\tau}{2\tau_z}-1\right)\frac{\partial^2}{\partial\nu^2}+\frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\left[\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right]. \tag{5.166}$$

Using Euler's formula, Eq. (5.166) can be rewritten as

$$2\tau\frac{\partial}{\partial t}\left[\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right] =$$
$$\frac{\sigma\tau}{\tau_z}\left[\left(\frac{e^{i2\eta}-e^{-i2\eta}}{2i}\right)\frac{\partial}{\partial\eta}+\left(e^{i2\eta}+e^{-i2\eta}\right)\right]\left[\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right]$$
$$+\,\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\Delta_{\theta,\nu}+\left(\frac{\tau}{2\tau_z}-1\right)\frac{\partial^2}{\partial\nu^2}+\frac{\tau}{2\tau_z}\frac{\partial^2}{\partial\eta^2}\right]\left[\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right]. \tag{5.167}$$

We then evaluate the derivatives in Eq. (5.167) to rewrite the equation (see Appendix 5.F.1) as

$$2\tau\frac{\partial}{\partial t}\left[\sum_{l,p,q}\frac{df_{pq}^{l}(t)}{dt}Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right] = \frac{\sigma\tau}{2\tau_z}\left[\sum_{l,p,q}(-q)\,f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)\overset{1}{\left[e^{-i(q-2)\eta}-e^{-i(q+2)\eta}\right]}\right.$$
$$\left.+\,2\sum_{l,p,q} f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)\overset{2}{\left[e^{-i(q-2)\eta}+e^{-i(q+2)\eta}\right]}\right]$$
$$+\,\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\sum_{l,p,q} f_{pq}^{l}(t)\overset{3}{\left(-l\left(l+1\right)\right)}Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right.$$
$$+\sum_{l,p,q}\left(-p^2\right)\overset{4}{\left(\frac{\tau}{2\tau_z}-1\right)}f_{pq}^{l}(t)Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}$$
$$\left.+\sum_{l,p,q} f_{pq}^{l}(t)\left(-q^2\right)\overset{5}{\left(\frac{\tau}{2\tau_z}\right)}Y_{lp}^{*}(\theta,\nu)e^{-iq\eta}\right]. \tag{5.168}$$

To obtain the differential-recurrence relation, we multiply both sides of Eq. (5.168) by $Y_{l'p'}(\theta,\nu)e^{iq'\eta}$ and then use the orthogonality properties of the spherical harmonics and the circular functions [2]

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} Y^*_{lp}(\theta,\nu)e^{-iq\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta = \delta_{ll'}\delta_{pp'}\delta_{qq'}2\pi. \tag{5.169}$$

Left Hand Side

$$\begin{aligned}
&\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\left(2\tau\sum_{l,p,q}\frac{df^l_{pq}(t)}{dt}Y^*_{lp}(\theta,\nu)e^{-iq\eta}\right)\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta\\
=&2\tau\sum_{l,p,q}\frac{df^l_{pq}(t)}{dt}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-iq\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta\\
=&2\tau\sum_{l,p,q}\frac{df^l_{pq}(t)}{dt}\delta_{ll'}\delta_{pp'}\delta_{qq'}2\pi\\
=&2\tau\,(2\pi)\,\frac{df^{l'}_{p'q'}(t)}{dt}.
\end{aligned}\tag{5.170}$$

Right Hand Side

1

$$\begin{aligned}
&\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{\sigma\tau}{2\tau_z}\left(\sum_{l,p,q}(-q)\,f^l_{pq}(t)Y^*_{lp}(\theta,\nu)\left[e^{-i(q-2)\eta}-e^{-i(q+2)\eta}\right]\right)\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta\\
=&\frac{\sigma\tau}{2\tau_z}\sum_{l,p,q}(-q)\,f^l_{pq}(t)\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)\left[e^{-i(q-2)\eta}-e^{-i(q+2)\eta}\right]\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta\\
=&\frac{\sigma\tau}{2\tau_z}\sum_{l,p,q}(-q)\,f^l_{pq}(t)\left[\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-i(q-2)\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta\right.\\
&\left.-\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-i(q+2)\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta\right]\\
=&\frac{\sigma\tau}{2\tau_z}\left[-\left(q'+2\right)f^{l'}_{p'q'+2}(t)2\pi+\left(q'-2\right)f^{l'}_{p'q'-2}(t)2\pi\right].
\end{aligned}\tag{5.171}$$

2

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{\sigma\tau}{2\tau_z}\left(2\sum_{l,p,q}f^l_{pq}(t)Y^*_{lp}(\theta,\nu)\left[e^{-i(q-2)\eta}+e^{-i(q+2)\eta}\right]\right)\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta$$
$$=\frac{\sigma\tau}{2\tau_z}\sum_{l,p,q}2f^l_{pq}(t)\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)\left[e^{-i(q-2)\eta}+e^{-i(q+2)\eta}\right]\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta$$
$$=\frac{\sigma\tau}{2\tau_z}\sum_{l,p,q}2f^l_{pq}(t)\left[\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-i(q-2)\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta\right.$$
$$\left.+\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-i(q+2)\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta\right]$$
$$=\frac{\sigma\tau}{2\tau_z}\left[2f^{l'}_{p'q'+2}(t)+2f^{l'}_{p'q'-2}(t)\right]2\pi. \tag{5.172}$$

3

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\left(\sum_{l,p,q}f^l_{pq}(t)\left(-l\left(l+1\right)\right)Y^*_{lp}(\theta,\nu)e^{-iq\eta}\right)\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta$$
$$=\sum_{l,p,q}f^l_{pq}(t)\left(-l\left(l+1\right)\right)\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-iq\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta$$
$$=\sum_{l,p,q}f^l_{pq}(t)\left(-l\left(l+1\right)\right)\delta_{ll'}\delta_{pp'}\delta_{qq'}2\pi$$
$$=\left(2\pi\right)f^{l'}_{p'q'}(t)\left(-l'\left(l'+1\right)\right). \tag{5.173}$$

4

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\left(\sum_{l,p,q}\left(-p^2\right)\left(\frac{\tau}{2\tau_z}-1\right)f^l_{pq}(t)Y^*_{lp}(\theta,\nu)e^{-iq\eta}\right)\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta$$
$$=\sum_{l,p,q}\left(-p^2\right)\left(\frac{\tau}{2\tau_z}-1\right)f^l_{pq}(t)\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-iq\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta$$
$$=\sum_{l,p,q}\left(-p^2\right)\left(\frac{\tau}{2\tau_z}-1\right)f^l_{pq}(t)\delta_{ll'}\delta_{pp'}\delta_{qq'}2\pi$$
$$=\left(2\pi\right)\left(-p'^2\right)\left(\frac{\tau}{2\tau_z}-1\right)f^{l'}_{p'q'}(t). \tag{5.174}$$

5

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\left(\sum_{l,p,q} f^l_{pq}(t)\left(-q^2\right)\left(\frac{\tau}{2\tau_z}\right)Y^*_{lp}(\theta,\nu)e^{-iq\eta}\right)\left(Y_{l'p'}(\theta,\nu)e^{iq'\eta}\right)\sin\theta d\theta d\nu d\eta$$
$$=\sum_{l,p,q}\left(-q^2\right)\left(\frac{\tau}{2\tau_z}\right)f^l_{pq}(t)\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}Y^*_{lp}(\theta,\nu)e^{-iq\eta}Y_{l'p'}(\theta,\nu)e^{iq'\eta}\sin\theta d\theta d\nu d\eta$$
$$=\sum_{l,p,q}\left(-q^2\right)\left(\frac{\tau}{2\tau_z}\right)f^l_{pq}(t)\delta_{ll'}\delta_{pp'}\delta_{qq'}2\pi$$
$$=(2\pi)\left(-q'^2\right)\left(\frac{\tau}{2\tau_z}\right)f^{l'}_{p'q'}(t). \tag{5.175}$$

Substituting Eqs. (5.171) - (5.175) into Eq. (5.168) we obtain

$$2\tau\,(2\pi)\,\frac{df^{l'}_{p'q'}(t)}{dt}$$
$$=\frac{\sigma\tau}{2\tau_z}\left[-\left(q'+2\right)f^{l'}_{p'q'+2}(t)\overset{1}{+}\left(q'-2\right)f^{l'}_{p'q'-2}(t)+2f^{l'}_{p'q'+2}(t)\overset{2}{+}2f^{l'}_{p'q'-2}(t)\right]2\pi$$
$$+\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[(2\pi)\,f^{l'}_{p'q'}(t)\overset{3}{\left(-l'\left(l'+1\right)\right)}+(2\pi)\left(-p'^2\right)\overset{4}{\left(\frac{\tau}{2\tau_z}-1\right)}f^{l'}_{p'q'}(t)\right.$$
$$\left.+\overset{5}{(2\pi)}\left(-q'^2\right)\left(\frac{\tau}{2\tau_z}\right)f^{l'}_{p'q'}(t)\right], \tag{5.176}$$

Eq. (5.176) can be rewritten as

$$2\tau\frac{d}{dt}f^l_{pq}(t)=\frac{\sigma\tau}{2\tau_z}q\left[f^l_{pq-2}(t)-f^l_{pq+2}(t)\right]$$
$$-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[\left(l\left(l+1\right)\right)+\left(p^2\right)\left(\frac{\tau}{2\tau_z}-1\right)+\left(q^2\right)\left(\frac{\tau}{2\tau_z}\right)\right]f^l_{pq}(t). \tag{5.177}$$

5.F.1 Evaluation of the partial derivatives in Eq. (5.167)

The spherical harmonics $Y_{lp}(\theta,\nu)$ are defined by

$$Y_{lp}\left(\theta,\nu\right)=\sqrt{\frac{\left(2l+1\right)}{4\pi}\frac{\left(l-p\right)!}{\left(l+p\right)!}}e^{ip\nu}P^p_l\left(\cos\left(\theta\right)\right)\ |p|\le l. \tag{5.178}$$

We seek a solution of the fractional Smoluchowski equation as the Fourier-Laplace series

$$f(\theta,\nu,\eta,t)=\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}. \tag{5.179}$$

The partial derivatives of $f(\theta,\nu,\eta,t)$ are given by

$$\begin{aligned}\frac{\partial}{\partial\nu}f\left(\theta,\nu,\eta,t\right)=&\frac{\partial}{\partial\nu}\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)\frac{\partial}{\partial\nu}Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)\left(-ip\right)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta},\end{aligned} \tag{5.180}$$

$$\begin{aligned}\frac{\partial^2}{\partial\nu^2}f\left(\theta,\nu,\eta,t\right)=&\frac{\partial^2}{\partial\nu^2}\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)\frac{\partial^2}{\partial\nu^2}Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)\left(-p^2\right)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta},\end{aligned} \tag{5.181}$$

$$\begin{aligned}\frac{\partial}{\partial\eta}f\left(\theta,\nu,\eta,t\right)=&\frac{\partial}{\partial\eta}\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)\frac{\partial}{\partial\eta}e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)\left(-iq\right)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta},\end{aligned} \tag{5.182}$$

$$\begin{aligned}\frac{\partial^2}{\partial\eta^2}f\left(\theta,\nu,\eta,t\right)=&\frac{\partial^2}{\partial\eta^2}\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)Y^{*}_{lp}(\theta,\nu)\frac{\partial^2}{\partial\eta^2}e^{-iq\eta}\\ =&\sum_{l,p,q} f^{l}_{pq}(t)\left(-q^2\right)Y^{*}_{lp}(\theta,\nu)e^{-iq\eta}.\end{aligned} \tag{5.183}$$

Using the properties of spherical harmonics, $\Delta_{\theta,\nu} f$ can be written as [2]

$$\begin{aligned}
\Delta_{\theta,\nu} f =& \Delta_{\theta,\nu}\left(\sum_{l,p,q} f_{pq}^{l}(t) Y_{lp}^{*}(\theta,\nu) e^{-iq\eta}\right) \\
=& \sum_{l,p,q} f_{pq}^{l}(t)\left(\Delta_{\theta,\nu} Y_{lp}^{*}(\theta,\nu)\right) e^{-iq\eta} \\
=& \sum_{l,p,q} f_{pq}^{l}(t)\left(-l\left(l+1\right) Y_{lp}^{*}(\theta,\nu)\right) e^{-iq\eta}.
\end{aligned} \tag{5.184}$$

5.G Derivation of the Differential-Recurrence Relation in terms of the Functions $a_{2q-1}^{c,s}(t)$

The associated Legendre functions $P_l^p(\cos\theta)$ are defined as [2]

$$P_l^p(\cos\theta) = \frac{(-1)^p}{2^l l!}(\sin\theta)^p \frac{d^{l+p}}{d(\cos\theta)^{l+p}}\left(\cos^2\theta - 1\right)^l, \ |p| \le l. \tag{5.185}$$

With $l = p = 1$, we have

$$P_1^1(\cos\theta) = -\sin\theta. \tag{5.186}$$

The spherical harmonics $Y_{lp}(\theta,\nu)$ are given by [2]

$$Y_{lp}(\theta,\nu) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-p)!}{(l+p)!}} e^{ip\nu} P_l^p(\cos\theta). \tag{5.187}$$

The spherical harmonic $Y_{11}(\theta,\nu)$ is given by

$$\begin{aligned}
Y_{11}(\theta,\nu) =& \sqrt{\frac{2(1)+1}{4\pi}\frac{(1-1)!}{(1+1)!}} e^{i(1)\nu} P_1^1(\cos\theta) \\
=& \sqrt{\frac{3}{8\pi}} e^{i\nu} P_1^1(\cos\theta) \\
=& -\sqrt{\frac{3}{8\pi}} e^{i\nu}\sin\theta.
\end{aligned} \tag{5.188}$$

Using the following property of spherical harmonics

$$Y_{l-m}(\theta,\nu) = (-1)^m Y_{lm}^{*}(\theta,\nu), \tag{5.189}$$

we have

$$Y_{1-1}(\theta,\nu) = (-1)^1 Y_{11}^*(\theta,\nu) = \sqrt{\frac{3}{8\pi}} e^{-i\nu}\sin\theta. \tag{5.190}$$

Recall that that the Fourier amplitudes $f_{pq}^l(t)$ are the statistical moments defined by

$$f_{pq}^l(t) = \int Y_{lp}(\theta,\nu)e^{iq\eta}f(\theta,\nu,\eta,t)d\Omega' = \left\langle Y_{lp}(\theta,\nu)e^{iq\eta}\right\rangle(t), \tag{5.191}$$

where $d\Omega' = \sin\theta d\theta d\nu d\eta$, $Y_{lp}(\theta,\nu)$ are spherical harmonics, with $l = 0,1,2,...$, $p = 0,\pm1,...,\pm l$ and $q = 0,\pm2,\pm4...$ for even values of p and $q = \pm1,\pm3...$ for odd values of p. For $l = 1$ and $p = -1$ we have

$$\begin{aligned} f_{-1q}^1(t) &= \left\langle Y_{1,-1}(\theta,\nu)e^{iq\eta}\right\rangle(t) \\ &= \left\langle Y_{1,-1}(\theta,\nu)\left[\cos(q\eta) + i\sin(q\eta)\right]\right\rangle(t) \\ &= \left\langle Y_{1,-1}(\theta,\nu)\cos(q\eta)\right\rangle(t) + i\left\langle Y_{1,-1}(\theta,\nu)\sin(q\eta)\right\rangle(t) \\ &= a_q^c(t) + ia_q^s(t). \end{aligned} \tag{5.192}$$

We recall that the differential-recurrence relation for $f_{pq}^l(t)$ is given by

$$\begin{aligned} 2\tau\frac{d}{dt}f_{pq}^l(t) = &\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[f_{pq-2}^l(t) - f_{pq+2}^l(t)\right]\right. \\ &\left. - \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[l(l+1) + p^2\left(\frac{\tau}{2\tau_z} - 1\right) + q^2\frac{\tau}{2\tau_z}\right]f_{pq}^l(t)\right\}. \end{aligned} \tag{5.193}$$

Substituting Eq. (5.192) into Eq. (5.193) we obtain

$$\begin{aligned} 2\tau\frac{d}{dt}\left[a_q^c(t) + ia_q^s(t)\right] = &\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[\left[a_{q-2}^c(t) + ia_{q-2}^s(t)\right] - \left[a_{q+2}^c(t) + ia_{q+2}^s(t)\right]\right]\right. \\ &\left. - \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[(1)(1+1) + (-1)^2\left(\frac{\tau}{2\tau_z} - 1\right) + q^2\frac{\tau}{2\tau_z}\right]\left[a_q^c(t) + ia_q^s(t)\right]\right\}. \end{aligned} \tag{5.194}$$

$$\begin{aligned} \Rightarrow 2\tau\frac{d}{dt}\left[a_q^c(t) + ia_q^s(t)\right] = &\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[\left[a_{q-2}^c(t) + ia_{q-2}^s(t)\right] - \left[a_{q+2}^c(t) + ia_{q+2}^s(t)\right]\right]\right. \\ &\left. - \tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2 + \left(\frac{\tau}{2\tau_z} - 1\right) + q^2\frac{\tau}{2\tau_z}\right]\left[a_q^c(t) + ia_q^s(t)\right]\right\}. \end{aligned} \tag{5.195}$$

From Eq. (5.195) we have

$$2\tau\frac{d}{dt}a_q^c(t)=\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[a_{q-2}^c(t)-a_{q+2}^c(t)\right]\right.$$
$$\left.-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2+\left(\frac{\tau}{2\tau_z}-1\right)+q^2\frac{\tau}{2\tau_z}\right]a_q^c(t)\right\}, \quad (5.196)$$

and

$$2\tau\frac{d}{dt}ia_q^s(t)=\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[ia_{q-2}^s(t)-ia_{q+2}^s(t)\right]\right.$$
$$\left.-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2+\left(\frac{\tau}{2\tau_z}-1\right)+q^2\frac{\tau}{2\tau_z}\right]ia_q^s(t)\right\}.$$
$$\Rightarrow 2\tau\frac{d}{dt}a_q^s(t)=\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[a_{q-2}^s(t)-a_{q+2}^s(t)\right]\right.$$
$$\left.-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2+\left(\frac{\tau}{2\tau_z}-1\right)+q^2\frac{\tau}{2\tau_z}\right]a_q^s(t)\right\}. \quad (5.197)$$

Eqs. (5.196) and (5.197) can be written more compactly as

$$2\tau\frac{d}{dt}a_q^{c,s}(t)=\left\{\frac{\tau\sigma_V}{2\tau_z}q\left[a_{q-2}^{c,s}(t)-a_{q+2}^{c,s}(t)\right]\right.$$
$$\left.-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2+\left(\frac{\tau}{2\tau_z}-1\right)+q^2\frac{\tau}{2\tau_z}\right]a_q^{c,s}(t)\right\}. \quad (5.198)$$

Replacing q with $2q-1$ in Eq. (5.198) we have

$$2\tau\frac{d}{dt}a_{2q-1}^{c,s}(t)=\left\{\frac{\tau\sigma_V}{2\tau_z}(2q-1)\left[a_{(2q-1)-2}^{c,s}(t)-a_{(2q-1)+2}^{c,s}(t)\right]\right.$$
$$\left.-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2+\left(\frac{\tau}{2\tau_z}-1\right)+(2q-1)^2\frac{\tau}{2\tau_z}\right]a_{2q-1}^{c,s}(t)\right\}. \quad (5.199)$$

$$\Rightarrow 2\tau\frac{d}{dt}a_{2q-1}^{c,s}(t)=\left\{\frac{\tau\sigma_V}{2\tau_z}(2q-1)\left[a_{2q-3}^{c,s}(t)-a_{2q+1}^{c,s}(t)\right]\right.$$
$$\left.-\tau^{1-\alpha}\,{}_0D_t^{1-\alpha}\left[2+\left(\frac{\tau}{2\tau_z}-1\right)+(2q-1)^2\frac{\tau}{2\tau_z}\right]a_{2q-1}^{c,s}(t)\right\}. \quad (5.200)$$

We define Q^{-}_{2q-1}, Q^{+}_{2q-1}, and Q_{2q-1} as

$$\begin{aligned} Q^{-}_{2q-1} =& \frac{\tau\sigma_V}{2\tau_z}(2q-1) \\ =& \sigma_V\left(\frac{\tau}{2\tau_z}\right)(2q-1) \\ =& \sigma_V\gamma(2q-1), \end{aligned} \tag{5.201}$$

$$\begin{aligned} Q^{+}_{2q-1} =& -\frac{\tau\sigma_V}{2\tau_z}(2q-1) \\ =& -\sigma_V\left(\frac{\tau}{2\tau_z}\right)(2q-1) \\ =& -\sigma_V\gamma(2q-1), \end{aligned} \tag{5.202}$$

$$\begin{aligned} Q_{2q-1} =& -2-\left(\frac{\tau}{2\tau_z}-1\right)-(2q-1)^2\frac{\tau}{2\tau_z} \\ =& -1-\frac{\tau}{2\tau_z}-(2q-1)^2\frac{\tau}{2\tau_z} \\ =& -1-\gamma-(2q-1)^2\gamma \\ =& -1-\gamma\left(1+(2q-1)^2\right). \end{aligned} \tag{5.203}$$

Using Eqs. (5.201) - (5.203) we may write Eq. (5.200) as the ordinary differential-recurrence relation

$$2\tau\frac{d}{dt}a^{c,s}_{2q-1}(t) = Q^{-}_{2q-1}a^{c,s}_{2q-3}(t)+Q^{+}_{2q-1}a^{c,s}_{2q+1}(t)+\tau^{1-\alpha}\,{}_0D^{1-\alpha}_t Q_{2q-1}a^{c,s}_{2q-1}(t). \tag{5.204}$$

Taking the Laplace transform of both sides of Eq. (5.204) we have (see Appendix 5.H)

$$2\tau\left[s\tilde{a}^{c,s}_{2q-1}(s) - a^{c,s}_{2q-1}(0)\right] = Q^{-}_{2q-1}\tilde{a}^{c,s}_{2q-3}(s) + Q^{+}_{2q-1}\tilde{a}^{c,s}_{2q+1}(s) + \frac{\tau^{1-\alpha}}{s^{\alpha-1}}Q_{2q-1}\tilde{a}^{c,s}_{2q-1}(s). \tag{5.205}$$

$$\Rightarrow -2\tau a^{c,s}_{2q-1}(0) = \left(-2\tau s + (\tau s)^{1-\alpha}Q_{2q-1}\right)\tilde{a}^{c,s}_{2q-1}(s) + Q^{-}_{2q-1}\tilde{a}^{c,s}_{2q-3}(s) + Q^{+}_{2q-1}\tilde{a}^{c,s}_{2q+1}(s). \tag{5.206}$$

$$\Rightarrow -2\tau a^{c,s}_{2q-1}(0) = \bar{Q}_{2q-1}\tilde{a}^{c,s}_{2q-1}(s) + Q^{-}_{2q-1}\tilde{a}^{c,s}_{2q-3}(s) + Q^{+}_{2q-1}\tilde{a}^{c,s}_{2q+1}(s), \tag{5.207}$$

where

$$\bar{Q}_{2q-1}(s) = (\tau s)^{1-\alpha}Q_{2q-1} - 2\tau s. \tag{5.208}$$

5.H The Laplace Transform of ${}_0D_t^{1-\alpha}Q_{2q-1}a^{c,s}_{2q-1}(t)$

The fractional operator ${}_0D_t^{1-\alpha} \equiv \frac{\partial}{\partial t}\,{}_0D_t^{-\alpha}$ is defined in terms of the convolution (the Riemann-Liouville definition)

$${}_0D_t^{-\alpha}f(\mathbf{\Omega}, t) = \frac{1}{\Gamma(\alpha)}\int_0^t \frac{f(\mathbf{\Omega}, t')dt'}{(t-t')^{1-\alpha}}, \tag{5.209}$$

where $\Gamma(\alpha)$ denotes the gamma function. Eq. (5.209) can be rewritten as

$$\begin{aligned}
{}_0D_t^{1-\alpha}f(\mathbf{\Omega}, t) =& {}_0D_t^{-(\alpha-1)}f(\mathbf{\Omega}, t)\\
=&\frac{1}{\Gamma(\alpha-1)}\int_0^t \frac{f(\mathbf{\Omega}, t')dt'}{(t-t')^{1-(\alpha-1)}}\\
=&\frac{1}{\Gamma(\alpha-1)}\int_0^t \frac{f(\mathbf{\Omega}, t')dt'}{(t-t')^{2-\alpha}}\\
=&\frac{1}{\Gamma(\alpha-1)}\left[f(\mathbf{\Omega}, t)u(t) * \frac{1}{(t)^{2-\alpha}}u(t)\right],
\end{aligned} \tag{5.210}$$

where the asterisk denotes linear convolution and $u(t)$ is the unit step function. Taking the Laplace transform of ${}_0D_t^{1-\alpha} f(\mathbf{\Omega}, t)$ we get

$$\mathcal{L}\left\{{}_0D_t^{1-\alpha} f(\mathbf{\Omega}, t)\right\} = \mathcal{L}\left\{\frac{1}{\Gamma(\alpha-1)}\left[f(\mathbf{\Omega}, t)u(t) * \frac{1}{(t)^{2-\alpha}}u(t)\right]\right\}. \tag{5.211}$$

Using the convolution property of the Laplace transform we can rewrite Eq. (5.211) as

$$\mathcal{L}\left\{{}_0D_t^{1-\alpha} f(\mathbf{\Omega}, t)\right\} = \frac{1}{\Gamma(\alpha-1)}\left[\mathcal{L}\left\{f(\mathbf{\Omega}, t)u(t)\right\} \times \mathcal{L}\left\{\frac{1}{(t)^{2-\alpha}}u(t)\right\}\right]. \tag{5.212}$$

We seek now to obtain the Laplace transform of $1/(t)^{2-\alpha}u(t)$. From the table of Laplace transforms [119] we have

$$\mathcal{L}\left\{\frac{(t)^{n-1}}{(n-1)!}u(t)\right\} = \frac{1}{s^n}, \ \mathrm{Re}\left\{s\right\} > 0. \tag{5.213}$$

Multiplying both sides of Eq. (5.213) by $(n-1)!$ we have

$$\mathcal{L}\left\{(t)^{n-1}u(t)\right\} = \frac{(n-1)!}{s^n}, \ \mathrm{Re}\left\{s\right\} > 0. \tag{5.214}$$

Replacing n by $n-1$ in Eq. (5.214) we obtain

$$\mathcal{L}\left\{(t)^{(n-1)-1}u(t)\right\} = \frac{((n-1)-1)!}{s^{(n-1)}}, \ \mathrm{Re}\left\{s\right\} > 0. \tag{5.215}$$

$$\Rightarrow \mathcal{L}\left\{(t)^{n-2}u(t)\right\} = \frac{(n-2)!}{s^{(n-1)}}, \ \mathrm{Re}\left\{s\right\} > 0. \tag{5.216}$$

With $n = \alpha$ in Eq. (5.216) we get

$$\mathcal{L}\left\{\frac{1}{(t)^{2-\alpha}}u(t)\right\} = \mathcal{L}\left\{(t)^{\alpha-2}u(t)\right\} = \frac{(\alpha-2)!}{s^{(\alpha-1)}}, \ \mathrm{Re}\left\{s\right\} > 0. \tag{5.217}$$

The Laplace transform of the functions $a_q^c(t)$ and $a_q^s(t)$ is given by

$$\begin{aligned}\mathcal{L}\left\{{}_0D_t^{1-\alpha}Q_{2q-1}a_{2q-1}^{c,s}(t)\right\} =& Q_{2q-1}\mathcal{L}\left\{{}_0D_t^{1-\alpha}a_{2q-1}^{c,s}(t)\right\}\\ =& Q_{2q-1}\tilde{a}_{2q-1}^{c,s}(s)\left[\frac{(\alpha-2)!}{s^{\alpha-1}}\right]\frac{1}{\Gamma(\alpha-1)}.\end{aligned} \tag{5.218}$$

Noting that $\Gamma(\alpha-1)=(\alpha-2)!$ we get for Eq. (5.218)

$$\begin{aligned}\mathcal{L}\left\{{}_0D_t^{1-\alpha}Q_{2q-1}a_{2q-1}^{c,s}(t)\right\} =& Q_{2q-1}\tilde{a}_{2q-1}^{c,s}(s)\left[\frac{(\alpha-2)!}{s^{\alpha-1}}\right]\frac{1}{(\alpha-2)!}\\ =& Q_{2q-1}\tilde{a}_{2q-1}^{c,s}(s)\frac{1}{s^{\alpha-1}}.\end{aligned} \tag{5.219}$$

5.I The Initial Values of the Functions $a_q^{c,s}(t)$

We have for the initial value $a_q^c(t)$

$$\begin{aligned}a_q^c(0) =& \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta\, e^{(\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta))+\sigma_V\cos 2\eta}d\Omega'}{\int e^{(\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta))+\sigma_V\cos 2\eta}d\Omega'}\\ =& \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta\, e^{(\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta))}e^{\sigma_V\cos 2\eta}d\Omega'}{\int e^{(\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta))}e^{\sigma_V\cos 2\eta}d\Omega'}.\end{aligned} \tag{5.220}$$

Since $\sigma_i \ll 1,\ i=1,2$, we may approximate $e^{(\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta))}$ as

$$e^{(\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta))} \approx \left[1+\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta)\right]. \tag{5.221}$$

Substituting Eq. (5.221) into Eq. (5.220) we get

$$a_q^c(0) \approx \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta\left[1+\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}{\int\left[1+\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}. \tag{5.222}$$

Eq. (5.222) may be written as

$$\begin{aligned}a_q^c(0) \approx& \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta e^{\sigma_V\cos 2\eta}d\Omega'}{\int\left[1+\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}\\ &+\frac{\int Y_{1-1}(\theta,\nu)\cos q\eta\left[\sigma_1\sin\theta\cos(\nu+\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}{\int\left[1+\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}\\ &+\frac{\int Y_{1-1}(\theta,\nu)\cos q\eta\left[\sigma_2\sin\theta\cos(\nu-\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}{\int\left[1+\sigma_1\sin\theta\cos(\nu+\eta)+\sigma_2\sin\theta\cos(\nu-\eta)\right]e^{\sigma_V\cos 2\eta}d\Omega'}.\end{aligned} \tag{5.223}$$

Note that since $\sigma_i \ll 1,\ i = 1, 2$, we can rewrite Eqn. (5.223) as

$$
\begin{aligned}
a_q^c(0) \approx & \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta e^{\sigma_V \cos 2\eta} d\Omega'}{\int e^{\sigma_V \cos 2\eta} d\Omega'} \\
& + \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta \left[\sigma_1 \sin\theta \cos(\nu+\eta)\right] e^{\sigma_V \cos 2\eta} d\Omega'}{\int e^{\sigma_V \cos 2\eta} d\Omega'} \\
& + \frac{\int Y_{1-1}(\theta,\nu)\cos q\eta \left[\sigma_2 \sin\theta \cos(\nu-\eta)\right] e^{\sigma_V \cos 2\eta} d\Omega'}{\int e^{\sigma_V \cos 2\eta} d\Omega'},
\end{aligned}
\tag{5.224}
$$

which can also be written as

$$
\begin{aligned}
a_q^c(0) \approx & \langle Y_{1-1}(\theta,\nu)\cos q\eta\rangle_0 + \langle Y_{1-1}(\theta,\nu)\cos q\eta \left[\sigma_1 \sin\theta\cos(\nu+\eta)\right]\rangle_0 \\
& + \langle Y_{1-1}(\theta,\nu)\cos q\eta \left[\sigma_2 \sin\theta\cos(\nu-\eta)\right]\rangle_0.
\end{aligned}
\tag{5.225}
$$

Since $\langle Y_{1-1}(\theta,\nu)\cos q\eta\rangle_0 = 0$ we have

$$
\begin{aligned}
a_q^c(0) \approx & \sigma_1 \langle Y_{1-1}(\theta,\nu)\cos q\eta \sin\theta\cos(\nu+\eta)\rangle_0 \\
& + \sigma_2 \langle Y_{1-1}(\theta,\nu)\cos q\eta \sin\theta\cos(\nu-\eta)\rangle_0.
\end{aligned}
\tag{5.226}
$$

Similarly, we have for the initial value $a_q^s(0)$

$$
\begin{aligned}
a_q^s(0) \approx & \langle Y_{1-1}(\theta,\nu)\sin q\eta\rangle_0 + \langle Y_{1-1}(\theta,\nu)\sin q\eta \left[\sigma_1 \sin\theta\cos(\nu+\eta)\right]\rangle_0 \\
& + \langle Y_{1-1}(\theta,\nu)\sin q\eta \left[\sigma_2 \sin\theta\cos(\nu-\eta)\right]\rangle_0.
\end{aligned}
\tag{5.227}
$$

Since $\langle Y_{1-1}(\theta,\nu)\sin q\eta\rangle_0 = 0$ we have

$$
\begin{aligned}
a_q^s(0) \approx & \sigma_1 \langle Y_{1-1}(\theta,\nu)\sin q\eta \sin\theta\cos(\nu+\eta)\rangle_0 \\
& + \sigma_2 \langle Y_{1-1}(\theta,\nu)\sin q\eta \sin\theta\cos(\nu-\eta)\rangle_0.
\end{aligned}
\tag{5.228}
$$

Using Euler's formula, we can write Eqs. (5.226) and (5.228) as

$$a_q^c(0) \approx \frac{\sigma_1}{2}\big\langle Y_{1-1}(\theta,\nu)\cos q\eta \sin\theta \left[e^{i\nu}e^{i\eta} + e^{-i\nu}e^{-i\eta}\right]\big\rangle_0 + \frac{\sigma_2}{2}\big\langle Y_{1-1}(\theta,\nu)\cos q\eta \sin\theta \left[e^{i\nu}e^{-i\eta} + e^{-i\nu}e^{i\eta}\right]\big\rangle_0, \tag{5.229}$$

$$a_q^s(0) \approx \frac{\sigma_1}{2}\big\langle Y_{1-1}(\theta,\nu)\sin q\eta \sin\theta \left[e^{i\nu}e^{i\eta} + e^{-i\nu}e^{-i\eta}\right]\big\rangle_0 + \frac{\sigma_2}{2}\big\langle Y_{1-1}(\theta,\nu)\sin q\eta \sin\theta \left[e^{i\nu}e^{-i\eta} + e^{-i\nu}e^{i\eta}\right]\big\rangle_0. \tag{5.230}$$

Since the spherical harmonic $Y_{1-1}(\theta,\nu)$ is given as

$$Y_{1-1}(\theta,\nu) = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\nu}, \tag{5.231}$$

we have

$$\sin\theta e^{-i\nu} = \sqrt{\frac{8\pi}{3}}Y_{1-1}(\theta,\nu), \tag{5.232}$$

whose complex conjugate is given by

$$\sin\theta e^{i\nu} = \sqrt{\frac{8\pi}{3}}Y^*_{1-1}(\theta,\nu), \tag{5.233}$$

where the asterisk denotes complex conjugation. Furthermore, using Eqs. (5.232) and (5.233) and Euler's formula, we may write Eq. (5.229) as

$$\begin{aligned} a_q^c(0) \approx &\frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}}\left(\big\langle Y_{1-1}(\theta,\nu)Y^*_{1-1}(\theta,\nu)\left[e^{i(q+1)\eta} + e^{-i(q-1)\eta}\right]\right. \\ &+ Y_{1-1}(\theta,\nu)Y_{1-1}(\theta,\nu)\ \left.\left[e^{i(q-1)\eta} + e^{-i(q+1)\eta}\right]\big\rangle_0\right) \\ &+ \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}}\left(\big\langle Y_{1-1}(\theta,\nu)Y^*_{1-1}(\theta,\nu)\left[e^{i(q-1)\eta} + e^{-i(q+1)\eta}\right]\right. \\ &+ Y_{1-1}(\theta,\nu)Y_{1-1}(\theta,\nu)\ \left.\left[e^{i(q+1)\eta} + e^{-i(q-1)\eta}\right]\big\rangle_0\right). \end{aligned} \tag{5.234}$$

Similarly using Eqs. (5.232) and (5.233) and Euler's formula we may write Eq. (5.230) as

$$\begin{aligned} a_q^s(0) \approx & \frac{\sigma_1}{4i}\sqrt{\frac{8\pi}{3}}\left(\left\langle Y_{1-1}(\theta,\nu)Y_{1-1}^*(\theta,\nu)\left[e^{i(q+1)\eta}-e^{-i(q-1)\eta}\right]\right.\right. \\ & \left.\left.+\,Y_{1-1}(\theta,\nu)Y_{1-1}(\theta,\nu)\ \left[e^{i(q-1)\eta}-e^{-i(q+1)\eta}\right]\right\rangle_0\right) \\ & +\frac{\sigma_2}{4i}\sqrt{\frac{8\pi}{3}}\left(\left\langle Y_{1-1}(\theta,\nu)Y_{1-1}^*(\theta,\nu)\left[e^{i(q-1)\eta}-e^{-i(q+1)\eta}\right]\right.\right. \\ & \left.\left.+\,Y_{1-1}(\theta,\nu)Y_{1-1}(\theta,\nu)\ \left[e^{i(q+1)\eta}-e^{-i(q-1)\eta}\right]\right\rangle_0\right). \end{aligned} \tag{5.235}$$

Consider the following properties of spherical harmonics

$$Y_{l-p}(\theta,\nu) = (-1)^p\, Y_{lp}^*, \tag{5.236}$$

and

$$\int_0^{2\pi}\int_0^{\pi} Y_{lp}(\theta,\nu)[Y_{l'p'}(\theta,\nu)]^*\sin\theta d\theta d\nu = \delta_{ll'}\delta_{pp'}. \tag{5.237}$$

Using Eqs. (5.236) and (5.237) we may write Eq. (5.234) as

$$\begin{aligned} a_q^c(0) \approx & \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}}\frac{\int_0^{2\pi}\left(e^{i(q+1)\eta}+e^{-i(q-1)\eta}\right)e^{\sigma_V\cos 2\eta}d\eta}{4\pi\int_0^{2\pi}e^{\sigma_V\cos 2\eta}d\eta} \\ & +\frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}}\frac{\int_0^{2\pi}\left(e^{i(q-1)\eta}+e^{-i(q+1)\eta}\right)e^{\sigma_V\cos 2\eta}d\eta}{4\pi\int_0^{2\pi}e^{\sigma_V\cos 2\eta}d\eta}, \end{aligned} \tag{5.238}$$

and we may write Eq. (5.235) as

$$\begin{aligned} a_q^s(0) \approx & \frac{\sigma_1}{4i}\sqrt{\frac{8\pi}{3}}\frac{\int_0^{2\pi}\left(e^{i(q+1)\eta}-e^{-i(q-1)\eta}\right)e^{\sigma_V\cos 2\eta}d\eta}{4\pi\int_0^{2\pi}e^{\sigma_V\cos 2\eta}d\eta} \\ & +\frac{\sigma_2}{4i}\sqrt{\frac{8\pi}{3}}\frac{\int_0^{2\pi}\left(e^{i(q-1)\eta}-e^{-i(q+1)\eta}\right)e^{\sigma_V\cos 2\eta}d\eta}{4\pi\int_0^{2\pi}e^{\sigma_V\cos 2\eta}d\eta}. \end{aligned} \tag{5.239}$$

The function $e^{\sigma_V\cos 2\eta}$ may be written as the Fourier series [83]

$$e^{\sigma_V\cos 2\eta} = \sum_{m=-\infty}^{\infty} I_m(\sigma_V)\,e^{i2m\eta}, \tag{5.240}$$

where $I_m(\sigma_V)$ is the modified Bessel function of the first kind of order m. From

Eq. (5.240), using the orthogonality property of circular functions and noting that $I_{-m}(\sigma_V) = I_m(\sigma_V)$, we have for Eq. (5.238)

$$a_q^c(0) \approx \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}} \frac{\int_0^{2\pi} e^{i(q+1)\eta}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] + e^{-i(q-1)\eta}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] d\eta}{4\pi \int_0^{2\pi}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] d\eta}$$
$$+ \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}} \frac{\int_0^{2\pi} e^{i(q-1)\eta}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] + e^{-i(q+1)\eta}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] d\eta}{4\pi \int_0^{2\pi}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] d\eta}. \tag{5.241}$$

$$\Rightarrow a_q^c(0) \approx \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}} \frac{\int_0^{2\pi}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i(q+1+2m)\eta}\right] + \left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i(1-q+2m)\eta}\right] d\eta}{4\pi \int_0^{2\pi}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] d\eta}$$
$$+ \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}} \frac{\int_0^{2\pi}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i(q-1+2m)\eta}\right] + \left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i(-1-q+2m)\eta}\right] d\eta}{4\pi \int_0^{2\pi}\left[\sum_{m=-\infty}^{\infty} I_m(\sigma_V)\, e^{i2m\eta}\right] d\eta}. \tag{5.242}$$

$$\Rightarrow a_q^c(0) \approx \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}} \frac{\sum_{m=-\infty}^{\infty} I_m(\sigma_V) \int_0^{2\pi} e^{i(q+1+2m)\eta} d\eta + \sum_{m=-\infty}^{\infty} I_m(\sigma_V) \int_0^{2\pi} e^{i(1-q+2m)\eta} d\eta}{4\pi \sum_{m=-\infty}^{\infty} I_m(\sigma_V) \int_0^{2\pi} e^{i2m\eta} d\eta}$$
$$+ \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}} \frac{\sum_{m=-\infty}^{\infty} I_m(\sigma_V) \int_0^{2\pi} e^{i(q-1+2m)\eta} d\eta + \sum_{m=-\infty}^{\infty} I_m(\sigma_V) \int_0^{2\pi} e^{i(-1-q+2m)\eta} d\eta}{4\pi \sum_{m=-\infty}^{\infty} I_m(\sigma_V) \int_0^{2\pi} e^{i2m\eta} d\eta}. \tag{5.243}$$

$$\Rightarrow a_q^c(0) \approx \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}}\frac{2\pi I_{(-(q+1)/2)}(\sigma_V) + 2\pi I_{((q-1)/2)}(\sigma_V)}{4\pi(2\pi I_0(\sigma_V))} + \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}}\frac{2\pi I_{(-(q-1)/2)}(\sigma_V) + 2\pi I_{((q+1)/2)}(\sigma_V)}{4\pi(2\pi I_0(\sigma_V))}. \tag{5.244}$$

$$\Rightarrow a_q^c(0) \approx \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}}\frac{I_{(-(q+1)/2)}(\sigma_V) + I_{((q-1)/2)}(\sigma_V)}{4\pi(I_0(\sigma_V))} + \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}}\frac{I_{(-(q-1)/2)}(\sigma_V) + I_{((q+1)/2)}(\sigma_V)}{4\pi(I_0(\sigma_V))}. \tag{5.245}$$

$$\Rightarrow a_q^c(0) \approx \frac{\sigma_1}{4}\sqrt{\frac{8\pi}{3}}\frac{I_{((q+1)/2)}(\sigma_V) + I_{((q-1)/2)}(\sigma_V)}{4\pi(I_0(\sigma_V))} + \frac{\sigma_2}{4}\sqrt{\frac{8\pi}{3}}\frac{I_{((q-1)/2)}(\sigma_V) + I_{((q+1)/2)}(\sigma_V)}{4\pi(I_0(\sigma_V))}. \tag{5.246}$$

$$\Rightarrow a_q^c(0) \approx \frac{\sigma_1+\sigma_2}{4(I_0(\sigma_V)4\pi)}\sqrt{\frac{8\pi}{3}}\left(I_{((q+1)/2)}(\sigma_V) + I_{((q-1)/2)}(\sigma_V)\right) = \frac{\sigma_1+\sigma_2}{4I_0(\sigma_V)}\sqrt{\frac{1}{6\pi}}\left(I_{((q+1)/2)}(\sigma_V) + I_{((q-1)/2)}(\sigma_V)\right). \tag{5.247}$$

Similarly, we have for Eq. (5.239)

$$a_q^s(0) \approx \frac{\sigma_1-\sigma_2}{4i(I_0(\sigma_V)4\pi)}\sqrt{\frac{8\pi}{3}}\left(I_{((q+1)/2)}(\sigma_V) - I_{((q-1)/2)}(\sigma_V)\right) = \frac{\sigma_1-\sigma_2}{4iI_0(\sigma_V)}\sqrt{\frac{1}{6\pi}}\left(I_{((q+1)/2)}(\sigma_V) - I_{((q-1)/2)}(\sigma_V)\right). \tag{5.248}$$

Eq. (5.248) may be written as

$$a_q^s(0) \approx \frac{i(\sigma_2-\sigma_1)}{4I_0(\sigma_V)}\sqrt{\frac{1}{6\pi}}\left(I_{((q+1)/2)}(\sigma_V) - I_{((q-1)/2)}(\sigma_V)\right). \tag{5.249}$$

Eqs. (5.247) and (5.249) may be written more compactly as

$$a_q^c(0) \approx \frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_{(q+1)/2}(\sigma_V) + I_{(q-1)/2}(\sigma_V) \right), \tag{5.250}$$

$$a_q^s(0) \approx \frac{i\sigma_1 \left(\kappa - 1\right)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_{(q+1)/2}(\sigma_V) - I_{(q-1)/2}(\sigma_V) \right), \tag{5.251}$$

where $\kappa = \mu_2/\mu_1$.

5.J Solving the Differential-Recurrence Relation via Continued Fractions

Recall that the three-term scalar differential recurrence relation is given by

$$2\tau \frac{d}{dt} a_{2p-1}^J(t) = Q_{2p-1}^- a_{2p-3}^J(t) + Q_{2p-1}^+ a_{2p+1}^J(t) + \tau^{1-\alpha} \, {}_0D_t^{1-\alpha} Q_{2p-1} a_{2p-1}^J(t), \tag{5.252}$$

where $J = c, s$, $p = 1, 2, 3, ...$, $a_{-1}^c(t) = a_1^c(t)$, $a_{-1}^s(t) = -a_1^s(t)$,

$$Q_{2q-1} = -\, 1 - \gamma \left(1 + (2q-1)^2\right), \tag{5.253}$$

$$Q_{2q-1}^{\pm} = \mp \, \sigma_V \gamma (2q-1), \tag{5.254}$$

$$a_p^c(t) = \langle Y_{1-1} \cos p\eta \rangle (t), \tag{5.255}$$

$$a_p^s(t) = \langle Y_{1-1} \sin p\eta \rangle (t). \tag{5.256}$$

and $\gamma = \tau/(2\tau_z)$ is a ratio of Debye times. Taking the Laplace transform of Eq. (5.252) we obtained a three-term recurrence relation in the s domain viz.

$$\left(1 - \delta_{p1}\right) Q_{2p-1}^- \tilde{a}_{2p-3}^J(s) + \left(\bar{Q}_{2p-1}(s) + b^J \delta_{p1}\right) \tilde{a}_{2p-1}^J(s) + Q_{2p-1}^+ \tilde{a}_{2p+1}^J(s) = -2\tau a_{2p-1}^J(0), \tag{5.257}$$

where $b^c = \gamma \sigma_V$, $b^s = -\gamma \sigma_V$,

$$\bar{Q}_p(s) = (\tau s)^{1-\alpha} Q_p - 2\tau s, \tag{5.258}$$

and

$$\tilde{a}_p^J(s) = \int_0^\infty a_p^J(t)e^{-st}dt. \tag{5.259}$$

We seek the solution of Eq. (5.257) as

$$\tilde{a}_{2p-1}^J(s) = S_{2p-1}(s)\,\tilde{a}_{2p-3}^J(s) + R_{2p-1}(s), \tag{5.260}$$

where

$$S_{2p-1}(s) = \left[-\bar{Q}_{2p-1}(s) - b^J\delta_{p1} - Q_{2p-1}^{+}S_{2p+1}(s)\right]^{-1}Q_{2p-1}^{-}. \tag{5.261}$$

The particular solution $R_{2p-1}(s)$ may be found by substituting Eq. (5.260) into Eq. (5.257) to obtain

$$\begin{aligned}&(1-\delta_{p1})\,Q_{2p-1}^{-}\tilde{a}_{2p-3}^J(s) + \left(\bar{Q}_{2p-1}(s) + b^J\delta_{p1}\right)\left[S_{2p-1}(s)\,\tilde{a}_{2p-3}^J(s) + R_{2p-1}(s)\right]\\&+ Q_{2p-1}^{+}\left\{S_{2p+1}(s)\,\tilde{a}_{2p-1}^J(s) + R_{2p+1}(s)\right\} = -2\tau a_{2p-1}^J(0),\end{aligned} \tag{5.262}$$

which can be written as

$$\begin{aligned}&(1-\delta_{p1})\,Q_{2p-1}^{-}\tilde{a}_{2p-3}^J(s) + \left(\bar{Q}_{2p-1}(s) + b^J\delta_{p1}\right)\left[S_{2p-1}(s)\,\tilde{a}_{2p-3}^J(s) + R_{2p-1}(s)\right]\\&+ Q_{2p-1}^{+}\left\{S_{2p+1}(s)\left[S_{2p-1}(s)\,\tilde{a}_{2p-3}^J(s) + R_{2p-1}(s)\right] + R_{2p+1}(s)\right\} = -2\tau a_{2p-1}^J(0).\end{aligned} \tag{5.263}$$

Eq. (5.263) can be further written as

$$\begin{aligned}&Q_{2p-1}^{-}\tilde{a}_{2p-3}^J(s) - \delta_{p1}Q_{2p-1}^{-}\tilde{a}_{2p-3}^J(s)\\&+\left[S_{2p-1}(s)\left(\bar{Q}_{2p-1}(s) + b^J\delta_{p1} + Q_{2p-1}^{+}S_{2p+1}(s)\right)\tilde{a}_{2p-3}^J(s)\right]\\&+\left[\bar{Q}_{2p-1}(s) + b^J\delta_{p1} + Q_{2p-1}^{+}S_{2p+1}(s)\right]R_{2p-1}(s) + Q_{2p-1}^{+}R_{2p+1}(s) = -2\tau a_{2p-1}^J(0).\end{aligned} \tag{5.264}$$

Eq. (5.261) can be written as

$$S_{2p-1}(s)\left[\bar{Q}_{2p-1}(s) + b^J\delta_{p1} + Q_{2p-1}^{+}S_{2p+1}(s)\right] = -Q_{2p-1}^{-}. \tag{5.265}$$

Substituting Eq. (5.265) into Eq. (5.264) we obtain

$$Q^{-}_{2p-1}\tilde{a}^{J}_{2p-3}(s) - \delta_{p1}Q^{-}_{2p-1}\tilde{a}^{J}_{2p-3}(s) + \left[-Q^{-}_{2p-1}\tilde{a}^{J}_{2p-3}\left(s\right)\right] \\ + \left[\bar{Q}_{2p-1}(s) + b^{J}\delta_{p1} + Q^{+}_{2p-1}S_{2p+1}\left(s\right)\right]R_{2p-1}\left(s\right) + Q^{+}_{2p-1}R_{2p+1}\left(s\right) = -2\tau a^{J}_{2p-1}(0). \tag{5.266}$$

$$\Rightarrow -\delta_{p1}Q^{-}_{2p-1}\tilde{a}^{J}_{2p-3}(s) + \left[\bar{Q}_{2p-1}(s) + b^{J}\delta_{p1} + Q^{+}_{2p-1}S_{2p+1}\left(s\right)\right]R_{2p-1}\left(s\right) \\ + Q^{+}_{2p-1}R_{2p+1}\left(s\right) = -2\tau a^{J}_{2p-1}(0). \tag{5.267}$$

Since $\delta_{p1} = 0$, $p \neq 1$, we have

$$-\delta_{p1}Q^{-}_{1}\tilde{a}^{J}_{-1}(s) + \left[\bar{Q}_{2p-1}(s) + b^{J}\delta_{p1} + Q^{+}_{2p-1}S_{2p+1}\left(s\right)\right]R_{2p-1}\left(s\right) \\ + Q^{+}_{2p-1}R_{2p+1}\left(s\right) = -2\tau a^{J}_{2p-1}(0). \tag{5.268}$$

$$\Rightarrow \left[-\bar{Q}_{2p-1}(s) - b^{J}\delta_{p1} - Q^{+}_{2p-1}S_{2p+1}\left(s\right)\right]R_{2p-1}\left(s\right) \\ - Q^{+}_{2p-1}R_{2p+1}\left(s\right) = 2\tau a^{J}_{2p-1}(0) - \delta_{p1}Q^{-}_{1}\tilde{a}^{J}_{-1}(s). \tag{5.269}$$

We obtain the following expression for $R_{2p-1}\left(s\right)$

$$R_{2p-1}\left(s\right) = \frac{2\tau a^{J}_{2p-1}(0) - \delta_{p1}Q^{-}_{1}\tilde{a}^{J}_{-1}(s) + Q^{+}_{2p-1}R_{2p+1}\left(s\right)}{\left[-\bar{Q}_{2p-1}(s) - b^{J}\delta_{p1} - Q^{+}_{2p-1}S_{2p+1}\left(s\right)\right]}. \tag{5.270}$$

With $p = 1$ we have

$$\begin{aligned} R_{1}\left(s\right) =& \frac{2\tau a^{J}_{1}(0) - Q^{-}_{1}\tilde{a}^{J}_{-1}(s) + Q^{+}_{1}R_{3}\left(s\right)}{\left[-\bar{Q}_{1}(s) - b^{J} - Q^{+}_{1}S_{3}\left(s\right)\right]} \\ =& \frac{2\tau a^{J}_{1}(0) - Q^{-}_{1}\tilde{a}^{J}_{-1}(s)}{\left[-\bar{Q}_{1}(s) - b^{J} - Q^{+}_{1}S_{3}\left(s\right)\right]} + \frac{Q^{+}_{1}R_{3}\left(s\right)}{\left[-\bar{Q}_{1}(s) - b^{J} - Q^{+}_{1}S_{3}\left(s\right)\right]}. \end{aligned} \tag{5.271}$$

Let $p = 2$, in Eq. (5.270)

$$R_{3}\left(s\right) = \frac{2\tau a^{J}_{3}(0) + Q^{+}_{3}R_{5}\left(s\right)}{\left[-\bar{Q}_{3}(s) - Q^{+}_{3}S_{5}\left(s\right)\right]}. \tag{5.272}$$

Substituting Eq. (5.272) into Eq. (5.271), we get

$$R_1(s) = \frac{2\tau a_1^J(0) - Q_1^- \tilde{a}_{-1}^J(s)}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ S_3(s)\right]} + \frac{Q_1^+ \left[2\tau a_3^J(0) + Q_3^+ R_5(s)\right]}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ S_3(s)\right]\left[-\bar{Q}_3(s) - Q_3^+ S_5(s)\right]}. \tag{5.273}$$

We introduce the continued fraction $\Delta_n(s)$

$$\Delta_{2n-1}(s) = \frac{S_{2n-1}(s)}{Q_{2n-1}^-(s)} = \left[-\bar{Q}_{2n-1}(s) - Q_{2n-1}^+(s)\,\Delta_{2n+1}(s)\,Q_{2n+1}^-\right]^{-1},\ n \geq 2. \tag{5.274}$$

$S_{2n-1}(s)$ can now be expressed as

$$S_{2n-1}(s) = \Delta_{2n-1}(s)\,Q_{2n-1}^-(s),\ n \geq 2. \tag{5.275}$$

With $n = 2$ in Eqs. (5.274) and (5.275) we have

$$\Delta_3(s) = \frac{S_3(s)}{Q_3^-(s)} = \frac{1}{\left[-\bar{Q}_3(s) - Q_3^+(s)\,\Delta_5(s)\,Q_5^-(s)\right]}, \tag{5.276}$$

$$S_3(s) = \Delta_3(s)\,Q_3^-(s). \tag{5.277}$$

Substituting Eqs. (5.276) and (5.277) into Eq. (5.273) we get

$$R_1(s) = \frac{2\tau a_1^J(0) - Q_1^- \tilde{a}_{-1}^J(s) + Q_1^+ \Delta_3(s)\left[2\tau a_3^J(0)\right] + Q_1^+ \Delta_3(s)\,Q_3^+ R_5(s)}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ \Delta_3(s)\,Q_3^-(s)\right]}. \tag{5.278}$$

Substituting for $R_5(s)$ in Eq. (5.278), and again using Eqs. (5.274) and (5.275) we obtain

$$R_1(s) = \frac{2\tau a_1^J(0) - Q_1^- \tilde{a}_{-1}^J(s) + Q_1^+ \Delta_3(s)\left[2\tau a_3^J(0)\right] + Q_1^+ \Delta_3(s)\,Q_3^+ \Delta_5(s)\left[2\tau a_5^J(0) + ...\right]}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ \Delta_3(s)\,Q_3^-(s)\right]}. \tag{5.279}$$

Substituting Eq. (5.279) into Eq. (5.260) with $p = 1$ yields

$$\begin{aligned}
\tilde{a}_1^J(s) =& S_1(s)\,\tilde{a}_{-1}^J(s) + R_1(s) \\
=& \frac{Q_1^- \tilde{a}_{-1}^J(s)}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ \Delta_3(s)\, Q_3^-(s)\right]} \\
&+ \frac{2\tau a_1^J(0) - Q_1^- \tilde{a}_{-1}^J(s) + Q_1^+ \Delta_3(s)\left[2\tau a_3^J(0) + Q_3^+ \Delta_5(s)\left(2\tau a_5^J(0) + ...\right)\right]}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ \Delta_3(s)\, Q_3^-(s)\right]} \\
=& \frac{Q_1^- \tilde{a}_{-1}^J(s) - Q_1^- \tilde{a}_{-1}^J(s) + 2\tau\left\{a_1^J(0) + Q_1^+ \Delta_3(s)\left[a_3^J(0) + Q_3^+ \Delta_5(s)\left(a_5^J(0) + ...\right)\right]\right\}}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ \Delta_3(s)\, Q_3^-(s)\right]}.
\end{aligned} \tag{5.280}$$

$$\Rightarrow \tilde{a}_1^J(s) = 2\tau \frac{\left\{a_1^J(0) + Q_1^+ \Delta_3(s)\left[a_3^J(0) + Q_3^+ \Delta_5(s)\left(a_5^J(0) + ...\right)\right]\right\}}{\left[-\bar{Q}_1(s) - b^J - Q_1^+ \Delta_3(s)\, Q_3^-(s)\right]}. \tag{5.281}$$

5.K Derivation of the Response Functions $c_1(t)$ and $c_2(t)$

Consider the spherical harmonic $Y_{lp}(\theta, \nu)$ for $l = 1$, $p = -1$

$$Y_{1-1}(\theta, \nu) = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\nu}. \tag{5.282}$$

We have

$$\sin(\theta)\, e^{-i\nu} = \sqrt{\frac{8\pi}{3}} Y_{1-1}(\theta, \nu), \tag{5.283}$$

and

$$\sin(\theta)\, e^{i\nu} = \sqrt{\frac{8\pi}{3}} Y_{1-1}^*(\theta, \nu), \tag{5.284}$$

where the asterisk denotes complex conjugation. We will use the following properties of spherical harmonics

$$\int_0^{2\pi}\int_0^{\pi} Y_{lp}^*(\theta, \nu) Y_{l'p'}(\theta, \nu) \sin\theta d\theta d\nu = \delta_{ll'}\delta_{pp'}, \tag{5.285}$$

and

$$Y_{l-p}(\theta, \nu) = (-1)^p\, Y_{lp}^*. \tag{5.286}$$

With $l=1$ and $p=1$ in Eq. (5.286), we have

$$Y_{1-1}(\theta,\nu) = (-1)^1 Y_{11}^*(\theta,\nu)\,. \tag{5.287}$$

Taking the complex conjugate of both sides of Eq. (5.287) we get

$$Y_{1-1}^*(\theta,\nu) = (-1)\,Y_{11}(\theta,\nu)\,. \tag{5.288}$$

$$\Rightarrow Y_{1-1}^*(\theta,\nu) = -\,Y_{11}(\theta,\nu)\,. \tag{5.289}$$

The after-effect function $c_1(t) = \langle \sin\theta\cos\psi_1\rangle(t)$ may be expressed in terms of the new variables $\nu = (\psi_1+\psi_2)/2$ and $\eta = (\psi_1-\psi_2)/2$ as

$$\begin{aligned} c_1(t) &= \langle \sin\theta\cos(\nu+\eta)\rangle(t) \\ &= \frac{1}{2}\left\langle \sin\theta\left(e^{i\nu}e^{i\eta} + e^{-i\nu}e^{-i\eta}\right)\right\rangle(t) \\ &= \frac{1}{2}\left\langle \sin\theta e^{i\nu}e^{i\eta} + \sin\theta e^{-i\nu}e^{-i\eta}\right\rangle(t). \end{aligned} \tag{5.290}$$

Substituting Eqs. (5.283) and (5.284) into Eq. (5.290) we get

$$\begin{aligned} c_1(t) &= \frac{1}{2}\left\langle \sqrt{\frac{8\pi}{3}}Y_{1-1}^*(\theta,\nu)e^{i\eta} + \sqrt{\frac{8\pi}{3}}Y_{1-1}(\theta,\nu)e^{-i\eta}\right\rangle(t) \\ &= \frac{1}{2}\left\langle \sqrt{\frac{8\pi}{3}}Y_{1-1}^*(\theta,\nu)e^{i\eta}\right\rangle(t) + \frac{1}{2}\left\langle \sqrt{\frac{8\pi}{3}}Y_{1-1}(\theta,\nu)e^{-i\eta}\right\rangle(t) \\ &= \sqrt{\frac{2\pi}{3}}\left[\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} Y_{1-1}^*(\theta,\nu)e^{i\eta}f(\theta,\nu,\eta,t)\sin\theta d\theta d\nu d\eta \right. \\ &\quad \left. + \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} Y_{1-1}(\theta,\nu)e^{-i\eta}f(\theta,\nu,\eta,t)\sin\theta d\theta d\nu d\eta\right]. \end{aligned} \tag{5.291}$$

Recall the solution for $f(\theta,\nu,\eta,t)$ expressed as a Fourier-Laplace series [8]

$$f(\theta,\nu,\eta,t) = \frac{1}{2\pi}\sum_{l,p,q} f_{pq}^l(t)Y_{lp}^*(\theta,\nu)e^{-iq\eta}, \tag{5.292}$$

where the Fourier amplitudes $f^l_{pq}(t)$ are the statistical moments defined by

$$f^l_{pq}(t) = \int Y_{lp}(\theta,\nu)e^{iq\eta}f(\theta,\nu,\eta,t)d\Omega' = \left\langle Y_{lp}(\theta,\nu)e^{iq\eta}\right\rangle(t). \tag{5.293}$$

Substituting Eq. (5.292) into Eq. (5.291), we get

$$\begin{aligned}c_1(t) =&\sqrt{\frac{2\pi}{3}}\left[\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{1}{2\pi}\sum_{l,p,q}f^l_{pq}(t)Y^*_{lp}(\theta,\nu)Y^*_{1-1}(\theta,\nu)e^{-i(q-1)\eta}\sin\theta d\theta d\nu d\eta\right.\\&\left.+\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{1}{2\pi}\sum_{l,p,q}f^l_{pq}(t)Y^*_{lp}(\theta,\nu)Y_{1-1}(\theta,\nu)e^{-i(q+1)\eta}\sin\theta d\theta d\nu d\eta\right].\end{aligned} \tag{5.294}$$

Using Eq. (5.289), this can be rewritten as

$$\begin{aligned}c_1(t) =&\sqrt{\frac{2\pi}{3}}\left[\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}-\frac{1}{2\pi}\sum_{l,p,q}f^l_{pq}(t)Y^*_{lp}(\theta,\nu)\left(Y_{11}(\theta,\nu)\right)e^{-i(q-1)\eta}\sin\theta d\theta d\nu d\eta\right.\\&\left.+\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{1}{2\pi}\sum_{l,p,q}f^l_{pq}(t)Y^*_{lp}(\theta,\nu)Y_{1-1}(\theta,\nu)e^{-i(q+1)\eta}\sin\theta d\theta d\nu d\eta\right].\end{aligned} \tag{5.295}$$

Using the orthogonality property of spherical harmonics (Eq. (5.285)), we get

$$\begin{aligned}c_1(t) =&\sqrt{\frac{2\pi}{3}}\left[\int_0^{2\pi}-\frac{1}{2\pi}\sum_{l,p,q}\delta_{l1}\delta_{p1}f^l_{pq}(t)e^{-i(q-1)\eta}d\eta+\int_0^{2\pi}\frac{1}{2\pi}\sum_{l,p,q}\delta_{l1}\delta_{p-1}f^l_{pq}(t)e^{-i(q+1)\eta}d\eta\right]\\=&\sqrt{\frac{2\pi}{3}}\left[\int_0^{2\pi}-\frac{1}{2\pi}f^1_{1q}\left(t\right)e^{-i(q-1)\eta}d\eta+\int_0^{2\pi}\frac{1}{2\pi}f^1_{-1q}\left(t\right)e^{-i(q+1)\eta}d\eta\right]\\=&\sqrt{\frac{2\pi}{3}}\left[-\frac{1}{2\pi}\left(2\pi f^1_{11}\left(t\right)\right)+\frac{1}{2\pi}\left(2\pi f^1_{-1-1}\left(t\right)\right)\right]\\=&\sqrt{\frac{2\pi}{3}}\left[-f^1_{11}\left(t\right)+f^1_{-1-1}\left(t\right)\right].\end{aligned} \tag{5.296}$$

Substituting Eq. (5.293) into Eq. (5.296) we get

$$\begin{aligned}c_1(t) =&\sqrt{\frac{2\pi}{3}}\left[-\left\langle Y_{11}(\theta,\nu)e^{i\eta}\right\rangle(t)+\left\langle Y_{1-1}(\theta,\nu)e^{-i\eta}\right\rangle(t)\right]\\=&\sqrt{\frac{2\pi}{3}}\left[\left\langle -Y_{11}(\theta,\nu)e^{i\eta}\right\rangle(t)+\left\langle Y_{1-1}(\theta,\nu)e^{-i\eta}\right\rangle(t)\right].\end{aligned} \tag{5.297}$$

Using Euler's formula and Eq. (5.289), we can rewrite Eq. (5.297) as

$$
\begin{aligned}
c_1(t) =& \sqrt{\frac{2\pi}{3}} \left[\left\langle Y^*_{1-1}(\theta,\nu)\left(\cos(\eta)+i\sin(\eta)\right)\right\rangle(t)\right.\\
&\left.+\left\langle Y_{1-1}(\theta,\nu)\left(\cos(\eta)-i\sin(\eta)\right)\right\rangle(t)\right]\\
=& \sqrt{\frac{2\pi}{3}} \left[\left\langle Y^*_{1-1}(\theta,\nu)\cos(\eta)\right\rangle(t) + i\left\langle Y^*_{1-1}(\theta,\nu)\sin(\eta)\right\rangle(t)\right.\\
&\left.+\left\langle Y_{1-1}(\theta,\nu)\cos(\eta)\right\rangle(t) - i\left\langle Y_{1-1}(\theta,\nu)\sin(\eta)\right\rangle(t)\right].
\end{aligned} \tag{5.298}
$$

Recall the functions

$$a^c_q(t) = \langle Y_{1-1}\cos q\eta\rangle(t), \tag{5.299}$$

$$a^s_q(t) = \langle Y_{1-1}\sin q\eta\rangle(t). \tag{5.300}$$

The complex conjugates of $a^c_q(t)$ and $a^s_q(t)$ are given by

$$a^{c*}_q(t) = \left[\langle Y_{1-1}\cos q\eta\rangle(t)\right]^* = \left\langle Y^*_{1-1}\cos q\eta\right\rangle(t), \tag{5.301}$$

$$a^{s*}_q(t) = \left[\langle Y_{1-1}\sin q\eta\rangle(t)\right]^* = \left\langle Y^*_{1-1}\sin q\eta\right\rangle(t). \tag{5.302}$$

Substituting Eqs. (5.299) - (5.302) into Eq. (5.298) we get

$$c_1(t) = \sqrt{\frac{2\pi}{3}}\left[a^c_1(t) + a^{c*}_1(t) - ia^s_1(t) + ia^{s*}_1(t)\right]. \tag{5.303}$$

With $t = 0$ we have

$$c_1(0) = \sqrt{\frac{2\pi}{3}}\left[a^{c*}_1(0) + ia^{s*}_1(0) + a^c_1(0) - ia^s_1(0)\right]. \tag{5.304}$$

In a similar manner we obtain the following expression for $c_2(t)$

$$c_2(t) = \sqrt{\frac{2\pi}{3}}\left[a^c_1(t) + a^{c*}_1(t) + ia^s_1(t) - ia^{s*}_1(t)\right]. \tag{5.305}$$

with $t = 0$ we have

$$c_2(0) = \sqrt{\frac{2\pi}{3}} \left[a_1^c(0) + a_1^{c*}(0) + ia_1^s(0) - ia_1^{s*}(0)\right]. \tag{5.306}$$

Eqs. (5.304) and (5.306) can be written in terms of the modified Bessel functions of the first kind (see Appendix 5.L). Next we determine the one sided Fourier transform of $c_1(t)$ given in Eq. (5.303). The Fourier transforms of $a_1^c(t)$ and $a_1^s(t)$ are given by

$$\tilde{a}_1^c(\omega) = \int_0^\infty a_1^c(t)e^{-i\omega t}dt, \tag{5.307}$$

$$\tilde{a}_1^s(\omega) = \int_0^\infty a_1^s(t)e^{-i\omega t}dt. \tag{5.308}$$

Taking the complex conjugate of both sides of Eqs. (5.307) and (5.308) we have

$$\begin{aligned}[\tilde{a}_1^c(\omega)]^* &= \left[\int_0^\infty a_1^c(t)e^{-i\omega t}dt\right]^* \\ &= \int_0^\infty a_1^{c*}(t)e^{i\omega t}dt,\end{aligned} \tag{5.309}$$

$$\begin{aligned}[\tilde{a}_1^s(\omega)]^* &= \left[\int_0^\infty a_1^s(t)e^{-i\omega t}dt\right]^* \\ &= \int_0^\infty a_1^{s*}(t)e^{i\omega t}dt.\end{aligned} \tag{5.310}$$

Replacing ω with $-\omega$ in Eqs. (5.309) and (5.310) we obtain

$$[\tilde{a}_1^c(-\omega)]^* = \int_0^\infty a_1^{c*}(t)e^{-i\omega t}dt = \mathcal{F}\left\{a_1^{c*}(t)\right\}, \tag{5.311}$$

$$[\tilde{a}_1^s(-\omega)]^* = \int_0^\infty a_1^{s*}(t)e^{-i\omega t}dt = \mathcal{F}\left\{a_1^{s*}(t)\right\}. \tag{5.312}$$

The Fourier transform of $c_1(t)$ in Eq. (5.303) is given by

$$\tilde{c}_1(\omega) = \sqrt{\frac{2\pi}{3}} \left(\tilde{a}_1^c(\omega) + \tilde{a}_1^{c*}(-\omega) - i\left(\tilde{a}_1^s(\omega) - \tilde{a}_1^{s*}(-\omega)\right)\right). \tag{5.313}$$

Similarly the one sided Fourier transform of $c_2(t)$ in Eq. (5.305) is given by

$$\tilde{c}_2(\omega) = \sqrt{\frac{2\pi}{3}} \left(\tilde{a}_1^c(\omega) + \tilde{a}_1^{c*}(-\omega) + i\left(\tilde{a}_1^s(\omega) - \tilde{a}_1^{s*}(-\omega)\right)\right). \tag{5.314}$$

5.L Response Function Initial Values written as Modified Bessel Functions of the First Kind

Recall that the initial values for $a_q^c(t)$ and $a_q^s(t)$ are given by

$$\begin{aligned} a_q^c(0) =& Z_F^{-1} \int Y_{1-1}(\theta,\nu) \cos q\eta \, e^{(\mu_1+\mu_2)\mathbf{F}/kT + \sigma_V \cos 2\eta} d\Omega' \\ \approx& \frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_{(q+1)/2}(\sigma_V) + I_{(q-1)/2}(\sigma_V)\right), \end{aligned} \tag{5.315}$$

$$\begin{aligned} a_q^s(0) =& Z_F^{-1} \int Y_{1-1}(\theta,\nu) \sin q\eta \, e^{(\mu_1+\mu_2)\mathbf{F}/kT + \sigma_V \cos 2\eta} d\Omega' \\ \approx& \frac{i\sigma_1(\kappa-1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_{(q+1)/2}(\sigma_V) - I_{(q-1)/2}(\sigma_V)\right). \end{aligned} \tag{5.316}$$

with $q = 1$, we have

$$a_1^c(0) = \frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) + I_0(\sigma_V)\right), \tag{5.317}$$

$$a_1^s(0) = \frac{i\sigma_1(\kappa-1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) - I_0(\sigma_V)\right). \tag{5.318}$$

Note that

$$[a_1^s(0)]^* = -\frac{i\sigma_1(\kappa-1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) - I_0(\sigma_V)\right). \tag{5.319}$$

Recall also that the initial values for $c_j(t)$ are given by

$$c_j(0) = \sqrt{\frac{2\pi}{3}} \left(a_1^c(0) + a_1^{c*}(0) + (-1)^j i\left(a_1^s(0) - a_1^{s*}(0)\right)\right), \; j = 1, 2. \tag{5.320}$$

Substituting Eqs. (5.317) and (5.318) into Eq. (5.320) for $j = 1$ we get

$$
\begin{aligned}
c_1(0) =& \sqrt{\frac{2\pi}{3}} \left(\frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) + I_0(\sigma_V)\right) + \frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) + I_0(\sigma_V)\right) \right. \\
& \left. - i \left(\frac{i\sigma_1 (\kappa - 1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) - I_0(\sigma_V)\right) + \frac{i\sigma_1 (\kappa - 1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(I_1(\sigma_V) - I_0(\sigma_V)\right) \right) \right).
\end{aligned}
\tag{5.321}
$$

Eq. (5.321) may be written as

$$
\begin{aligned}
c_1(0) =& \sqrt{\frac{2\pi}{3}} \left(\frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(2I_1(\sigma_V) + 2I_0(\sigma_V)\right) \right. \\
& \left. - i \left[\frac{i\sigma_1 (\kappa - 1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(2I_1(\sigma_V) - 2I_0(\sigma_V)\right) \right] \right) \\
=& \sqrt{\frac{2\pi}{3}} \left(\frac{\sigma_1(1+\kappa)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(2I_1(\sigma_V) + 2I_0(\sigma_V)\right) \right. \\
& \left. + \frac{\sigma_1 (\kappa - 1)}{4\sqrt{6\pi} I_0(\sigma_V)} \left(2I_1(\sigma_V) - 2I_0(\sigma_V)\right) \right).
\end{aligned}
\tag{5.322}
$$

$$
\begin{aligned}
\Rightarrow c_1(0) =& \frac{\sigma_1}{12 I_0(\sigma_V)} \left[(1+\kappa) \left(2I_1(\sigma_V) + 2I_0(\sigma_V)\right) + (\kappa - 1) \left(2I_1(\sigma_V) - 2I_0(\sigma_V)\right) \right] \\
=& \frac{\sigma_1}{12 I_0(\sigma_V)} \left[4I_0(\sigma_V) + \kappa 4 I_1(\sigma_V) \right].
\end{aligned}
\tag{5.323}
$$

$$
\Rightarrow c_1(0) = \frac{\sigma_1}{3 I_0(\sigma_V)} \left[I_0(\sigma_V) + \kappa I_1(\sigma_V) \right]. \tag{5.324}
$$

Similarly for $j = 2$ in Eq. (5.320) we get

$$
c_2(0) = \frac{\sigma_1}{3 I_0(\sigma_V)} \left[I_1(\sigma_V) + \kappa I_0(\sigma_V) \right]. \tag{5.325}
$$

These Appendices show how very detailed calculations compared to the original Debye problem are required even for the very simple two body interaction considered.

5.M Wolfram Mathematica Code Used for the Calculation of the Observables

```
(***************************************************)
(* Q expressions in the recurrence relation
 (see equations (24) and (26) of the paper "Generalization to anomalous diffusion*)
(*of Budó's treatment of polar molecules containing interacting rotating groups*)
(*" by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov, M.H.Al Bayyari,
  and W.J.Dowling) you can also see Eqs. (5.24) and (5.26) of the thesis.
  Furthermore, you can see Appendices 5.F and 5.G for information on how the
  differential-recurrence relation needed for the calculation was derived.*)

(* Qq *)
Q[q_, γ_] := -1 - γ * (1 + (q) ^2)

(* Q̄q(s) *)
Qhat[q_, γ_, ω_, α_] := (((I * ω) ^ (1 - α)) * Q[q, γ]) - 2 * (I * ω)

(* Qq- *)
Qminus[q_, γ_, σv_] := σv * γ * (q)

(* Qq+ *)
Qplus[q_, γ_, σv_] := -σv * γ * (q)

(***************************************************)

(* initial values of aq^c(0) and aq^s(0)
 (see equations (28) and (29) of the paper "Generalization to anomalous diffusion*)
(* of Budó's treatment of polar molecules containing interacting rotating groups" *)
(* by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov,
   M.H.Al Bayyari, and W.J.Dowling). The derivation of the formulas
 for aq^c(0) and aq^s(0) is given in Appendix 5.K of the thesis. *)

(* aq^c(0) *)
acinitial[q_, σ1_, σ2_, σv_, κ_] := (-σ1 * ((1 + κ) / (4 * Sqrt[6 * π] * BesselI[0, σv]))) *
  (BesselI[(q + 1) / 2, σv] + BesselI[(q - 1) / 2, σv])

(* aq^s(0) *)
asinitial[q_, σ1_, σ2_, σv_, κ_] :=
 (-σ1 * ((I * (κ - 1)) / (4 * Sqrt[6 * π] * BesselI[0, σv]))) *
  (BesselI[(q + 1) / 2, σv] - BesselI[(q - 1) / 2, σv])

(***************************************************)

(* The following functions works to solve for the laplace
 transform of the relaxation function C(iω) seen in equation
 (32) of the paper "Generalization to anomalous diffusion*)
(* of Budó's treatment of polar molecules containing interacting
 rotating groups" by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov,
   M.H.Al Bayyari, and W.J.Dowling or Eq. (5.32) of the thesis. *)

(*-----------------------------------------------*)

(* Continued Fraction from equation (31) of
 the paper "Generalization to anomalous diffusion *)
```

```
(* of Budó’s treatment of polar molecules containing interacting
 rotating groups" by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov,
   M.H.Al Bayyari, and W.J.Dowling or Eq. (5.31) of the thesis. *)

(* The purpose of this continued fraction is to provide an explicit solution
 for the desired spectrum ã1J(s) in the form of a scalar continued fraction
 viz. Eq. (30) of the paper "Generalization to anomalous diffusion *)
(* of Budó’s treatment of polar molecules containing interacting
 rotating groups" by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov,
   M.H.Al Bayyari, and W.J.Dowling or Eq. (5.30) of the thesis. *)

Δ[n_, t_, γ_, σv_, ω_, α_] := (Block[{a, i},
   a = 0;

   (*This for loop evaluates the scalar continued
     fraction by starting with the max iteration value i=2*t+1,
   and then iterating for decreasing values i=i-2, until we iterate the
    necessary number of times to obtain the answer we seek (Sn)*)
   (*For every iteration of the For loop, the variable a stores the
    previously evaluated answer so that it can be further iterated on.*)

   For[i = 2 * t + 1, i ≥ n, i -= 2,
    a = (-Qhat[i, γ, ω, α] - Qplus[i, γ, σv] * a * Qminus[i + 2, γ, σv]) ^ (-1)];
   a
  ])

(*--------------------------------------------------*)
(* The following functions work to solve for the desired spectrum ã1J(s)
 which we will later use to solve for the response functions c̃j(iω) *)

(* These two functions generate the numerator of
 Eq.(30) of the paper "Generalization to anomalous diffusion *)
(* of Budó’s treatment of polar molecules containing interacting rotating
 groups" by S.V. Titov, W.T. Coffey, M. Zarifakis, Y.P. Kalmykov, M.H. Al
   Bayyari, and W.J. Dowling or Eq. (5.30) of the thesis. The procedure to *)
(* generate the numerator of Eq.(30) is similar to that of Eq. 2.7.11 of the
 4th edition of the book "The Langevin Equation: With Applications to Stochastic
   Problems in Physics, Chemistry and Electrical Engineering" where *)
(* we are solving for the column vector formed from statistical moments C̃1(s) *)

(* Numerator of Eq.(30) when solving for ã1c(s) *)
Ac[n_, t_, γ_, σ1_, σ2_, σv_, ω_, α_, κ_] :=
 acinitial[1, σ1, σ2, σv, κ] + Sum[acinitial[2 * i + 1, σ1, σ2, σv, κ] *
    Product[Qplus[2 * j - 1, γ, σv] * Δ[2 * j + 1, t, γ, σv, ω, α], {j, 1, i}], {i, 1, n, 1}]

(* Numerator of Eq.(30) when solving for ã1s(s) *)
As[n_, t_, γ_, σ1_, σ2_, σv_, ω_, α_, κ_] :=
 asinitial[1, σ1, σ2, σv, κ] + Sum[asinitial[2 * i + 1, σ1, σ2, σv, κ] *
    Product[Qplus[2 * j - 1, γ, σv] * Δ[2 * j + 1, t, γ, σv, ω, α], {j, 1, i}], {i, 1, n, 1}]

(*--------------------------------------------------*)

(* Eq.(30) of the paper "Generalization to anomalous diffusion *)
(* of Budó’s treatment of polar molecules containing interacting rotating groups *)
```

```
(* " by S.V. Titov, W.T. Coffey, M. Zarifakis, Y.P. Kalmykov, M.H. Al Bayyari,
  and W.J.Dowling or Eq. (5.30) of the thesis used to solve for ã1^J(s).
  These will later be used to solve for the response functions c̃j^J(iω) *)

(* Eq.(30) when solving for ã1^c(s) *)
a1laplacec[n_, t_, γ_, σ1_, σ2_, σv_, ω_, α_, κ_] :=
 2 * ((Ac[n, t, γ, σ1, σ2, σv, ω, α, κ]) /
    (-Qhat[1, γ, ω, α] - σv * γ - Qplus[1, γ, σv] * Δ[3, t, γ, σv, ω, α] * Qminus[3, γ, σv]))

(* Eq.(30) when solving for ã1^s(s) *)
a1laplaces[n_, t_, γ_, σ1_, σ2_, σv_, ω_, α_, κ_] :=
 2 * ((As[n, t, γ, σ1, σ2, σv, ω, α, κ]) /
    (-Qhat[1, γ, ω, α] + σv * γ - Qplus[1, γ, σv] * Δ[3, t, γ, σv, ω, α] * Qminus[3, γ, σv]))

(*-------------------------------------------------*)

(* Here we seek to obtain the initial conditions (cj(0)) of
 the response functions c̃j(iω) which are rendered in closed form via
 Eq. (34) of the paper "Generalization to anomalous diffusion *)
(* of Budó’s treatment of polar molecules containing interacting
 rotating groups" by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov,
   M.H.Al Bayyari, and W.J.Dowling or Eq. (5.34) of the thesis. *)

c0[i_, σ1_, σ2_, σv_, κ_] :=
 -((σ1) / (3)) * ((BesselI[(i - 1), σv] + κ * BesselI[(2 - i), σv]) / (BesselI[0, σv]))

(*-------------------------------------------------*)

(* Here we make use of the previously calculated desired
 spectrums ã1^J(s) to solve for the response functions c̃j^J(iω) via
 Eq. (33) of the paper "Generalization to anomalous diffusion *)
(* of Budó’s treatment of polar molecules containing interacting
 rotating groups" by S.V.Titov, W.T.Coffey, M.Zarifakis, Y.P.Kalmykov,
   M.H.Al Bayyari, and W.J.Dowling or Eq. (5.33) of the thesis. *)

claplace[i_, n_, t_, γ_, σ1_, σ2_, σv_, ω_, α_, κ_] :=
 Sqrt[(2 * π) / 3] * (a1laplacec[n, t, γ, σ1, σ2, σv, ω, α, κ] +
    Conjugate[a1laplacec[n, t, γ, σ1, σ2, σv, -ω, α, κ]] +
    ((-1)^i) * I * (a1laplaces[n, t, γ, σ1, σ2, σv, ω, α, κ] -
       Conjugate[a1laplaces[n, t, γ, σ1, σ2, σv, -ω, α, κ]]))

(*-------------------------------------------------*)

(* Here we make use of the previously calculated response functions c̃j^J
 (iω) to calculate the spectrum of the desired relaxation function C(iω)
 via Eq. (32) of the paper "Generalization to anomalous diffusion *)
(* of Budó’s treatment of polar molecules containing interacting rotating
 groups " by S.V. Titov, W.T. Coffey, M. Zarifakis, Y.P. Kalmykov,
   M.H. Al Bayyari, and W.J. Dowling or Eq. (5.32) of the thesis. *)
(* This will be later used to solve for the complex susceptibility χ(ω)=
 χ'(ω)-iχ''(ω) via Eq. *)(* (16) of the paper or Eq. (5.16) of the thesis. *)

Claplace[n_, t_, γ_, σ1_, σ2_, σv_, ω_, α_, κ_] :=
```

```
(claplace[1, n, t, γ, σ1, σ2, σv, ω, α, κ] + κ * claplace[2, n, t, γ, σ1, σ2, σv, ω, α, κ]) /
  (c0[1, σ1, σ2, σv, κ] + κ * c0[2, σ1, σ2, σv, κ])
(*-----------------------------------------------------*)
```

6. Frequency Dependent Linear Response

The equations in Chapter 5 lend themselves to numerical analysis of the (normalized) susceptibility $\chi(\omega)/\chi$ for both the normal and the anomalous diffusion extension of Budó's treatment of the dynamical effects on polar molecules containing rotating polar groups so causing hindered rotation. $\chi(\omega)/\chi$ is calculated through making use of the differential recurrence relation in Eq. (5.25) by implementing it as *Wolfram* language code in the *Wolfram Mathematica* software package. The $\bar{Q}_p(s)$ and $Q_p^{\pm}$ in Eq. (5.25) are expressed in the code. Upon doing so, Eqs. (5.28) and (5.29) are then implemented in the Wolfram language to be used as a part of the calculation of the desired spectrum $\tilde{a}_1^J(s)$ via Eq. (5.30), which itself requires the implementation of the continued fraction in Eq. (5.31). We iterate on both Eqs. (5.30) and (5.31) until we get a converging answer such that the answer will not change and/or undergo negligible change upon further iteration. Upon doing so, we then make use of Eqs. (5.32) - (5.34), implemented in the Wolfram language, in order to obtain the spectrum of the relaxation function $C(t)$ (Eq. (5.33) relies on the answers given by Eq. (5.30) and Eq. (5.34) relies on the answers given by Eqs. (5.28)). Once we obtain the desired value for Eq. (5.32), this is then substituted into Eq. (5.16) (again implemented in the Wolfram language) to obtain the desired normalised susceptibility. This is done for a range of values of the frequency ω.

Throughout this procedure, we choose values for the ratio of Debye times $\gamma = \tau/(2\tau_z)$, the dipole moment ratio $\kappa = \mu_2/\mu_1$, the dimensionless interaction parameter $\sigma_V = V_0/kT$, and the anomalous exponent α at our discretion to obtain the plots seen in Figures 6.1 - 6.3. In Figure 6.1 we show the susceptibility for a selection of typical values of the anomalous exponent α.

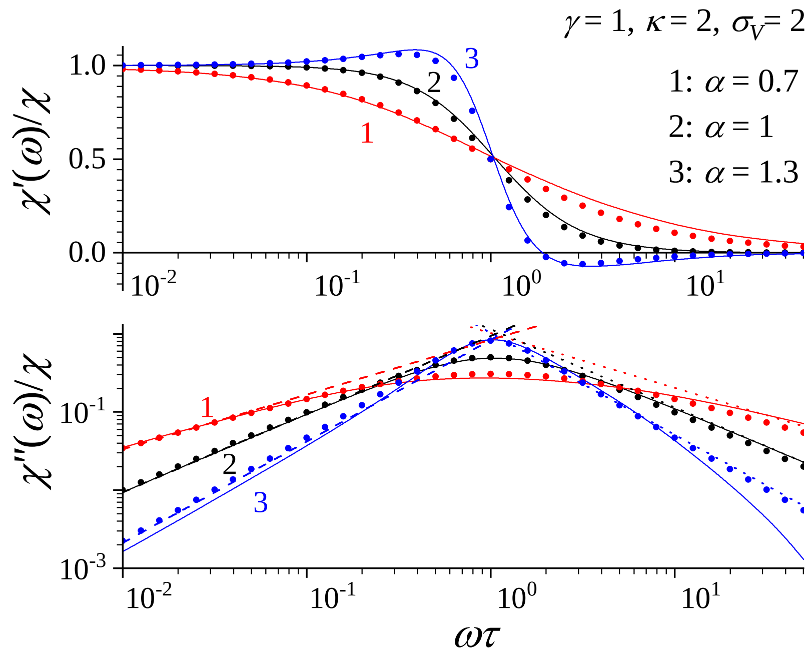

Figure 6.1: (Colour on line) Real and imaginary parts of susceptibility vs. $\omega\tau$ for various α. Solid lines: numerically exact solution from Eqs. (5.16), (5.32), and (5.33); symbols: the approximate equation (6.1). The low-frequency (dashed lines) and high-frequency (dotted lines) asymptotes are calculated from Eq. (6.2).

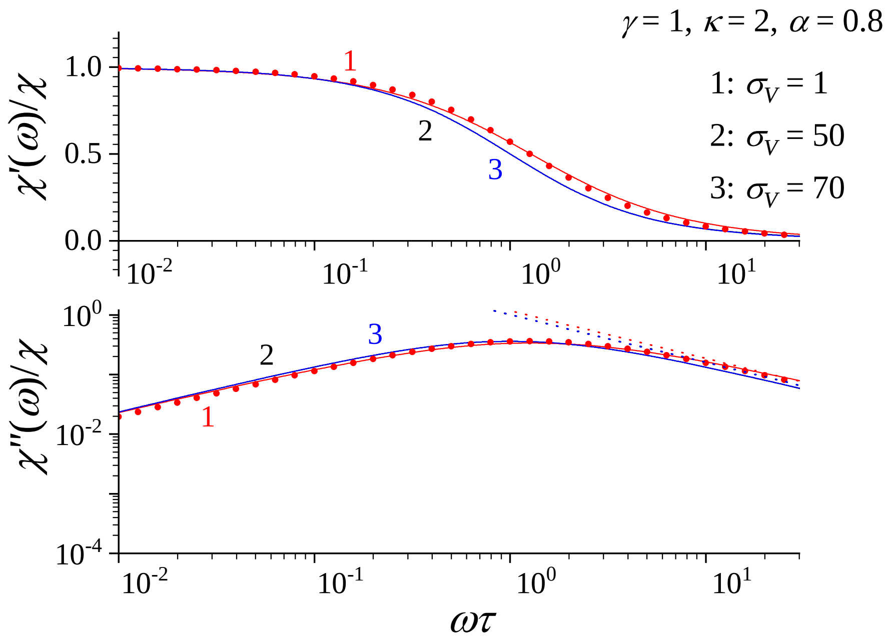

Figure 6.2: (Color on line) Real and imaginary parts of susceptibility vs. $\omega\tau$ for various σ_V. Solid lines: numerically exact solution from Eqs. (5.16), (5.32), and (5.33); symbols: the approximate equation (6.1). The high-frequency (dotted lines) asymptotes are calculated from Eq. (6.2).

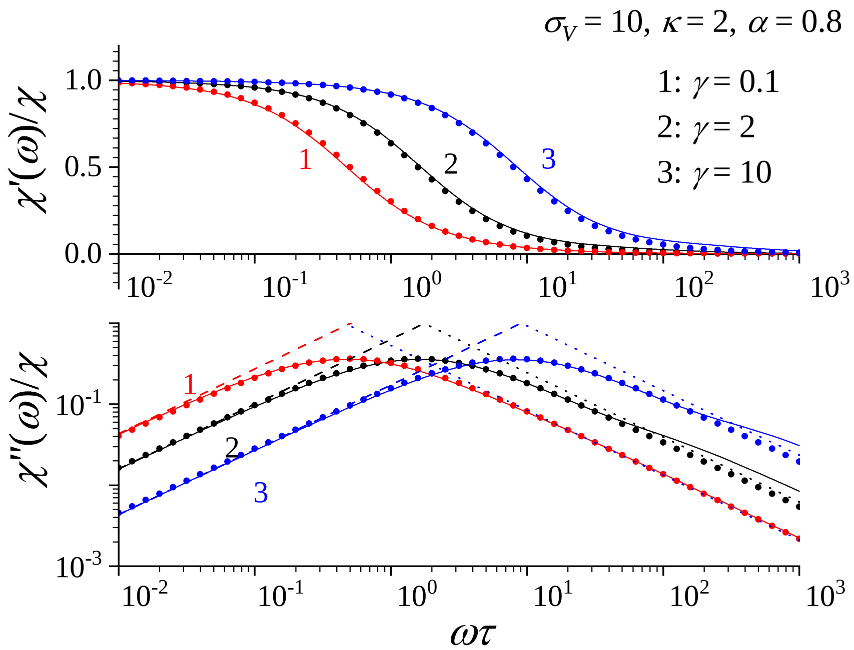

Figure 6.3: (Color on line) Real and imaginary parts of susceptibility vs. $\omega\tau$ for various γ. Solid lines: numerically exact solution from Eqs. (5.16), (5.32), and (5.33); symbols: the approximate equation (6.1). the low-frequency (dashed lines) and high-frequency (dotted lines) asymptotes are calculated from Eq. (6.2).

In general the spectral characteristics, i.e., the half-width, characteristic frequency and shape, vary significantly with α. For subdiffusion ($\alpha = 0.7$) the real part of the susceptibility is smaller at lower frequencies ($\omega\tau < 1$) than is so for normal diffusion ($\alpha = 1$) while at high frequencies ($\omega\tau > 1$) it exceeds that for normal diffusion. For superdiffusion ($\alpha = 1.3$) the real part is effectively constant at low frequencies while for high frequencies it decreases very rapidly. In Figure 6.1 we also perceive how α influences the imaginary part, noting in particular how the maxima for all α occur near the turnover frequency defined by $\omega\tau = 1$. Moreover, as α increases the maxima become more and more pronounced. Furthermore, by inspection of Figure 6.1 *et seq.*, the susceptibility can be accurately approximated for all α by the simple Cole-Cole equation viz.,

$$\frac{\chi(\omega)}{\chi} = \frac{1}{1 + (i\omega/\omega_R)^{\alpha}}, \tag{6.1}$$

where $\omega_R = \tau^{-1}$ is the frequency at which the imaginary part of susceptibility attains it maximum [6]. The advantage of such a simple representation of the susceptibility is that it may be used to accurately determine both the low and high frequency asymptotes of our solution using methods described in Chapter 12, Sections 12.3 and 12.4.2 of [2]. We then have from Eq. (5.16) (using the methods alluded to above) in the low and high frequency limits

$$\frac{\chi(\omega)}{\chi} \approx \begin{cases} 1 - (i\omega\tau)^{\alpha}\tau_{\text{int}}/\tau, & \omega \to 0, \\ (i\omega\tau)^{-\alpha}\tau/\tau_{\text{ef}}, & \omega \to \infty, \end{cases} \tag{6.2}$$

where

$$\frac{\tau_{\text{int}}}{\tau} = \tilde{C}(0) = \int_0^{\infty} C(t)dt, \quad \frac{\tau_{\text{ef}}}{\tau} = -\frac{1}{\dot{C}(0)}, \tag{6.3}$$

are the characteristic times of normal diffusion ($\alpha = 1$), τ_{int} is the integral relaxation time defined as the area under the decay curve $C(t)$, which may be calculated by taking the zero-frequency limit of Eq. (5.32), and τ_{ef} is the effective relaxation time yielding precise information on the initial decay of $C(t)$. The zero-time limit $\dot{C}(0)$

is calculated from Eqs. (5.12) and (5.23) yielding

$$\begin{aligned}\dot{C}(0) =& \frac{\dot{c}_1(0) + \kappa \dot{c}_2(0)}{c_1(0) + \kappa c_2(0)} \\ =& \frac{(1+\kappa)\mathrm{Re}[\dot{a}_1^c(0)] + (1-\kappa)\mathrm{Im}[\dot{a}_1^s(0)]}{(1+\kappa)\mathrm{Re}[a_1^c(0)] + (1-\kappa)\mathrm{Im}[a_1^s(0)]},\end{aligned} \tag{6.4}$$

where

$$2\tau \dot{a}_1^J(0) = (Q_1 + b^J) a_1^J(0) + Q_1^+ a_3^J(0), \tag{6.5}$$

and $a_q^J(0)$ are given by Eqs. (5.28) and (5.29). By substituting the initial values Eqs. (5.28), (5.29), and (6.5) into Eq. (6.4) we then have the closed form

$$\tau \dot{C}(0) = \frac{\kappa \gamma \sigma_V \left(I_0(\sigma_V) - I_2(\sigma_V)\right)}{(1+\kappa^2) I_0(\sigma_V) + 2k I_1(\sigma_V)} - \gamma - \frac{1}{2}. \tag{6.6}$$

By inspection of Figures 6.1 - 6.3 it is apparent that the asymptotes so determined correctly reproduce both the low and high frequency limits of the susceptibility. Figure 6.2 shows the frequency dependence of the susceptibility for various interaction parameters σ_V for subdiffusion ($\alpha = 0.8, \gamma = 1, \kappa = 2$). It would appear that the effects of σ_V on the shapes of the real and imaginary parts of $\chi(\omega)$ is *small*. With very strong binding ($\sigma_V = 50$ and $\sigma_V = 70$) the real and imaginary plots of $\chi(\omega)$ appear to nearly overlap one another while for $\sigma_V = 1$, the real part of $\chi(\omega)$ overlaps the plots for $\sigma_V = 50$ and $\sigma_V = 70$ at low frequencies ($10^{-2} \leq \omega\tau \leq 10^{-1}$). The imaginary parts of $\chi(\omega)$ for all three values of σ_V all appear to nearly overlap one another with some discrepancies between $\sigma_V = 1$ and $\sigma_V = 50, 70$ near the left side of the peak and at frequencies beyond $\omega\tau = 1$. The real part, having attained a maximum value starts to decrease monotonically. For weak interaction ($\sigma_V = 1$), Eq. (6.1) is obviously a good approximation to the spectra. In Figure 6.3 the spectra for three Debye time ratios $\gamma = \tau/(2\tau_z)$ for subdiffusion is shown. Clearly small γ has little effect on the plots as the shapes appear similar. However, for low frequencies we see that the imaginary part decreases with increasing γ. On the other hand, for higher frequencies the absorption becomes larger. Clearly for increasing γ, the loss peak shifts to higher frequencies, corresponding, of course, to a decreasing friction ratio $2\xi_z/\xi$.

Regarding Figure 3 of the published paper "Generalization to anomalous diffusion of Budó's treatment of polar molecules containing interacting rotating groups" [19] we emphasise that this figure is misleading and should be replaced by Figure 6.2 in that paper. The reason being that an insufficient number of iterations were originally taken in plotting that figure so as to achieve convergence. More precisely speaking it turns out that the number of iterations that were originally used for obtaining Figure 3 were not enough to guarantee convergence ($n = 11$ was used for Figure 3 in [19] with the continued fraction being iterated on 17 times). When I recalculated the same Figure I used $n = 51$ iterations to ensure that I had convergence, as well as 57 (convergents) iterations of the continued fraction. In the light of this I took Figure 3 (i.e., Figure 6.2) and I replaced the old data with the new one in the software package Origin by OriginLab Corporation in order to reproduce the plot with my answers. In addition to this I have also rewritten the part of the original discussion of results in the paper [19] in order to talk about the patterns observed in the new Figure 6.2. The new Figure shows that the simple Cole-Cole expression accurately reproduces the behaviour of the susceptibility for moderate to very strong coupling σ_V unlike the statement in the paper [19] that this approximation is really only accurate for $\sigma_V = 1$.

7. Dipole-Dipole and Exchange Interaction Effects on the magnetisation Relaxation of Two Macrospins: Compared

7.1 Transformation of the Stochastic Landau-Lifshitz-Gilbert (Langevin) Equation to Differential-Recurrence Relations for the Statistical Moments

As far as dipole-dipole interaction in magnetic relaxation by traversing a potential barrier is concerned, we consider [21] the transient response of two interacting macrospins subjected to a uniform external dc magnetic field, which alters in step-like fashion, i.e., the magnitude of that field suddenly changes by an arbitrary amount at time $t = 0$ from $\mathbf{H}^{\mathrm{I}}$ to a new value $\mathbf{H}^{\mathrm{II}}$ (the fields $\mathbf{H}^{\mathrm{I}}$ and $\mathbf{H}^{\mathrm{II}}$ are assumed to be applied parallel to the Z axis of the laboratory coordinate system). Consequently, we are treating the transient longitudinal magnetisation relaxation of two macroscopic interacting spins starting from an equilibrium state I say to a new equilibrium state II. The magnetic dipole moment of an individual macrospin is represented by $\boldsymbol{\mu}_p(t) = \mu \mathbf{s}_p(t), (p = 1, 2)$, where $\mathbf{s}_p$ is the unit vector along $\mu_p(t)$

defined as

$$\mathbf{s}_p = \mathbf{i}\sin\vartheta_p\cos\varphi_p + \mathbf{j}\sin\vartheta_p\sin\varphi_p + \mathbf{k}\cos\vartheta_p, \tag{7.1}$$

μ is the nominal value of the magnetic dipole moment, and ϑ_p and φ_p are the respective polar and azimuthal angles of spin p. The total normalised free energy E_i ($i = \mathrm{I}, \mathrm{II}$) including dipole-dipole interaction, anisotropy and Zeeman energies may be compactly written in vector form as [21]

$$\begin{aligned} E_i =& \varsigma\left[(\mathbf{s}_1\cdot\mathbf{s}_2) - 3\,(\mathbf{u}_r\cdot\mathbf{s}_1)\,(\mathbf{u}_r\cdot\mathbf{s}_2)\right] - \sum_{p=1,2}\left[\xi_i\,(\mathbf{e}_Z\cdot\mathbf{s}_p) + \sigma(\mathbf{e}_Z\cdot\mathbf{s}_p)^2\right] \\ =& \varsigma\left[\sin\vartheta_1\sin\vartheta_2\cos(\varphi_1-\varphi_2) - 2\cos\vartheta_1\cos\vartheta_2\right] - \xi_i\,(\cos\vartheta_1+\cos\vartheta_2) \\ &- \sigma\left(\cos^2\vartheta_1 + \cos^2\vartheta_2\right). \end{aligned} \tag{7.2}$$

Here $\mathbf{u}_r = \mathbf{r}/r$ is a unit vector with $r = |\mathbf{r}|$ specifying the separation between the two spins, $\mathbf{e}_Z$ is the unit vector along the (polar) Z axis (assuming that $\mathbf{e}_Z \parallel \mathbf{u}_r$), $\xi_i = \mu_0\mu H_Z^i/(kT)$ and $\sigma = K/(kT)$ are dimensionless field and anisotropy parameters, respectively, $\mu_0 = 4\pi\cdot 10^{-7}\ \mathrm{J}\cdot\mathrm{A}^{-2}\cdot\mathrm{m}^{-1}$ in SI units, H_Z^i represents the (arbitrary) magnitude of an external applied (spatially) uniform dc magnetic field $\mathbf{H}_Z^i$, K is the anisotropy constant, $\varsigma = \mu_0\mu^2/(kTr^3)$ is the *dimensionless dipole-dipole interaction parameter*, k is the Boltzmann constant, and T is the temperature. The geometry of the problem for an individual macrospin is shown in Figure 7.1. As mentioned, the two easy axes of magnetisation are supposed parallel to each other and to the applied dc field, which is in turn assumed parallel to the reference (Z) axis. Thus, omitting the dipole-dipole term the problem just represents the well studied [2] relaxation in a *circularly symmetric anisotropy* Zeeman energy potential $\sigma\cos^2\vartheta$. Next the results for the two-spin system above will be compared with those for spins coupled solely by *exchange* interaction, namely, for the compact form [22]

$$E_i = -\varsigma\,(\mathbf{s}_1\cdot\mathbf{s}_2) - \sum_{p=1,2}\left[\xi_i\,(\mathbf{e}_Z\cdot\mathbf{s}_p) + \sigma(\mathbf{e}_Z\cdot\mathbf{s}_p)^2\right], \tag{7.3}$$

where now $\varsigma = \mu_0\mu^2 J/(kT)$ and J is the exchange coupling constant.

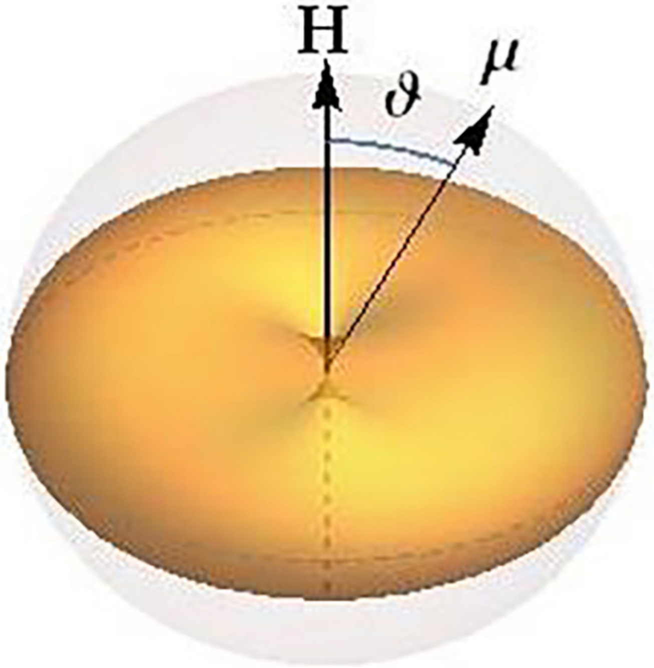

Figure 7.1: Geometry of the task: uniaxial anisotropy potential $E(\vartheta) = \sigma \sin^2 \vartheta$ with vertical easy axis (dashed line), a uniform external dc magnetic field $\mathbf{H}$ parallel to the easy axis and the magnetic dipole moment of an individual macrospin $\boldsymbol{\mu}$.

The effective magnetic field $\mathbf{H}_p$ acting on a spin comprises the externally applied crystalline anisotropy and dipole-dipole coupling fields, so that in spherical polar coordinates

$$\mathbf{H}_p = \frac{kT}{\mu_0 \mu} \left(0, -\frac{\partial E_i}{\partial \vartheta_p}, -\frac{1}{\sin \vartheta_p} \frac{\partial E_i}{\partial \varphi_p} \right). \tag{7.4}$$

In magnetisation relaxation, the relevant observables are obviously time-dependent orientational ensemble averages involving the spherical harmonics $Y_{l\,m}(\vartheta, \varphi)$, defined as in our previous chapter by [2, 120]

$$Y_{l\,m}(\vartheta, \varphi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\varphi} P_l^m(\cos \vartheta)\ |m| \leq l, \tag{7.5}$$

where $P_l^m(x)(|m| \leq l)$ are the associated Legendre functions, consequently we rewrite the free energy, Eq. (7.2), as [21] (see Appendix 7.A)

$$
\begin{aligned}
E_i = & -\frac{4\pi}{6}\varsigma \sum_{m=-1}^{1} (3+(-1)^m) Y_{1\,m}(\vartheta_1,\varphi_1) Y_{1\,-m}(\vartheta_2,\varphi_2) \\
& - \sum_{p=1,2}\left[\xi_i \sqrt{\frac{4\pi}{3}} Y_{1\,0}(\vartheta_p,\varphi_p) + \sigma\frac{4}{3}\sqrt{\frac{\pi}{5}} Y_{2\,0}(\vartheta_p,\varphi_p)\right] + \text{const.}
\end{aligned} \tag{7.6}
$$

The form of the dipole-dipole coupling potential, Eq. (7.6), again suggests as in the pure exchange interaction studied by Titov *et al.* [22] introducing as new stochastic variables the time-dependent product of spherical harmonics of arguments (ϑ_1,φ_1) and (ϑ_2,φ_2) respectively [21]

$$
M_{l_1\,l_2\,m} = Y_{l_1\,m}(\vartheta_1,\varphi_1) Y_{l_2\,-m}(\vartheta_2,\varphi_2). \tag{7.7}
$$

Eq. (7.7) then represents a complete set of orthogonal functions characterising the orientational dynamics of the two interacting spins. The *equilibrium* averages $\langle M_{l_1\,l_2\,m}\rangle_i$, corresponding to the spatial distributions of the initial and final states of the two-spin system, are given by

$$
\langle M_{l_1\,l_2\,m}\rangle_i = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} M_{l_1\,l_2\,m} W_i(\vartheta_1,\varphi_1,\vartheta_2,\varphi_2)\sin\vartheta_2\sin\vartheta_1 d\vartheta_2 d\vartheta_1 d\varphi_2 d\varphi_1, \tag{7.8}
$$

where $W_i(\vartheta_1,\varphi_1,\vartheta_2,\varphi_2) = Z_i^{-1} e^{-E_i(\vartheta_1,\varphi_1,\vartheta_2,\varphi_2)}$ are the relevant Boltzmann distribution functions and Z_i are the corresponding partition functions. Now as we saw the magnetisation dynamics of a typical macrospin are described by the stochastic Landau-Lifshitz-Gilbert equation, i.e., the deterministic Landau-Lifshitz-Gilbert equation augmented by a random noise field $\mathbf{h}_p(t')$ originating from the thermal bath fluctuations [2]

$$
\begin{aligned}
\dot{\mathbf{s}}_p = & \frac{\mu_0\mu}{2kT\tau_N}\left(\alpha^{-1}\left[(\mathbf{H}_p(t') + \mathbf{h}_p(t')) \times \mathbf{s}_p(t')\right]\right. \\
& \left. - \left[\mathbf{s}_p(t') \times \left[\mathbf{s}_p(t') \times (\mathbf{H}_p(t') + \mathbf{h}_p(t'))\right]\right]\right),
\end{aligned} \tag{7.9}
$$

where $\tau_N = \mu_0\mu(1+\alpha^2)/(2\gamma\alpha kT)$ is a characteristic (free diffusion of the magnetic moment) time, γ is the gyromagnetic ratio, α is the dimensionless damping parameter representing the dissipative coupling to the heat bath and $\mathbf{h}_p(t')$ has white noise properties with zero mean and δ-correlated viz.,

$$\overline{h_p^L(t')} = 0,\ \overline{h_p^L(t)h_p^M(t')} = 2kT\alpha(\gamma\mu_0\mu)^{-1}\delta_{LM}\delta(t-t'). \tag{7.10}$$

Here the individual $h_p^L(t')$ are the components of $\mathbf{h}_p(t)$ in the laboratory coordinate system so that $L, M = X, Y, Z$, δ_{LM} is Kronecker's delta, $\delta(t-t')$ is the Dirac-delta function, and the overbar denotes the statistical averaging over an ensemble of dipoles. The vector stochastic differential equation (Eq. (7.9)) as rewritten in spherical polar coordinates then represents a set of coupled non-linear scalar stochastic differential equations [21] (see Appendix 7.B)

$$\begin{aligned}
\dot{\vartheta}_p(t') =& \frac{\mu_0\mu}{2kT\tau_N}\left[h_{\vartheta_p}(t') + \alpha^{-1}h_{\varphi_p}(t')\right] - \frac{1}{2\tau_N}\left(\frac{\partial E_i}{\partial\vartheta_p} + \frac{1}{\alpha\sin\vartheta_p(t')}\frac{\partial E_i}{\partial\varphi_p}\right), \\
\dot{\varphi}_p(t') =& \frac{\mu_0\mu}{2kT\tau_N\sin\vartheta_p}\left[h_{\varphi_p}(t') - \alpha^{-1}h_{\vartheta_p}(t')\right] - \frac{1}{2\tau_N}\left(\frac{1}{\sin^2\vartheta_p(t')}\frac{\partial E_i}{\partial\varphi_p} - \frac{1}{\alpha\sin\vartheta_p(t')}\frac{\partial E_i}{\partial\vartheta_p}\right),
\end{aligned} \tag{7.11}$$

where $h_{\vartheta_{p(t')}}, h_{\varphi_{p(t')}}$ are the spherical components of the random field $\mathbf{h}_p(t)$ which can be expressed via the cartesian components $h_p^L(t')$ [2]. The set of Eq. (7.11) is solved by supposing as usual that the solutions $\{\vartheta_1(t'), \varphi_1(t'), \vartheta_2(t'), \varphi_2(t')\}$ at a given time t had the sharp values $\{\vartheta_1(t) = \vartheta_1, \varphi_1(t') = \varphi_1, \vartheta_2(t) = \vartheta_2, \varphi_2(t) = \varphi_2\}$, i.e., all macrospins had the same initial orientations at an earlier time t.

Because the set of Eq. (7.11) are *Stratonovich* stochastic differential equations, and since in transformations of such equations one may use the ordinary rules of calculus [2], we have from Eqs. (7.9) - (7.11) a *stochastic* differential equation for the functions $M_{l_1l_2m}(t') = M_{l_1l_2m}(\vartheta_1(t'), \varphi_1(t'), \vartheta_2(t'), \varphi_2(t'))$ defined by Eq. (7.7) [21], viz.,

$$\frac{d}{dt}M_{l_1\,l_2\,m}(t') = \sum_{p=1,2}\left(\dot{\vartheta}_p(t')\frac{\partial M_{l_1\,l_2\,m}}{\partial\vartheta_p}(t') + \dot{\varphi}_p(t')\frac{\partial M_{l_1\,l_2\,m}}{\partial\varphi_p}(t')\right). \tag{7.12}$$

This stochastic equation will ultimately yield (after many lengthy and tedious calculations via Appendix 7.D) the *deterministic* evolution equation for the sharp values $M_{l_1\,l_2\,m}$ at time t. In order to accomplish this we must first average Eq. (7.12) over its realizations in configuration space in an infinitesimal time as prescribed by Einstein and described in [2]. Hence we have a differential-recurrence relation for $M_{l_1\, l_2\, m}$ in the three recurring indices l_1, l_2, m [21], viz.,

$$\tau_N \dot{M}_{l_1\, l_2\, m} = \sum_{i,j=-2}^{2} \sum_{k=-1}^{1} d_{l_1+i\, l_2+j\, m+k}^{l_1\, l_2\, m} M_{l_1+i\, l_2+j\, m+k}. \tag{7.13}$$

The various expansion coefficients $d_{l_1+i\, l_2+j\, m+k}^{l_1\, l_2\, m}$ obtained via the theory of angular momentum again as described in [2] are explicitly given in Appendix 7.C. However, the $M_{l_1\, l_2\, m}$ so obtained are obviously functions of the sharp values ϑ_p, φ_p, which are themselves *random variables* with *spatial distribution function* $W(\vartheta_1, \varphi_1, \vartheta_2, \varphi_2, t)$. Hence taking the ensemble (i.e., spatial) average of Eq. (7.13) over $W(\vartheta_1, \varphi_1, \vartheta_2, \varphi_2, t)$, we finally have an infinite hierarchy of differential-recurrence relations (in the manner described in [2, 121] for non-interacting magnetic dipoles) for the observables, namely, the relaxation functions $c_{l_1\, l_2\, m}(t) = \langle M_{l_1\, l_2\, m} \rangle (t) - \langle M_{l_1\, l_2\, m} \rangle_{\text{II}}$ of the two-spin system, viz.,

$$\tau_N \dot{c}_{l_1\, l_2\, m} = \sum_{i,j=-2}^{2} \sum_{k=-1}^{1} d_{l_1+i\, l_2+j\, m+k}^{l_1\, l_2\, m} c_{l_1+i\, l_2+j\, m+k}, \tag{7.14}$$

where the angular brackets $\langle\rangle(t)$ denote ensemble averaging of the sharp values over $W(\vartheta_1, \varphi_1, \vartheta_2, \varphi_2, t)$. In writing Eq. (7.14) we have also used the fact that the equilibrium averages $\langle M_{l_1\, l_2\, m} \rangle_i$ satisfy the time-independent recurrence relation:

$$\sum_{i,j=-2}^{2} \sum_{k=-1}^{1} d_{l_1+i\, l_2+j\, m+k}^{l_1\, l_2\, m} \langle M_{l_1+i\, l_2+j\, m+k} \rangle_i = 0. \tag{7.15}$$

The hierarchy of recurrence relations for the relaxation functions $c_{l_1\, l_2\, m}(t)$ must be solved subject to the initial conditions $c_{l_1\, l_2\, m}(0) = \langle M_{l_1\, l_2\, m} \rangle_{\text{I}} - \langle M_{l_1\, l_2\, m} \rangle_{\text{II}}$, where the equilibrium averages $\langle M_{l_1, l_2, m} \rangle_i$ can be evaluated either from Eq. (7.15) or from Eq. (7.8).

Next continuing with the solution of Eq. (7.14), we introduce the column vectors

$$\mathbf{C}_n(t) = \begin{pmatrix} \mathbf{c}_{2n-1\,0}(t) \\ \mathbf{c}_{2n-2\,1}(t) \\ \vdots \\ \mathbf{c}_{0\,2n-1}(t) \\ \mathbf{c}_{2n\,0}(t) \\ \mathbf{c}_{2n-1\,1}(t) \\ \vdots \\ \mathbf{c}_{0\,2n}(t) \end{pmatrix}_{4n^2+2n+1}, \quad \mathbf{c}_{nm}(t) = \begin{pmatrix} c_{nm-r}(t) \\ c_{nm-r+1}(t) \\ \vdots \\ c_{nmr}(t) \end{pmatrix}, \tag{7.16}$$

($r = \min[n, m]$) indicating that Eq. (7.14) can be transformed into the tractable [2] tridiagonal vector recurrence relation (admitting of a *formally exact* matrix continued fraction solution in the frequency domain, e.g., Eq. (7.18) below)

$$\tau_N \frac{d}{dt}\mathbf{C}_n(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}(t) + \mathbf{Q}_n \mathbf{C}_n(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t), \tag{7.17}$$

with $\mathbf{C}_0(t) = \mathbf{0}$. The matrix coefficients $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, $\mathbf{Q}_n^-$ are explicitly given in Appendix 7.E and derived in Appendix 7.F. Eq. (7.17) then yields [2] the formal solution for the Laplace transform $\tilde{\mathbf{C}}_1(s)$, which is exactly rendered as a rapidly converging sum of products of matrix continued fractions just like the dielectric case

$$\tilde{\mathbf{C}}_1(s) = \tau_N \boldsymbol{\Delta}_1(s) \left\{ \mathbf{C}_1(0) + \sum_{n=2}^{\infty} \left(\prod_{k=2}^{n} \mathbf{Q}_{k-1}^+ \boldsymbol{\Delta}_k(s) \right) \mathbf{C}_n(0) \right\}, \tag{7.18}$$

where the matrix continued fraction $\boldsymbol{\Delta}_n(s)$ is defined [2] by the algebraic recurrence equation

$$\boldsymbol{\Delta}_n(s) = \left[s\tau_N \mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \boldsymbol{\Delta}_{n+1}(s) \mathbf{Q}_{n+1}^- \right]^{-1}, \tag{7.19}$$

and the tilde denotes the Laplace transform, viz.,

$$\tilde{\mathbf{C}}_1(s) = \int_0^\infty \mathbf{C}_1(t) e^{-st} dt. \tag{7.20}$$

The initial value column vector $\mathbf{C}_n(0)$ in Eq. (7.18) can also be calculated via continued fractions (see Ref. [22]). In solving Eq. (7.18) the summation is restricted by selecting an $n_{\max}$, which is large enough to ensure convergence. For the parameters used in our calculations $n_{\max} = 15$ is sufficient to arrive at an accuracy of not less than 5 significant digits in the majority of cases.

7.2 Calculation of Observables for Two Interacting Spins Coupled by Dipole-Dipole Interaction

The response of spin p immediately following a step-like alteration of the dc field is represented via the normalised (by the final equilibrium value) relaxation function

$$f_p(t) = \frac{\langle \mathbf{s}_p \cdot \mathbf{e}_Z \rangle (t) - \langle \mathbf{s}_p \cdot \mathbf{e}_Z \rangle_{\mathrm{II}}}{\langle \mathbf{s}_p \cdot \mathbf{e}_Z \rangle_{\mathrm{I}} - \langle \mathbf{s}_p \cdot \mathbf{e}_Z \rangle_{\mathrm{II}}}. \tag{7.21}$$

Thus with $\tilde{\mathbf{C}}_1(s)$ obtained from the numerical solution of Eq. (7.18), which as mentioned already will in general comprise an infinite set of decaying exponentials characterized by a set of distinct eigenvalues of the system matrix and their corresponding amplitudes, we have the *integral relaxation time* τ_{int} [2], namely the area under decay curve $f_p(t)$ [2, 22]

$$\tau_{\mathrm{int}} = \int_0^\infty f_1(t)dt = \int_0^\infty f_2(t)dt = \frac{\tilde{c}_{1\,0\,0}(0)}{c_{1\,0\,0}(0)}. \tag{7.22}$$

The *integral relaxation time* contains contributions from all the eigenvalues of the two spin system. The individual relaxation functions $f_1(t)$ or $f_2(t)$ and the (global) τ_{int} describe the transient response of the *longitudinal component* of the magnetic moment of the two-spin system because the Z component of the total dipole moment $m_Z(t) = \mu \langle (\mathbf{s}_1 + \mathbf{s}_2) \cdot \mathbf{e}_Z \rangle (t)$ may always be written as

$$m_Z(t) = 2\mu \left[\langle \mathbf{s}_1 \cdot \mathbf{e}_Z \rangle_{\mathrm{II}} + \left(\langle \mathbf{s}_1 \cdot \mathbf{e}_Z \rangle_{\mathrm{I}} - \langle \mathbf{s}_1 \cdot \mathbf{e}_Z \rangle_{\mathrm{II}} \right) f_1(t) \right]. \tag{7.23}$$

This (in general) *non-linear response* contains as a special case the *linear response* to *infinitesimally* small step changes in the strength of the (arbitrarily) strong applied dc field $\mathbf{H}_Z^{\mathrm{I}}$, i.e., for $\mathbf{H}_Z^{\mathrm{II}} = \mathbf{H}_Z^{\mathrm{I}} - \kappa$ as $\kappa \to \mathbf{0}$, where κ is regarded as a small external perturbation. Hence $f_1(t)$ as defined by Eq. (7.21) then coincides with the normalised longitudinal dipole equilibrium correlation function $C_{\|}(t)$, that is

$$\lim_{\kappa\to 0} f_1(t) = C_{\|}(t) = \frac{\langle m_Z(0)m_Z(t)\rangle_{\mathrm{II}} - \langle m_Z(0)\rangle_{\mathrm{II}}^2}{\langle m_Z^2(0)\rangle_{\mathrm{II}} - \langle m_Z(0)\rangle_{\mathrm{II}}^2}. \tag{7.24}$$

Thus according to linear response theory (see, e.g., [2]), via the one-sided Fourier transform $\tilde{C}_{\|}(i\omega)$ [i.e., the spectrum of $C_{\|}(t)$], we have τ_{int} for linear response, viz. the correlation time $\tau = \tilde{C}_{\|}(0)$, and also the normalised dynamic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ [2] since

$$\chi(\omega) = 1 - i\omega\tilde{C}_{\|}(i\omega) = 1 - i\omega\frac{\tilde{c}_{1\,0\,0}(i\omega)}{c_{1\,0\,0}(0)}. \tag{7.25}$$

Furthermore, the asymptotic behaviour of $\chi(\omega)$ in the extrema of very low and very high frequencies is explicitly given by [2, 22],

$$\chi(\omega) \sim \begin{cases} 1 - i\omega\int_0^\infty C_{\|}(t)dt = 1 - i\omega\tau_{\mathrm{int}} + \ldots, & \omega \to 0, \\ -\frac{\dot{C}_{\|}(0)}{i\omega} + \ldots = -\frac{i}{\omega\tau_{\|}^{ef}} + \ldots, & \omega \to \infty, \end{cases} \tag{7.26}$$

where (see Appendix 7.H)

$$\tau_{\mathrm{ef}} = -\frac{1}{\dot{C}_{\|}(0)} = 2\tau_N \frac{\left\langle(\cos\vartheta_1 + \cos\vartheta_2)^2\right\rangle_{\mathrm{II}} - \langle\cos\vartheta_1 + \cos\vartheta_2\rangle_{\mathrm{II}}^2}{\left\langle\sin^2\vartheta_1 + \sin^2\vartheta_2\right\rangle_{\mathrm{II}}}, \tag{7.27}$$

is the *effective* relaxation time governing the initial decay of $C_{\|}(0)$. Here τ_{int} and τ_{ef} [2] characterize the global and the short-time behaviour of $C_{\|}(t)$ respectively. The time τ_{ef} is evaluated (see Appendix 7.H) in terms of equilibrium averages as in [22]. Moreover if the potential wells are approximately equivalent (as is true [2] for a *small* external field), τ_{int} is approximately the magnetisation reversal time τ (see Figure 8.2 below) $\tau_{\mathrm{int}} \approx \tau = 1/\lambda_1$ so that the response is now dominated by the slow reversal-over-barrier mode. Here λ_1 is the smallest non-vanishing eigenvalue of the system matrix, corresponding to the hierarchy of differential-recurrence relations seen in Eq. (7.14) [2]. Using matrix continued fractions, we then have λ_1 numerically from the secular equation of the two-spin system [2], namely

$$\det\left[\lambda_1\tau_N\mathbf{I}+\mathbf{Q}_1+\mathbf{Q}_1^{+}\boldsymbol{\Delta}_2(-\lambda_1)\mathbf{Q}_2^{-}\right]=0. \tag{7.28}$$

The inverse $\tau = 1/\lambda_1$ characterises the long-time behaviour of $C_{\|}(t)$ [2]. Moreover, λ_1 can also be determined either from the half-width of the spectrum $\tilde{C}_{\|}(i\omega)$ or, equivalently, from the low-frequency maximum of the loss spectrum $\chi''(\omega)$.

Appendices - Details of the various calculations

7.A The Total Normalised Free Energy Equation in terms of Spherical Harmonics

Recall that the total normalised free energy E_i (i = I,II) including dipole-dipole interaction, anisotropy and Zeeman energies may be written in terms of spherical harmonics $Y_{l\,m}(\vartheta,\varphi)$ as

$$\begin{aligned}
E_i =& -\frac{4\pi}{6}\varsigma\sum_{m=-1}^{1}(3+(-1)^m)Y_{1\,m}(\vartheta_1,\varphi_1)Y_{1\,-m}(\vartheta_2,\varphi_2)\\
&-\sum_{p=1,2}\left[\xi_i\sqrt{\frac{4\pi}{3}}Y_{1\,0}(\vartheta_p,\varphi_p)+\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{2\,0}(\vartheta_p,\varphi_p)\right]+\text{const.}\\
=& -\frac{4\pi}{6}\varsigma\left[(3-1)\,Y_{1\,-1}(\vartheta_1,\varphi_1)Y_{1\,1}(\vartheta_2,\varphi_2)+(3+1)\,Y_{1\,0}(\vartheta_1,\varphi_1)Y_{1\,0}(\vartheta_2,\varphi_2)\right.\\
&\left.+(3-1)\,Y_{1\,1}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right]\\
&-\left[\xi_i\sqrt{\frac{4\pi}{3}}Y_{1\,0}(\vartheta_1,\varphi_1)+\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{2\,0}(\vartheta_1,\varphi_1)+\xi_i\sqrt{\frac{4\pi}{3}}Y_{1\,0}(\vartheta_2,\varphi_2)\right.\\
&\left.+\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{2\,0}(\vartheta_2,\varphi_2)\right]+\text{const.}
\end{aligned} \tag{7.29}$$

The spherical harmonics $Y_{l\,m}(\vartheta,\varphi)$ are given by

$$Y_{l\,m}(\vartheta,\varphi)=(-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}e^{im\varphi}P_l^m(\cos\vartheta)\ |m|\le l, \tag{7.30}$$

where $P_l^m(x)(|m| \leq l)$ are the associated Legendre functions.

I will now show that Eq. (7.29) is equivalent to Eq. (7.2). We substitute the following spherical harmonics $Y_{l\,m}(\vartheta_p, \varphi_p),\ (p = 1, 2)$ into Eq. (7.29)

$$Y_{1-1}\left(\vartheta_p, \varphi_p\right) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{-i\varphi}\sin\vartheta, \tag{7.31}$$

$$Y_{11}\left(\vartheta_p, \varphi_p\right) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{i\varphi}\sin\vartheta, \tag{7.32}$$

$$Y_{10}\left(\vartheta_p, \varphi_p\right) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\vartheta, \tag{7.33}$$

$$Y_{20}\left(\vartheta_p, \varphi_p\right) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2\vartheta - 1\right), \tag{7.34}$$

to get

$$\begin{aligned}
E_i = & -\frac{4\pi}{6}\varsigma\left[(2)\left(\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{-i\varphi_1}\sin\vartheta_1\right)\left(-\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{i\varphi_2}\sin\vartheta_2\right)\right.\\
& + (4)\left(\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\vartheta_1)\right)\left(\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\vartheta_2)\right)\\
& \left. + (2)\left(-\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{i\varphi_1}\sin\vartheta_1\right)\left(\frac{1}{2}\sqrt{\frac{3}{2\pi}}e^{-i\varphi_2}\sin\vartheta_2\right)\right]\\
& - \left[\xi_i\sqrt{\frac{4\pi}{3}}\left(\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\vartheta_1\right) + \sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\left(\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2\vartheta_1 - 1\right)\right)\right.\\
& \left. + \xi_i\sqrt{\frac{4\pi}{3}}\left(\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\vartheta_2\right) + \sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\left(\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\cos^2\vartheta_2 - 1\right)\right)\right],
\end{aligned} \tag{7.35}$$

which can be written as

$$
\begin{aligned}
E_i =& -\frac{4\pi}{6}\varsigma\left[2\left(-\frac{3}{8\pi}e^{i(\varphi_2-\varphi_1)}\sin\vartheta_1\sin\vartheta_2\right)\right.\\
&+4\left(\frac{3}{4\pi}\right)\cos\vartheta_1\cos\vartheta_2\\
&\left.+2\left(-\frac{3}{8\pi}e^{i(\varphi_1-\varphi_2)}\sin\vartheta_1\sin\vartheta_2\right)\right]\\
&-\xi_i\left(\cos\vartheta_1+\cos\vartheta_2\right)\\
&-\sigma\left(\cos^2\vartheta_1+\cos^2\vartheta_2-\frac{2}{3}\right).
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow E_i =&\varsigma\left[\frac{1}{2}\left(e^{i(\varphi_2-\varphi_1)}+e^{i(\varphi_1-\varphi_2)}\right)\sin\vartheta_1\sin\vartheta_2-2\cos\vartheta_1\cos\vartheta_2\right]\\
&-\xi_i\left(\cos\vartheta_1+\cos\vartheta_2\right)-\sigma\left(\cos^2\vartheta_1+\cos^2\vartheta_2-\frac{2}{3}\right)\\
=&\varsigma\left[\frac{1}{2}\left(e^{-i(\varphi_1-\varphi_2)}+e^{i(\varphi_1-\varphi_2)}\right)\sin\vartheta_1\sin\vartheta_2-2\cos\vartheta_1\cos\vartheta_2\right]\\
&-\xi_i\left(\cos\vartheta_1+\cos\vartheta_2\right)-\sigma\left(\cos^2\vartheta_1+\cos^2\vartheta_2-\frac{2}{3}\right). \qquad (7.36)
\end{aligned}
$$

Using Euler's formula

$$
e^{ix} = \cos x + i\sin x, \qquad (7.37)
$$

$$
e^{-ix} = \cos\left(-x\right)+i\sin\left(-x\right) = \cos x - i\sin x, \qquad (7.38)
$$

we can rewrite Eq. (7.36) as

$$
\begin{aligned}
E_i =&\varsigma\left[\frac{1}{2}\left(\cos\left(\varphi_1-\varphi_2\right)-i\sin\left(\varphi_1-\varphi_2\right)\right.\right.\\
&\left.\left.+\cos\left(\varphi_1-\varphi_2\right)+i\sin\left(\varphi_1-\varphi_2\right)\right)\sin\vartheta_1\sin\vartheta_2-2\cos\vartheta_1\cos\vartheta_2\right]\\
&-\xi_i\left(\cos\vartheta_1+\cos\vartheta_2\right)-\sigma\left(\cos^2\vartheta_1+\cos^2\vartheta_2-\frac{2}{3}\right), \qquad (7.39)
\end{aligned}
$$

which can be written as

$$E_i = \varsigma \left[\sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2) - 2\cos\vartheta_1 \cos\vartheta_2\right]] \\ - \xi_i (\cos\vartheta_1 + \cos\vartheta_2) - \sigma\left(\cos^2\vartheta_1 + \cos^2\vartheta_2\right) + \frac{2}{3}\sigma. \tag{7.40}$$

Note that the constant in Eq. (7.29) is $-(2/3)\sigma$.

7.B Derivation of the Two Coupled Scalar Stochastic Differential Equations

The magnetic dipole moment of an individual macrospin is represented by $\boldsymbol{\mu}_p(t) = \mu\mathbf{s}_p(t)$ $(p = 1, 2)$, where $\mathbf{s}_p$ is the unit vector along $\boldsymbol{\mu}_p$ defined as

$$\mathbf{s}_p = \mathbf{i}\sin\vartheta_p \cos\varphi_p + \mathbf{j}\sin\vartheta_p \sin\varphi_p + \mathbf{k}\cos\vartheta_p, \tag{7.41}$$

or

$$\mathbf{s}_1 = \mathbf{i}\sin\vartheta_1 \cos\varphi_1 + \mathbf{j}\sin\vartheta_1 \sin\varphi_1 + \mathbf{k}\cos\vartheta_1, \tag{7.42}$$

$$\mathbf{s}_2 = \mathbf{i}\sin\vartheta_2 \cos\varphi_2 + \mathbf{j}\sin\vartheta_2 \sin\varphi_2 + \mathbf{k}\cos\vartheta_2, \tag{7.43}$$

μ is the nominal value of the magnetic dipole moment, and ϑ_p and φ_p are the respective polar and azimuthal angles of spin p. The dot product of Eqs. (7.42) and (7.43) is given by

$$\begin{aligned} \mathbf{s}_1 \cdot \mathbf{s}_2 &= \sin\vartheta_1 \sin\vartheta_2 \cos\varphi_1 \cos\varphi_2 + \sin\vartheta_1 \sin\vartheta_2 \sin\varphi_1 \sin\varphi_2 + \cos\vartheta_1 \cos\vartheta_2 \\ &= \sin\vartheta_1 \sin\vartheta_2 \left[\cos\varphi_1 \cos\varphi_2 + \sin\varphi_1 \sin\varphi_2\right] + \cos\vartheta_1 \cos\vartheta_2 \\ &= \sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2) + \cos\vartheta_1 \cos\vartheta_2. \end{aligned} \tag{7.44}$$

Recall that the total normalised free energy E_i $(i = \mathrm{I}, \mathrm{II})$ including dipole-dipole interaction, anisotropy and Zeeman energies may be compactly written in vector form as

$$E_i = \varsigma \left[(\mathbf{s}_1 \cdot \mathbf{s}_2) - 3 \left(\mathbf{u}_r \cdot \mathbf{s}_1 \right) \left(\mathbf{u}_r \cdot \mathbf{s}_2 \right) \right] - \sum_{p=1,2} \left[\xi_i \left(\mathbf{e}_Z \cdot \mathbf{s}_p \right) + \sigma (\mathbf{e}_Z \cdot \mathbf{s}_p)^2 \right], \tag{7.45}$$

where $\mathbf{u}_r = \mathbf{r}/r$ is a unit vector with $r = |\mathbf{r}|$ specifying the separation between the two spins, $\mathbf{e}_Z$ is the unit vector along the (polar) Z axis (assuming that $\mathbf{e}_Z \parallel \mathbf{u}_r$). Since it is assumed that $\mathbf{e}_Z \parallel \mathbf{u}_r$, we have

$$\mathbf{u}_r \cdot \mathbf{s}_1 = |\mathbf{u}_r| \, |\mathbf{s}_1| \cos \vartheta_1 = \cos \vartheta_1, \tag{7.46}$$

$$\mathbf{e}_Z \cdot \mathbf{s}_1 = |\mathbf{e}_Z| \, |\mathbf{s}_1| \cos \vartheta_1 = \cos \vartheta_1, \tag{7.47}$$

and

$$\mathbf{u}_r \cdot \mathbf{s}_2 = |\mathbf{u}_r| \, |\mathbf{s}_2| \cos \vartheta_2 = \cos \vartheta_2, \tag{7.48}$$

$$\mathbf{e}_Z \cdot \mathbf{s}_2 = |\mathbf{e}_Z| \, |\mathbf{s}_2| \cos \vartheta_2 = \cos \vartheta_2. \tag{7.49}$$

Substituting Eqs. (7.46) - (7.49) into Eq. (7.45), we have

$$\begin{aligned} E_i =& \varsigma \left[(\mathbf{s}_1 \cdot \mathbf{s}_2) - 3 \left(\mathbf{u}_r \cdot \mathbf{s}_1 \right) \left(\mathbf{u}_r \cdot \mathbf{s}_2 \right) \right] \\ & - \sum_{p=1,2} \left[\xi_i \left(\mathbf{e}_Z \cdot \mathbf{s}_p \right) + \sigma (\mathbf{e}_Z \cdot \mathbf{s}_p)^2 \right] \\ =& \varsigma \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_1 - \varphi_2) + \varsigma \cos \vartheta_1 \cos \vartheta_2 - 3 \varsigma \cos \vartheta_1 \cos \vartheta_2 \\ & - \xi_i \left(\cos \vartheta_1 + \cos \vartheta_2 \right) - \sigma \left(\cos^2 \vartheta_1 + \cos^2 \vartheta_2 \right) \\ =& \varsigma \left[\sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_1 - \varphi_2) - 2 \cos \vartheta_1 \cos \vartheta_2 \right] \\ & - \xi_i \left(\cos \vartheta_1 + \cos \vartheta_2 \right) - \sigma \left(\cos^2 \vartheta_1 + \cos^2 \vartheta_2 \right). \end{aligned} \tag{7.50}$$

We describe the dynamics of the magnetic moments $\mathbf{M}_p(t)$ ($p = 1, 2$) by the system of stochastic Landau-Lifshitz-Gilbert equations

$$\dot{\mathbf{M}}_p + \gamma \eta \left[\mathbf{M}_p \times \dot{\mathbf{M}}_p \right] = \gamma \left[\mathbf{M}_p \times \left(\mathbf{H}_p + \mathbf{h}_p \right) \right], \tag{7.51}$$

where γ is the gyromagnetic ratio, and η is the damping parameter specifying the dissipative coupling between the spin and its thermal bath. The magnetic field $\mathbf{H}_p(t)$ acting on the particle may consist of externally applied magnetic fields, the crystalline anisotropy field and a field produced by the other nanoparticles. The random Gaussian white noise field $\mathbf{h}_p(t)$ has the properties

$$\overline{h_p^L(t')} = 0, \; \overline{h_p^L(t)h_p^M(t')} = 2kT\alpha(\gamma\mu_0\mu)^{-1}\delta_{LM}\delta(t-t'). \tag{7.52}$$

Cross multiplying both sides of Eq. (7.51) by $\mathbf{M}_p$ we obtain

$$\mathbf{M}_p \times \dot{\mathbf{M}}_p + \gamma\eta\left[\mathbf{M}_p \times \left(\mathbf{M}_p \times \dot{\mathbf{M}}_p\right)\right] = \gamma\left[\mathbf{M}_p \times \{\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right]. \tag{7.53}$$

$$\Rightarrow \mathbf{M}_p \times \dot{\mathbf{M}}_p = \gamma\left[\mathbf{M}_p \times \{\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right] - \gamma\eta\left[\mathbf{M}_p \times \left(\mathbf{M}_p \times \dot{\mathbf{M}}_p\right)\right]. \tag{7.54}$$

Using the vector identity

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c})\,\mathbf{b} - (\mathbf{a} \cdot \mathbf{b})\,\mathbf{c}, \tag{7.55}$$

we may write

$$\begin{aligned} \mathbf{M}_p \times \left(\mathbf{M}_p \times \dot{\mathbf{M}}_p\right) &= \left(\mathbf{M}_p \cdot \dot{\mathbf{M}}_p\right)\mathbf{M}_p - (\mathbf{M}_p \cdot \mathbf{M}_p)\,\dot{\mathbf{M}}_p \\ &= -\,M_S^2\dot{\mathbf{M}}_p, \end{aligned} \tag{7.56}$$

since $\mathbf{M}_p \cdot \dot{\mathbf{M}}_p = 0$. Using Eq. (7.56), we may rewrite Eq. (7.53) as

$$\mathbf{M}_p \times \dot{\mathbf{M}}_p = \gamma\left[\mathbf{M}_p \times \{\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right] + \gamma\eta M_S^2\dot{\mathbf{M}}_p. \tag{7.57}$$

Using Eq. (7.57) we can substitute for $\mathbf{M}_p \times \dot{\mathbf{M}}_p$ in Eq. (7.51) to obtain

$$\dot{\mathbf{M}}_p + \gamma^2\eta\left[\mathbf{M}_p \times \{\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right] + \gamma^2\eta^2 M_S^2\dot{\mathbf{M}}_p = \gamma\left[\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\right]. \tag{7.58}$$

$$\Rightarrow \dot{\mathbf{M}}_p = \frac{\gamma}{1+\gamma^2\eta^2 M_S^2}\left[\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\right] - \frac{\gamma^2\eta}{1+\gamma^2\eta^2 M_S^2}\left[\mathbf{M}_p \times \{\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right]. \tag{7.59}$$

Eq. (7.59) may be written as

$$\dot{\mathbf{M}}_p = \frac{bM_S}{\alpha}\left[\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\right] - b\left[\mathbf{M}_p \times \{\mathbf{M}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right], \tag{7.60}$$

where M_S is the saturation magnetisation of the nanoparticle and

$$\alpha = \gamma\eta M_S, \ b = \frac{\beta}{2\tau_N}, \ \tau_N = \frac{\beta M_S(1+\alpha^2)}{2\gamma\alpha}. \tag{7.61}$$

To analyse the dynamics of magnetisation, it is convenient to introduce polar coordinates

$$\mathbf{M}_p = M_S\left(\sin\vartheta_p\cos\varphi_p, \sin\vartheta_p\sin\varphi_p, \cos\vartheta_p\right). \tag{7.62}$$

If the free energy per unit volume V of the single domain particle is expressed as a function of components of $\mathbf{M}_p$, then

$$\mathbf{H}_p = -\frac{\partial V}{\partial \mathbf{M}_p} = \frac{1}{M_S}\left(0, -\frac{\partial V}{\partial \vartheta_p}, -\frac{1}{\sin\vartheta_p}\frac{\partial V}{\partial \varphi_p}\right), \tag{7.63}$$

where

$$\frac{\partial V}{\partial \mathbf{M}_p} = \frac{\partial V}{\partial \mathbf{M}_X}\mathbf{i} + \frac{\partial V}{\partial \mathbf{M}_Y}\mathbf{j} + \frac{\partial V}{\partial \mathbf{M}_Z}\mathbf{k}. \tag{7.64}$$

Note that

$$\mathbf{M}_p(t) = \boldsymbol{\mu}_p(t) = \mu\mathbf{s}_p(t), \ (p = 1, 2), \tag{7.65}$$

$$\dot{\mathbf{M}}_p(t) = \dot{\boldsymbol{\mu}}_p(t) = \mu\dot{\mathbf{s}}_p(t), \ (p = 1, 2), \tag{7.66}$$

$$\mu = M_S. \tag{7.67}$$

Using Eqs. (7.65) - (7.67) we can rewrite Eq. (7.60) as

$$\mu\dot{\mathbf{s}}_p = \frac{b\mu}{\alpha}\left[\mu\mathbf{s}_p \times (\mathbf{H}_p + \mathbf{h}_p)\right] - b\left[\mu\mathbf{s}_p \times \{\mu\mathbf{s}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right]. \tag{7.68}$$

Noting that $\mathbf{A} \times \mathbf{B} = -\mathbf{B} \times \mathbf{A}$ we may rewrite Eq. (7.68) as

$$\begin{aligned}\dot{\mathbf{s}}_p =& -\frac{b\mu}{\alpha}\left[(\mathbf{H}_p + \mathbf{h}_p) \times \mathbf{s}_p\right] - b\mu\left[\mathbf{s}_p \times \{\mathbf{s}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right] \\ =& -\frac{\mu_0\mu}{2kT\tau_N}\left(\frac{1}{\alpha}\left[(\mathbf{H}_p + \mathbf{h}_p) \times \mathbf{s}_p\right] + \left[\mathbf{s}_p \times \{\mathbf{s}_p \times (\mathbf{H}_p + \mathbf{h}_p)\}\right]\right), \end{aligned} \tag{7.69}$$

where $\mathbf{s}_p$ is a unit vector, which in spherical coordinates is given by

$$\mathbf{s}_p = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \tag{7.70}$$

$$\dot{\mathbf{s}}_p = \begin{pmatrix} 0 \\ \dot{\vartheta}_p \\ \sin\vartheta_p \dot{\varphi}_p \end{pmatrix}. \tag{7.71}$$

Note that

$$\mathbf{H}_p = -\frac{kT}{\mu_0\mu}\frac{\partial E_p}{\partial \mathbf{s}_p}, \tag{7.72}$$

where $\partial/\partial\mathbf{s}_p$ is the gradient on the surface of a unit sphere explicitly defined in spherical coordinates as

$$\frac{\partial}{\partial \mathbf{s}_p} = \frac{\partial}{\partial \vartheta_p}\mathbf{e}_{\vartheta_p} + \frac{1}{\sin\vartheta_p}\frac{\partial}{\partial \varphi_p}\mathbf{e}_{\varphi_p}. \tag{7.73}$$

Substituting Eq. (7.73) into Eq. (7.72) we get

$$\mathbf{H}_p = -\frac{kT}{\mu_0\mu}\begin{pmatrix} 0 \\ \frac{\partial E_p}{\partial \vartheta_p} \\ \frac{1}{\sin\vartheta_p}\frac{\partial E_p}{\partial \varphi_p} \end{pmatrix}. \tag{7.74}$$

Furthermore

$$\mathbf{h}_p = h_{r_p}\mathbf{e}_{r_p} + h_{\vartheta_p}\mathbf{e}_{\vartheta_p} + h_{\varphi_p}\mathbf{e}_{\varphi_p}, \tag{7.75}$$

which can be written as

$$\mathbf{h}_p = \begin{pmatrix} h_{r_p} \\ h_{\vartheta_p} \\ h_{\varphi_p} \end{pmatrix}. \tag{7.76}$$

Thus

$$\mathbf{H}_p + \mathbf{h}_p = \begin{pmatrix} h_{r_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) + h_{\vartheta_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial \varphi_p}\right) + h_{\varphi_p} \end{pmatrix}, \tag{7.77}$$

$$\begin{aligned}(\mathbf{H}_p + \mathbf{h}_p) \times \mathbf{s}_p &= \begin{pmatrix} h_{r_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) + h_{\vartheta_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_p}{\partial \varphi_p}\right) + h_{\varphi_p} \end{pmatrix} \times \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\ &= \left[\left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial \varphi_p}\right) + h_{\varphi_p}\right]\mathbf{e}_{\vartheta_p} + \left[\left(\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) - h_{\vartheta_p}\right]\mathbf{e}_{\varphi_p},\end{aligned} \tag{7.78}$$

$$\begin{aligned}\mathbf{s}_p \times (\mathbf{H}_p + \mathbf{h}_p) &= \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \times \begin{pmatrix} h_{r_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) + h_{\vartheta_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial \varphi_p}\right) + h_{\varphi_p} \end{pmatrix} \\ &= \left[\left(\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial \varphi_p}\right) - h_{\varphi_p}\right]\mathbf{e}_{\vartheta_p} + \left[\left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) + h_{\vartheta_p}\right]\mathbf{e}_{\varphi_p},\end{aligned} \tag{7.79}$$

$$\begin{aligned}\mathbf{s}_p \times [\mathbf{s}_p \times (\mathbf{H}_p + \mathbf{h}_p)] &= \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ \left(\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial \varphi_p}\right) - h_{\varphi_p} \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) + h_{\vartheta_p} \end{pmatrix} \\ &= \left[\left(\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial \vartheta_p}\right) - h_{\vartheta_p}\right]\mathbf{e}_{\vartheta_p} + \left[\left(\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial \varphi_p}\right) - h_{\varphi_p}\right]\mathbf{e}_{\varphi_p}.\end{aligned} \tag{7.80}$$

Substituting Eqs. (7.71), (7.78) and (7.80) into Eq. (7.69) we have

$$\begin{pmatrix} 0 \\ \dot{\vartheta}_p \\ \sin\vartheta_p \dot{\varphi}_p \end{pmatrix} = \frac{\mu_0\mu}{2kT\tau_N}\left[\frac{1}{\alpha}\begin{pmatrix} 0 \\ \left(-\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial\varphi_p}\right) + h_{\varphi_p} \\ \left(\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial\vartheta_p}\right) - h_{\vartheta_p} \end{pmatrix} - \begin{pmatrix} 0 \\ \left(\frac{kT}{\mu_0\mu}\right)\left(\frac{\partial E_i}{\partial\vartheta_p}\right) - h_{\vartheta_p} \\ \left(\frac{kT}{\mu_0\mu}\right)\left(\frac{1}{\sin\vartheta_p}\frac{\partial E_i}{\partial\varphi_p}\right) - h_{\varphi_p} \end{pmatrix}\right], \tag{7.81}$$

which can be written as

$$\dot{\vartheta}_p = \frac{\mu_0\mu}{2kT\tau_N}\left(h_{\vartheta_p} + \alpha^{-1}h_{\varphi_p}\right) - \frac{1}{2\tau_N}\left(\frac{\partial E_i}{\partial\vartheta_p} + \frac{1}{\alpha\sin\vartheta_p}\frac{\partial E_i}{\partial\varphi_p}\right), \tag{7.82}$$

$$\dot{\varphi}_p = \frac{\mu_0\mu}{2kT\tau_N\sin\vartheta_p}\left(h_{\varphi_p} - \alpha^{-1}h_{\vartheta_p}\right) - \frac{1}{2\tau_N}\left(\frac{1}{\sin^2\vartheta_p}\frac{\partial E_i}{\partial\varphi_p} - \frac{1}{\alpha\sin\vartheta_p}\frac{\partial E_i}{\partial\vartheta_p}\right). \tag{7.83}$$

7.C Coefficients $d^{l_1\,l_2\,m}_{l_1+i\,l_2+j\,m+k}$

From the methods described in [2] and [22] using the theory of angular momentum and the Clebsch-Gordan series as well as the expansion of the potential E_i in terms of spherical harmonics, Eq. (7.5), we have after lengthy calculations (given in detail in Appendix 7.D) the various coefficients $d^{l_1\,l_2\,m}_{l_1+i\,l_2+j\,m+k}$ for dipole-dipole interaction, which are

$$d^{l_1\,l_2\,m}_{l_1\,l_2\,m} = p_{l_1\,l_2\,m} = -\sum_{l=l_1,l_2}\left(\frac{1}{2}l(l+1) - \sigma\frac{l(l+1)-3m^2}{(2l-1)(2l+3)}\right),$$

$$d^{l_1\,l_2\,m}_{l_1+2\,l_2\,m} = \bar{u}_{l_1\,l_2\,m} = -\sigma\frac{l_1}{2l_1+3}\sqrt{\frac{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}{(2l_1+1)(2l_1+5)}},$$

$$d^{l_1\,l_2\,m}_{l_1\,l_2+2\,m} = \bar{u}_{l_2\,l_1\,m} = -\sigma\frac{l_2}{2l_2+3}\sqrt{\frac{((l_2+1)^2-m^2)((l_2+2)^2-m^2)}{(2l_2+1)(2l_2+5)}},$$

$$d^{l_1\,l_2\,m}_{l_1-2\,l_2\,m} = \bar{v}_{l_2\,l_1\,m} = \sigma\frac{l_1+1}{2l_1-1}\sqrt{\frac{(l_1^2-m^2)((l_1-1)^2-m^2)}{(2l_1+1)(2l_1-3)}},$$

$$
\begin{aligned}
d^{l_1\,l_2\,m}_{l_1\,l_2-2\,m} =&\bar{v}_{l_1\,l_2\,m} = \sigma\frac{l_2+1}{2l_2-1}\sqrt{\frac{(l_2^2-m^2)((l_2-1)^2-m^2)}{(2l_2+1)(2l_2-3)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2\,m} =&(s_{l_1\,l_2\,m})^* = -\left(\frac{\xi_{\mathrm{II}}}{2}l_1 - \frac{i(\sigma-\varsigma)}{\alpha}m\right)\sqrt{\frac{(l_1+1)^2-m^2}{4(l_1+1)^2-1}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2+1\,m} =&s_{l_2\,l_1\,m} = -\left(\frac{\xi_{\mathrm{II}}}{2}l_2 + \frac{i(\sigma-\varsigma)}{\alpha}m\right)\sqrt{\frac{(l_2+1)^2-m^2}{4(l_2+1)^2-1}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2\,m} =&r_{l_2\,l_1\,m} = \left(\frac{\xi_{\mathrm{II}}}{2}(l_1+1) + \frac{i(\sigma-\varsigma)}{\alpha}m\right)\sqrt{\frac{l_1^2-m^2}{4l_1^2-1}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2-1\,m} =&(r_{l_1\,l_2\,m})^* = \left(\frac{\xi_{\mathrm{II}}}{2}(l_2+1) - \frac{i(\sigma-\varsigma)}{\alpha}m\right)\sqrt{\frac{l_2^2-m^2}{4l_2^2-1}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2+1\,m} =&u_{l_1\,l_2\,m} = -\varsigma(l_1+l_2)\sqrt{\frac{((l_1+1)^2-m^2)((l_2+1)^2-m^2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2-1\,m} =&v_{l_1\,l_2\,m} = \varsigma(l_1+l_2+2)\sqrt{\frac{(l_1^2-m^2)(l_2^2-m^2)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2-1\,m} =&\bar{p}_{l_1\,l_2\,m} = \varsigma(l_2-l_1+1)\sqrt{\frac{((l_1+1)^2-m^2)(l_2^2-m^2)}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2+1\,m} =&\bar{p}_{l_2\,l_1\,m} = \varsigma(l_1-l_2+1)\sqrt{\frac{((l_2+1)^2-m^2)(l_1^2-m^2)}{(2l_2+1)\,(2l_2+3)\,(2l_1-1)\,(2l_1+1)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2+1\,m\pm1} =&u^{\pm}_{l_1\,l_2\,m} = -\frac{1}{4}\varsigma(l_1+l_2)\sqrt{\frac{(l_1\pm m+1)\,(l_1\pm m+2)\,(l_2\pm m+1)\,(l_2\pm m+2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2-1\,m\pm1} =&\bar{p}^{\pm}_{l_1\,l_2\,m} = -\frac{1}{4}\varsigma(l_2-l_1+1)\sqrt{\frac{(l_1\pm m+1)\,(l_1\pm m+2)\,(l_2\mp m-1)\,(l_2\mp m)}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2+1\,m\pm1} =&\bar{p}^{\pm}_{l_2\,l_1\,m} = -\frac{1}{4}\varsigma(l_1-l_2+1)\sqrt{\frac{(l_2\pm m+1)\,(l_2\pm m+2)\,(l_1\mp m-1)\,(l_1\mp m)}{(2l_2+1)\,(2l_2+3)\,(2l_1-1)\,(2l_1+1)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2-1\,m\pm1} =&v^{\pm}_{l_1\,l_2\,m} = \frac{1}{4}\varsigma(l_1+l_2+2)\sqrt{\frac{(l_1\mp m-1)\,(l_1\mp m)\,(l_2\mp m-1)\,(l_2\mp m)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2\,m\pm1} =&\left(s^{\pm}_{l_1\,l_2\,m}\right)^* = \pm\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_1\pm m+1)\,(l_1\pm m+2)\,(l_2\pm m+1)(l_2\mp m)}{(2l_1+1)\,(2l_1+3)}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2+1\,m\pm1} =&s^{\pm}_{l_2\,l_1\,m} = \mp\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_2\pm m+1)\,(l_2\pm m+2)\,(l_1\pm m+1)(l_1\mp m)}{(2l_2+1)\,(2l_2+3)}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2-1\,m\pm1} =&\left(r^{\pm}_{l_1\,l_2\,m}\right)^* = \pm\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_1\pm m+1)(l_1\mp m)\,(l_2\mp m-1)\,(l_2\mp m)}{(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2\,m\pm1} =&r^{\pm}_{l_2\,l_1\,m} = \mp\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_2\pm m+1)(l_2\mp m)\,(l_1\mp m-1)\,(l_1\mp m)}{(2l_1-1)\,(2l_1+1)}}.
\end{aligned}
$$

We note that

$$d^{l_i\,l_j\,m}_{l_i+x\,l_j+y\,m\pm1} = \left(d^{l_j\,l_i\,m}_{l_j+y\,l_i+x\,m\pm1}\right)^*. \tag{7.84}$$

It is useful to compare the coefficients for dipole-dipole coupling with the corresponding ones for exchange interaction [22] (Eq. (7.3)). We have

$$\begin{aligned}
d^{l_1\,l_2\,m}_{l_1\,l_2\,m} =& p_{l_1\,l_2\,m} = -\sum_{l=l_1,l_2}\left(\frac{1}{2}l(l+1) - \sigma\frac{l(l+1)-3m^2}{(2l-1)(2l+3)}\right),\\
d^{l_1\,l_2\,m}_{l_1+2\,l_2\,m} =& \bar{u}_{l_1\,l_2\,m} = -\sigma\frac{l_1}{2l_1+3}\sqrt{\frac{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}{(2l_1+1)(2l_1+5)}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2+2\,m} =& \bar{u}_{l_2\,l_1\,m} = -\sigma\frac{l_2}{2l_2+3}\sqrt{\frac{((l_2+1)^2-m^2)((l_2+2)^2-m^2)}{(2l_2+1)(2l_2+5)}},\\
d^{l_1\,l_2\,m}_{l_1-2\,l_2\,m} =& \bar{v}_{l_2\,l_1\,m} = \sigma\frac{l_1+1}{2l_1-1}\sqrt{\frac{(l_1^2-m^2)((l_1-1)^2-m^2)}{(2l_1+1)(2l_1-3)}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2-2\,m} =& \bar{v}_{l_1\,l_2\,m} = \sigma\frac{l_2+1}{2l_2-1}\sqrt{\frac{(l_2^2-m^2)((l_2-1)^2-m^2)}{(2l_2+1)(2l_2-3)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2\,m} =& (s_{l_1\,l_2\,m})^* = -\left(\frac{\xi_{\mathrm{II}}}{2}l_1 - \frac{i(2\sigma-\varsigma)}{2\alpha}m\right)\sqrt{\frac{(l_1+1)^2-m^2}{4(l_1+1)^2-1}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2+1\,m} =& s_{l_2\,l_1\,m} = -\left(\frac{\xi_{\mathrm{II}}}{2}l_2 + \frac{i(2\sigma-\varsigma)}{2\alpha}m\right)\sqrt{\frac{(l_2+1)^2-m^2}{4(l_2+1)^2-1}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2\,m} =& r_{l_2\,l_1\,m} = \left(\frac{\xi_{\mathrm{II}}}{2}(l_1+1) + \frac{i(2\sigma-\varsigma)}{2\alpha}m\right)\sqrt{\frac{l_1^2-m^2}{4l_1^2-1}},\\
d^{l_1\,l_2\,m}_{l_1\,l_2-1\,m} =& (r_{l_1\,l_2\,m})^* = \left(\frac{\xi_{\mathrm{II}}}{2}(l_2+1) - \frac{i(2\sigma-\varsigma)}{2\alpha}m\right)\sqrt{\frac{l_2^2-m^2}{4l_2^2-1}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2+1\,m} =& u_{l_1\,l_2\,m} = -\frac{1}{2}\varsigma(l_1+l_2)\sqrt{\frac{((l_1+1)^2-m^2)((l_2+1)^2-m^2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2-1\,m} =& v_{l_1\,l_2\,m} = \frac{1}{2}\varsigma(l_1+l_2+2)\sqrt{\frac{(l_1^2-m^2)(l_2^2-m^2)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1+1\,l_2-1\,m} =& \bar{p}_{l_1\,l_2\,m} = \frac{1}{2}\varsigma(l_2-l_1+1)\sqrt{\frac{((l_1+1)^2-m^2)(l_2^2-m^2)}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}},\\
d^{l_1\,l_2\,m}_{l_1-1\,l_2+1\,m} =& \bar{p}_{l_2\,l_1\,m} = \frac{1}{2}\varsigma(l_1-l_2+1)\sqrt{\frac{((l_2+1)^2-m^2)(l_1^2-m^2)}{(2l_2+1)\,(2l_2+3)\,(2l_1-1)\,(2l_1+1)}},
\end{aligned}$$

$$d^{l_1\,l_2\,m}_{l_1+1\,l_2+1\,m\pm1} = u^{\pm}_{l_1\,l_2\,m} = \frac{1}{4}\varsigma(l_1+l_2)\sqrt{\frac{(l_1\pm m+1)\,(l_1\pm m+2)\,(l_2\pm m+1)\,(l_2\pm m+2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}},$$

$$d^{l_1\,l_2\,m}_{l_1+1\,l_2-1\,m\pm1} = \bar{p}^{\pm}_{l_1\,l_2\,m} = \frac{1}{4}\varsigma(l_2-l_1+1)\sqrt{\frac{(l_1\pm m+1)\,(l_1\pm m+2)\,(l_2\mp m-1)\,(l_2\mp m)}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}},$$

$$d^{l_1\,l_2\,m}_{l_1-1\,l_2+1\,m\pm1} = \bar{p}^{\pm}_{l_2\,l_1\,m} = \frac{1}{4}\varsigma(l_1-l_2+1)\sqrt{\frac{(l_2\pm m+1)\,(l_2\pm m+2)\,(l_1\mp m-1)\,(l_1\mp m)}{(2l_2+1)\,(2l_2+3)\,(2l_1-1)\,(2l_1+1)}},$$

$$d^{l_1\,l_2\,m}_{l_1-1\,l_2-1\,m\pm1} = v^{\pm}_{l_1\,l_2\,m} = -\frac{1}{4}\varsigma(l_1+l_2+2)\sqrt{\frac{(l_1\mp m-1)\,(l_1\mp m)\,(l_2\mp m-1)\,(l_2\mp m)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}},$$

$$d^{l_1\,l_2\,m}_{l_1+1\,l_2\,m\pm1} = \left(s^{\pm}_{l_1\,l_2\,m}\right)^* = \mp\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_1\pm m+1)\,(l_1\pm m+2)\,(l_2\pm m+1)(l_2\mp m)}{(2l_1+1)\,(2l_1+3)}},$$

$$d^{l_1\,l_2\,m}_{l_1\,l_2+1\,m\pm1} = s^{\pm}_{l_2\,l_1\,m} = \pm\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_2\pm m+1)\,(l_2\pm m+2)\,(l_1\pm m+1)(l_1\mp m)}{(2l_2+1)\,(2l_2+3)}},$$

$$d^{l_1\,l_2\,m}_{l_1\,l_2-1\,m\pm1} = \left(r^{\pm}_{l_1\,l_2\,m}\right)^* = \mp\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_1\pm m+1)(l_1\mp m)\,(l_2\mp m-1)\,(l_2\mp m)}{(2l_2-1)\,(2l_2+1)}},$$

$$d^{l_1\,l_2\,m}_{l_1-1\,l_2\,m\pm1} = r^{\pm}_{l_2\,l_1\,m} = \pm\frac{i\varsigma}{4\alpha}\sqrt{\frac{(l_2\pm m+1)(l_2\mp m)\,(l_1\mp m-1)\,(l_1\mp m)}{(2l_1-1)\,(2l_1+1)}}.$$

We describe in detail how the above results are obtained in Appendix 7.D.

7.D Deriving the expansion Coefficients $d^{l_1\,l_2\,m}_{l_1+i\,l_2+j\,m+k}$

Recall that the normalised free energy, E_i is given by

$$\begin{aligned} E_i = &-\frac{4\pi}{6}\varsigma\sum_{m=-1}^{1}(3+(-1)^m)Y_{1m}(\vartheta_1,\varphi_1)Y_{1-m}(\vartheta_2,\varphi_2) \\ &-\sum_{p=1,2}\left[\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_p,\varphi_p)+\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_p,\varphi_p)\right]+\text{const.},\quad \text{i}=\text{I},\text{II}. \end{aligned} \tag{7.85}$$

We define (because we wish to use a general expression provided by Coffey, Kalmykov and Titov. (see Eq. (1.103) of [34]) See Eq. (7.95) below)

$$
\begin{aligned}
E_i^{(p)} =&E_{i,+}^{(p)} + E_{i,-}^{(p)},\\
E_{i,+}^{(p)} =&\sum_{R=1}^{\infty}\sum_{S=0}^{R} v_{RS}^{(p)} Y_{RS}^{(p)}(\vartheta_p,\varphi_p),\\
E_{i,-}^{(p)} =&\sum_{R=1}^{\infty}\sum_{S=-R}^{-1} v_{RS}^{(p)} Y_{RS}^{(p)}(\vartheta_p,\varphi_p),\\
p =&1,2.
\end{aligned}
\tag{7.86}
$$

From Eq. (7.86) we have for Eq. (7.85):

$$
\begin{aligned}
E_i^{(1)} =& -\frac{4\pi}{6}\varsigma\sum_{m=-1}^{1}(3+(-1)^m)Y_{1m}(\vartheta_1,\varphi_1)Y_{1-m}(\vartheta_2,\varphi_2)\\
&-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\\
=& -\frac{4\pi}{6}\varsigma\,[2Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+4Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\\
&+2Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)]\\
&-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_1,\varphi_1),
\end{aligned}
\tag{7.87}
$$

$$
\begin{aligned}
E_i^{(2)} =& -\frac{4\pi}{6}\varsigma\,[2Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\ +4Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\\
&+\ 2Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)]\\
&-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_2,\varphi_2),
\end{aligned}
\tag{7.88}
$$

$$
\begin{aligned}
E_{i,+}^{(1)} =& -\frac{4\pi}{6}\varsigma\,[4Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+2Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)]\\
&-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\\
=& -\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\\
=&\mathrm{A}_{1,1,0}^{(1)}\left(\varsigma\right)Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\mathrm{A}_{1,1,1}^{(1)}\left(\varsigma\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&+\mathrm{A}_{1,0,0}^{(1)}Y_{10}(\vartheta_1,\varphi_1)+\mathrm{A}_{2,0,0}^{(1)}Y_{20}(\vartheta_1,\varphi_1),
\end{aligned}
\tag{7.89}
$$

$$
\begin{aligned}
E_{i,-}^{(1)} =& -\frac{4\pi}{6}\varsigma\left[2Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right] \\
=& -\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2) \\
=& \mathrm{A}_{1,1,-1}^{(1)}\left(\varsigma\right)Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2),
\end{aligned}
\tag{7.90}
$$

$$
\begin{aligned}
E_{i,+}^{(2)} =& -\frac{4\pi}{6}\varsigma\left[2Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+4Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right] \\
& -\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_2,\varphi_2) \\
=& -\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2) \\
& -\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_2,\varphi_2) \\
=& \mathrm{A}_{1,1,-1}^{(2)}\left(\varsigma\right)Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+\mathrm{A}_{1,1,0}^{(2)}\left(\varsigma\right)Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2) \\
& +\mathrm{A}_{0,1,0}^{(2)}Y_{10}(\vartheta_2,\varphi_2)+\mathrm{A}_{0,2,0}^{(2)}Y_{20}(\vartheta_2,\varphi_2),
\end{aligned}
\tag{7.91}
$$

$$
\begin{aligned}
E_{i,-}^{(2)} =& -\frac{4\pi}{6}\varsigma\left[2Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right] \\
=& -\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) \\
=& \mathrm{A}_{1,1,1}^{(2)}\left(\varsigma\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2).
\end{aligned}
\tag{7.92}
$$

Having written the split potentials as products of spherical harmonics of arguments (ϑ_1,φ_1) and (ϑ_2,φ_2), we now introduce as new variables (whose form is suggested by the potential) the time dependent product of spherical harmonics of arguments (ϑ_1,φ_1) and (ϑ_2,φ_2) respectively expressed as

$$
M_{l_1\,l_2\,m}=Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2). \tag{7.93}
$$

The stochastic equation of motion for the functions $M_{l_1\,l_2\,m}(t)$ is given by

$$
\frac{d}{dt}M_{l_1\,l_2\,m}=\sum_{p=1,2}\dot{\vartheta}_p\frac{\partial M_{l_1\,l_2\,m}}{\partial\vartheta_p}+\dot{\varphi}_p\frac{\partial M_{l_1\,l_2\,m}}{\partial\varphi_p}. \tag{7.94}
$$

Upon averaging Eq. (7.94) over its realisations in an infinitesimal time, we obtain by essentially adapting the formal method of Coffey, Kalmykov and Titov (See Eq.

(1.102) of [34])

$$\begin{aligned}
\tau_N \dot{M}_{l_1 l_2 m} = & \sum_{i=1}^{2} \frac{1}{4} \Big[\big(L^{(p)}\big)^2 \Big(E_i^{(p)} M_{l_1 l_2 m} \Big) - E_i^{(p)} \big(L^{(p)}\big)^2 M_{l_1 l_2 m} \\
& - M_{l_1 l_2 m} \big(L^{(p)}\big)^2 E_i^{(p)} \Big] - \frac{1}{2} \sum_{i=1}^{2} \big(L^{(p)}\big)^2 M_{l_1 l_2 m} \\
& + \sum_{i=1}^{2} \frac{i}{4\alpha} \sqrt{\frac{3}{2\pi}} \Big\{ \Big(Y_{1,1}^{(p)} \Big)^{-1} \Big[\Big(L_Z^{(p)} E_{i+}^{(p)} \Big) \Big(L_+^{(p)} M_{l_1 l_2 m} \Big) \\
& - \Big(L_+^{(p)} E_{i+}^{(p)} \Big) \Big(L_Z^{(p)} M_{l_1 l_2 m} \Big) \Big] \\
& + \Big(Y_{1,-1}^{(i)} \Big)^{-1} \Big[\Big(L_Z^{(p)} E_{i-}^{(p)} \Big) \Big(L_-^{(p)} M_{l_1 l_2 m} \Big) \\
& - \Big(L_-^{(p)} E_{i-}^{(p)} \Big) \Big(L_Z^{(p)} M_{l_1 l_2 m} \Big) \Big] \Big\}, \qquad (7.95)
\end{aligned}$$

where

$$\big(L^{(p)}\big)^2 = - \frac{1}{\sin\vartheta_p} \frac{\partial}{\partial\vartheta_p} \left(\sin\vartheta_p \frac{\partial}{\partial\vartheta_p} \right) - \frac{1}{\sin^2\vartheta_p} \frac{\partial^2}{\partial\varphi_p^2}, \qquad (7.96)$$

$$L_Z^{(p)} = - i \frac{\partial}{\partial\varphi_p}, \qquad (7.97)$$

$$L_\pm^{(p)} = e^{\pm\varphi_p} \left(\pm \frac{\partial}{\partial\vartheta_p} + i \cot\vartheta_p \frac{\partial}{\partial\varphi_p} \right), \qquad (7.98)$$

are the orbital angular momentum operators [34,120]. Using Eqs. (7.87) - (7.92) we may substitute for the free energy terms in Eq. (7.95) to obtain

$$\tau_N \dot{M}_{l_1 l_2 m} =$$

1

$$\frac{1}{4}\left[\left(L^{(1)}\right)^2 \left(\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2) - \frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\right.\right.$$
$$- \frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) - \xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)$$
$$\left.\left. -\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right) Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)$$

2

$$- \left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2) - \frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.$$
$$- \frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) - \xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)$$
$$\left. - \sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right) \left(L^{(1)}\right)^2 Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)$$

3

$$- Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(L^{(1)}\right)^2 \left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.$$
$$- \frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)$$
$$\left.- \frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) - \xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1) - \sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right)$$

4

$$+ \left(L^{(2)}\right)^2 \left(\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2) - \frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\right.$$
$$- \frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) - \xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)$$
$$\left.\left. - \sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\right) Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)$$

5

$$- \left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2) - \frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.$$
$$- \frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) - \xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)$$
$$\left. - \sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\right) \left(L^{(2)}\right)^2 Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)$$

6

$$-\,Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\big(L^{(2)}\big)^2\Bigg(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)$$

$$-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)$$

$$-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\Bigg)\Bigg]$$

7

$$-\frac{1}{2}\Big[\big(L^{(1)}\big)^2Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)+\big(L^{(2)}\big)^2Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big]$$

8

$$+\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left\{\left(Y^{(1)}_{1,1}\right)^{-1}\Big[\Big(L^{(1)}_Z\Big(\mathrm{A}^{(1)}_{1,1,0}(\varsigma)\,Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.$$

$$+\mathrm{A}^{(1)}_{1,1,1}(\varsigma)\,Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\mathrm{A}^{(1)}_{1,0,0}Y_{10}(\vartheta_1,\varphi_1)$$

$$+\ \mathrm{A}^{(1)}_{2,0,0}Y_{20}(\vartheta_1,\varphi_1)\Big)\Big)\Big(L^{(1)}_+Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)$$

9

$$-\Big(L^{(1)}_+\Big(\mathrm{A}^{(1)}_{1,1,0}(\varsigma)\,Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)$$

$$+\mathrm{A}^{(1)}_{1,1,1}(\varsigma)\,Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\mathrm{A}^{(1)}_{1,0,0}Y_{10}(\vartheta_1,\varphi_1)$$

$$+\ \mathrm{A}^{(1)}_{2,0,0}Y_{20}(\vartheta_1,\varphi_1)\Big)\Big)\Big(L^{(1)}_ZY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)\Big]$$

10

$$+\left(Y^{(1)}_{1,-1}\right)^{-1}\Big[\Big(L^{(1)}_Z\Big(\mathrm{A}^{(1)}_{1,1,-1}(\varsigma)\,Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\Big)\Big)\Big(L^{(1)}_-Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)$$

$$-\ \Big(L^{(1)}_-\Big(\mathrm{A}^{(1)}_{1,1,-1}(\varsigma)\,Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\Big)\Big)\Big(L^{(1)}_ZY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)\Big]$$

11

$$+\left(Y^{(2)}_{1,1}\right)^{-1}\Big[\Big(L^{(2)}_Z\Big(\mathrm{A}^{(2)}_{1,1,-1}(\varsigma)\,Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\ +\mathrm{A}^{(2)}_{1,1,0}(\varsigma)\,Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)$$

$$+\mathrm{A}^{(2)}_{0,1,0}Y_{10}(\vartheta_2,\varphi_2)+\ \mathrm{A}^{(2)}_{0,2,0}Y_{20}(\vartheta_2,\varphi_2)\Big)\Big)\Big(L^{(2)}_+Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)$$

12

$$-\Big(L^{(2)}_+\Big(\mathrm{A}^{(2)}_{1,1,-1}(\varsigma)\,Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\ +\mathrm{A}^{(2)}_{1,1,0}(\varsigma)\,Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)$$

$$+\mathrm{A}^{(2)}_{0,1,0}Y_{10}(\vartheta_2,\varphi_2)+\ \mathrm{A}^{(2)}_{0,2,0}Y_{20}(\vartheta_2,\varphi_2)\Big)\Big)\Big(L^{(2)}_ZY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)\Big]$$

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$$+\left(Y^{(2)}_{1,-1}\right)^{-1}\Big[\Big(L^{(2)}_Z\Big(\mathrm{A}^{(2)}_{1,1,1}(\varsigma)\,Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\Big)\Big)\Big(L^{(2)}_-Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)$$

$$-\ \Big(L^{(2)}_-\Big(\mathrm{A}^{(2)}_{1,1,1}(\varsigma)\,Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\Big)\Big)\Big(L^{(2)}_ZY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)\Big]\Big\}\,. \tag{7.99}$$

In the following sections, we shall use the following identities for the product of two spherical harmonics [2]

$$\begin{aligned}
\sqrt{\frac{8\pi}{3}}Y_{1\pm1}Y_{lm} =&\sqrt{\frac{(l\pm m+1)\,(l\pm m+2)}{(2l+1)\,(2l+3)}}Y_{l+1m\pm1}\\
&-\sqrt{\frac{(l\mp m-1)\,(l\mp m)}{(2l-1)\,(2l+1)}}Y_{l-1m\pm1},\\
\Rightarrow Y_{1\pm1}Y_{lm} =&\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l\pm m+1)\,(l\pm m+2)}{(2l+1)\,(2l+3)}}Y_{l+1m\pm1}\\
&-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l\mp m-1)\,(l\mp m)}{(2l-1)\,(2l+1)}}Y_{l-1m\pm1},
\end{aligned}\tag{7.100}$$

$$\begin{aligned}
\sqrt{\frac{4\pi}{3}}Y_{10}Y_{lm} =&\sqrt{\frac{(l+m+1)\,(l-m+1)}{(2l+1)\,(2l+3)}}Y_{l+1m}\\
&+\sqrt{\frac{(l-m)\,(l+m)}{(2l-1)\,(2l+1)}}Y_{l-1m},\\
\Rightarrow Y_{10}Y_{lm} =&\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l+m+1)\,(l-m+1)}{(2l+1)\,(2l+3)}}Y_{l+1m}\\
&+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l-m)\,(l+m)}{(2l-1)\,(2l+1)}}Y_{l-1m},
\end{aligned}\tag{7.101}$$

$$\begin{aligned}
\sqrt{\frac{4\pi}{5}}Y_{20}Y_{lm} =&\frac{l(l+1)-3m^2}{(2l-1)(2l+3)}Y_{lm}\\
&+\frac{3\sqrt{(l^2-m^2)((l-1)^2-m^2)}}{2(2l-1)\sqrt{(2l+1)(2l-3)}}Y_{l-2m}\\
&+\frac{3\sqrt{((l+1)^2-m^2)((l+2)^2-m^2)}}{2(2l+3)\sqrt{(2l+1)(2l+5)}}Y_{l+2m},\\
\Rightarrow Y_{20}Y_{lm} =&\sqrt{\frac{5}{4\pi}}\frac{l(l+1)-3m^2}{(2l-1)(2l+3)}Y_{lm}\\
&+\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{(l^2-m^2)((l-1)^2-m^2)}}{2(2l-1)\sqrt{(2l+1)(2l-3)}}Y_{l-2m}\\
&+\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{((l+1)^2-m^2)((l+2)^2-m^2)}}{2(2l+3)\sqrt{(2l+1)(2l+5)}}Y_{l+2m}.
\end{aligned}\tag{7.102}$$

Furthermore, the action of the angular momentum operator L^2 on a spherical harmonic Y_{lm} is given by

$$L^2 Y_{lm} = l\,(l+1)\,Y_{lm}. \tag{7.103}$$

We shall now evaluate the effects of the various operators on the components of Eq. (7.99) individually

1

$$\begin{aligned}
&\frac{1}{4}\big(L^{(1)}\big)^2 \Bigg(\bigg(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2) - \frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\\
&- \frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2) - \xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)\\
&- \sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\bigg)\,Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Bigg)\\
=&\big(L^{(1)}\big)^2\bigg(-\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\;Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{11}(\vartheta_2,\varphi_2)\\
&- \frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{10}(\vartheta_2,\varphi_2)\\
&- \frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{1-1}(\vartheta_2,\varphi_2)\\
&- \xi_i\sqrt{\frac{\pi}{12}}Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&- \sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{20}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\bigg)
\end{aligned}$$

$$
\begin{aligned}
=&\left(L^{(1)}\right)^2\Bigg[-\frac{\pi}{3}\varsigma\left(\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m+1)(l_1-m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m-1}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m-1)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m-1}\right)\times\\
&\left(\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2+(-m)+1)(l_2+(-m)+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1(-m)+1}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-(-m)-1)(l_2-(-m))}{(2l_2-1)(2l_2+1)}}Y_{l_2-1(-m)+1}\right)\\
&-\frac{2\pi}{3}\varsigma\left(\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m}\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}\right)\times\\
&\left(\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1(-m)}\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2-(-m))(l_2+(-m))}{(2l_2-1)(2l_2+1)}}Y_{l_2-1(-m)}\right)\\
&-\frac{\pi}{3}\varsigma\left(\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m+1)(l_1+m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m+1}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m-1)(l_1-m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m+1}\right)\times\\
&\left(\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-(-m)+1)(l_2-(-m)+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1(-m)-1}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l+(-m)-1)(l+(-m))}{(2l_2-1)(2l_2+1)}}Y_{l_2-1(-m)-1}\right)\\
&-\xi_i\sqrt{\frac{\pi}{12}}\left(\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m}\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}\right)(Y_{l_2-m})\\
&-\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\left(\sqrt{\frac{5}{4\pi}}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}Y_{l_1m}\right.
\end{aligned}
$$

$$+\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{2(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}Y_{l_1-2m}$$

$$\left.+\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{2(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}Y_{l_1+2m}\right)(Y_{l_2-m})\Big]$$

$$=\left(L^{(1)}\right)^2\left(-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}Y_{l_1+1m-1}Y_{l_2+11-m}\right.$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2+m-1)(l_2-(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}Y_{l_1+1m-1}Y_{l_2-11-m}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2-m+1)(l_2-m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}Y_{l_1-1m-1}Y_{l_2+11-m}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}Y_{l_1-1m-1}Y_{l_2-11-m}$$

$$-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}Y_{l_1+1m}Y_{l_2+1-m}$$

$$-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-(-m))(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}Y_{l_1+1m}Y_{l_2-1-m}$$

$$-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}Y_{l_1-1m}Y_{l_2+1-m}$$

$$-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-(-m))(l_2+(-m))}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}Y_{l_1-1m}Y_{l_2-1-m}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-(-m)+1)(l_2-(-m)+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}Y_{l_1+1m+1}Y_{l_2+1-m-1}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+(-m)-1)(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}Y_{l_1+1m+1}Y_{l_2-1-m-1}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-(-m)+1)(l_2-(-m)+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}Y_{l_1-1m+1}Y_{l_2+1-m-1}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+(-m)-1)(l_2+(-m))}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}Y_{l_1-1m+1}Y_{l_2-1-m-1}$$

$$-\frac{1}{4}\xi_i\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m}Y_{l_2-m}$$

$$-\frac{1}{4}\xi_i\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}Y_{l_2-m}$$

$$
\begin{aligned}
&- \sigma \frac{1}{6} \frac{l_1(l_1+1) - 3m^2}{(2l_1-1)(2l_1+3)} Y_{l_1 m} Y_{l_2 -m} \\
&- \sigma \frac{1}{4} \frac{\sqrt{(l_1^2 - m^2)((l_1-1)^2 - m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} Y_{l_1-2 m} Y_{l_2 -m} \\
&- \sigma \frac{1}{4} \frac{\sqrt{((l_1+1)^2 - m^2)((l_1+2)^2 - m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}} Y_{l_1+2 m} Y_{l_2 -m} \Bigg) \\
=& \left(L^{(1)}\right)^2 \Bigg(- \frac{1}{8} \varsigma \sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} M_{l_1+1 l_2+1 m-1} \\
&+ \frac{1}{8} \varsigma \sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2+m-1)(l_2-(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} M_{l_1+1 l_2-1 m-1} \\
&+ \frac{1}{8} \varsigma \sqrt{\frac{(l_1+m-1)(l_1+m)(l_2-m+1)(l_2-m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} M_{l_1-1 l_2+1 m-1} \\
&- \frac{1}{8} \varsigma \sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} M_{l_1-1 l_2-1 m-1} \\
&- \frac{1}{2} \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} M_{l_1+1 l_2+1 m} \\
&- \frac{1}{2} \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-(-m))(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} M_{l_1+1 l_2-1 m} \\
&- \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} M_{l_1-1 l_2+1 m} \\
&- \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-(-m))(l_2+(-m))}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} M_{l_1-1 l_2-1 m} \\
&- \frac{1}{8} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-(-m)+1)(l_2-(-m)+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} M_{l_1+1 l_2+1 m+1} \\
&+ \frac{1}{8} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+(-m)-1)(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} M_{l_1+1 l_2-1 m+1} \\
&+ \frac{1}{8} \varsigma \sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-(-m)+1)(l_2-(-m)+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} M_{l_1-1 l_2+1 m+1} \\
&- \frac{1}{8} \varsigma \sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+(-m)-1)(l_2+(-m))}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} M_{l_1-1 l_2-1 m+1} \\
&- \frac{1}{4} \xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} M_{l_1+1 l_2 m}
\end{aligned}
$$

$$- \frac{1}{4}\xi_i\sqrt{\frac{(l_1-m)\,(l_1+m)}{(2l_1-1)\,(2l_1+1)}}M_{l_1-1\,l_2\,m}$$

$$- \sigma\frac{1}{6}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}M_{l_1\,l_2\,m}$$

$$- \frac{1}{4}\sigma\frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}M_{l_1-2\,l_2\,m}$$

$$- \frac{1}{4}\,\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}M_{l_1+2l_2\,m}\Bigg)$$

$$= -\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)\,(l_1-m+2)\,(l_2-m+1)\,(l_2-m+2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}}\times$$

$$(l_1+1)\,((l_1+1)+1)\,M_{l_1+1l_2+1\,m-1}$$

$$+ \frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)\,(l_1-m+2)\,(l_2+m-1)\,(l_2-(-m))}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}}\times$$

$$(l_1+1)\,((l_1+1)+1)\,M_{l_1+1l_2-1\,m-1}$$

$$+ \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)\,(l_1+m)\,(l_2-m+1)\,(l_2-m+2)}{(2l_1-1)\,(2l_1+1)\,(2l_2+1)\,(2l_2+3)}}\times$$

$$(l_1-1)\,((l_1-1)+1)\,M_{l_1-1l_2+1\,m-1}$$

$$- \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)\,(l_1+m)\,(l_2+m-1)\,(l_2+m)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}}\times$$

$$(l_1-1)\,((l_1-1)+1)\,M_{l_1-1l_2-1\,m-1}$$

$$- \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)\,(l_1-m+1)\,(l_2+(-m)+1)\,(l_2-(-m)+1)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}}\times$$

$$(l_1+1)\,((l_1+1)+1)\,M_{l_1+1l_2+1\,m}$$

$$- \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)\,(l_1-m+1)\,(l_2-(-m))\,(l_2+(-m))}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}}\times$$

$$(l_1+1)\,((l_1+1)+1)\,M_{l_1+1l_2-1\,m}$$

$$- \frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)\,(l_1+m)\,(l_2+(-m)+1)\,(l_2-(-m)+1)}{(2l_1-1)\,(2l_1+1)\,(2l_2+1)\,(2l_2+3)}}\times$$

$$(l_1-1)\,((l_1-1)+1)\,M_{l_1-1l_2+1m}$$

$$
-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)\,(l_1+m)\,(l_2-(-m))\,(l_2+(-m))}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}}\times
$$

$$
(l_1-1)\,((l_1-1)+1)\,M_{l_1-1 l_2-1\, m}
$$

$$
-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)\,(l_1+m+2)\,(l_2-(-m)+1)\,(l_2-(-m)+2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}}\times
$$

$$
(l_1+1)\,((l_1+1)+1)\,M_{l_1+1 l_2+1\, m+1}
$$

$$
+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)\,(l_1+m+2)\,(l_2+(-m)-1)\,(l_2+(-m))}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}}\times
$$

$$
(l_1+1)\,((l_1+1)+1)\,M_{l_1+1 l_2-1\, m+1}
$$

$$
+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)\,(l_1-m)\,(l_2-(-m)+1)\,(l_2-(-m)+2)}{(2l_1-1)\,(2l_1+1)\,(2l_2+1)\,(2l_2+3)}}\times
$$

$$
(l_1-1)\,((l_1-1)+1)\,M_{l_1-1\, l_2+1\, m+1}
$$

$$
-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)\,(l_1-m)\,(l_2+(-m)-1)\,(l_2+(-m))}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}}\times
$$

$$
(l_1-1)\,((l_1-1)+1)\,M_{l_1-1 l_2-1\, m+1}
$$

$$
-\frac{1}{4}\xi_i\sqrt{\frac{(l_1+m+1)\,(l_1-m+1)}{(2l_1+1)\,(2l_1+3)}}\times
$$

$$
(l_1+1)\,((l_1+1)+1)\,M_{l_1+1 l_2\, m}
$$

$$
-\frac{1}{4}\xi_i\sqrt{\frac{(l_1-m)\,(l_1+m)}{(2l_1-1)\,(2l_1+1)}}\times
$$

$$
(l_1-1)\,((l_1-1)+1)\,M_{l_1-1\, l_2\, m}
$$

$$
-\sigma\frac{1}{6}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}l_1\,(l_1+1)\,M_{l_1\, l_2\, m}
$$

$$
-\frac{1}{4}\sigma\frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}\times
$$

$$
(l_1-2)\,((l_1-2)+1)\,M_{l_1-2\, l_2\, m}
$$

$$
-\frac{1}{4}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\times
$$

$$
(l_1+2)\,((l_1+2)+1)\,M_{l_1+2 l_2\, m}. \tag{7.104}
$$

Thus the first term '1' on the RHS of Eq. (7.99) has been expressed as a *linear combination of the desired products* M. Likewise all the other terms follow, whence we can can by orthogonality hive off the expansion coefficients in the Fourier-Laplace series. Notice that in general it is much easier to use the Clebsch-Gordan coefficients which exist in Mathematica in order to avoid those complicated calculations. We have for the second term '2':

2

$$
\begin{aligned}
&\frac{1}{4}\left(\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&+\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)\\
&\left.+\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right)\left(L^{(1)}\right)^2 Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\left(\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&+\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\xi_i\sqrt{\frac{\pi}{12}}Y_{10}(\vartheta_1,\varphi_1)\\
&\left.+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{20}(\vartheta_1,\varphi_1)\right)\left(l_1\left(l_1+1\right)\right)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&l_1\left(l_1+1\right)\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{11}(\vartheta_2,\varphi_2)\\
&+l_1\left(l_1+1\right)\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{10}(\vartheta_2,\varphi_2)\\
&+l_1\left(l_1+1\right)\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{1-1}(\vartheta_2,\varphi_2)\\
&+l_1\left(l_1+1\right)\xi_i\sqrt{\frac{\pi}{12}}Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+l_1\left(l_1+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{20}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\left[l_1\left(l_1+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m-1}\right.\\
&\left.-l_1\left(l_1+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m-1}\right]\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+11-m}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-11-m}\right]
\end{aligned}
$$

$$
\begin{aligned}
&+\left[l_1\left(l_1+1\right)\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1-m+1\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m}\right.\\
&\left.+l_1\left(l_1+1\right)\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_1-m\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m}\right]\times\\
&\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2+m+1\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+1-m}\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_2+m\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-1-m}\right]\\
&+\left[l_1\left(l_1+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m+1}\right.\\
&\left.-l_1\left(l_1+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m+1}\right]\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+1-m-1}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-1-m-1}\right]\\
&+\left[l_1\left(l_1+1\right)\xi_i\sqrt{\frac{\pi}{12}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1-m+1\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m}Y_{l_2-m}\right.\\
&\left.+l_1\left(l_1+1\right)\xi_i\sqrt{\frac{\pi}{12}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_1-m\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m}Y_{l_2-m}\right]\\
&+\left[l_1\left(l_1+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\sqrt{\frac{5}{4\pi}}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}Y_{l_1m}Y_{l_2-m}\right.\\
&+l_1\left(l_1+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{2(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}Y_{l_1-2m}Y_{l_2-m}\\
&\left.+l_1\left(l_1+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{2(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}Y_{l_1+2m}Y_{l_2-m}\right]\\
=&\frac{1}{8}\varsigma\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)\left(2l_2+1\right)\left(2l_2+3\right)}}l_1\left(l_1+1\right)M_{l_1+1l_2+1\,m-1}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_1+1\right)\left(2l_1+3\right)\left(2l_2-1\right)\left(2l_2+1\right)}}l_1\left(l_1+1\right)M_{l_1+1l_2-1\,m-1}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_1-1\right)\left(2l_1+1\right)\left(2l_2+1\right)\left(2l_2+3\right)}}l_1\left(l_1+1\right)M_{l_1-1l_2+1\,m-1}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_1(l_1+1)M_{l_1-1l_2-1\,m-1}\\
&+\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}l_1(l_1+1)M_{l_1+1l_2+1\,m}\\
&+\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_1(l_1+1)M_{l_1+1l_2-1\,m}\\
&+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}l_1(l_1+1)M_{l_1-1l_2+1\,m}\\
&+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_1(l_1+1)M_{l_1-1l_2-1\,m}\\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}l_1(l_1+1)M_{l_1+1l_2+1\,m+1}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-m-1)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_1(l_1+1)M_{l_1+1l_2-1\,m+1}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+m+1)(l_2+m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}l_1(l_1+1)M_{l_1-1l_2+1\,m+1}\\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-m-1)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_1(l_1+1)M_{l_1-1l_2-1\,m+1}\\
&+\frac{1}{4}\xi_i\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}l_1(l_1+1)M_{l_1+1l_2\,m}\\
&+\frac{1}{4}\xi_i\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}l_1(l_1+1)M_{l_1-1l_2\,m}\\
&+\sigma\frac{1}{6}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}l_1(l_1+1)M_{l_1\,l_2\,m}\\
&+\sigma\frac{1}{4}\frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}l_1(l_1+1)M_{l_1-2\,l_2\,m}\\
&+\sigma\frac{1}{4}\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}l_1(l_1+1)M_{l_1+2\,l_2\,m}. \qquad (7.105)
\end{aligned}
$$

3

$$
\begin{aligned}
&\frac{1}{4}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(L^{(1)}\right)^2\left(\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&+\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.+\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)+\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right)\\
=&Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(\frac{\pi}{3}\varsigma\left(L^{(1)}\right)^2Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&+\frac{2\pi}{3}\varsigma\left(L^{(1)}\right)^2Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\frac{\pi}{3}\varsigma\left(L^{(1)}\right)^2Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.+\xi_i\sqrt{\frac{\pi}{12}}\left(L^{(1)}\right)^2Y_{10}(\vartheta_1,\varphi_1)+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\left(L^{(1)}\right)^2Y_{20}(\vartheta_1,\varphi_1)\right)\\
=&Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(\frac{\pi}{3}\varsigma\left(1\left(1+1\right)\right)Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&+\frac{2\pi}{3}\varsigma\left(1\left(1+1\right)\right)Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\frac{\pi}{3}\varsigma\left(1\left(1+1\right)\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.+\xi_i\sqrt{\frac{\pi}{12}}\left(1\left(1+1\right)\right)Y_{10}(\vartheta_1,\varphi_1)+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\left(2\left(2+1\right)\right)Y_{20}(\vartheta_1,\varphi_1)\right)\\
=&Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(\frac{2\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&+\frac{4\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\frac{2\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.+\xi_i\sqrt{\frac{\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)+\sigma\frac{2}{3}\sqrt{\frac{9\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right)\\
=&\frac{2\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{11}(\vartheta_2,\varphi_2)\\
&+\frac{4\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{10}(\vartheta_2,\varphi_2)\\
&+\frac{2\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{1-1}(\vartheta_2,\varphi_2)\\
&+\xi_i\sqrt{\frac{\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+\sigma\frac{2}{3}\sqrt{\frac{9\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)
\end{aligned}
$$

$$
\begin{aligned}
= \Bigg[& \frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m+1)(l_1-m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m-1} \\
& - \frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m-1)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m-1}\Bigg] \times \\
& \Bigg[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-m+1)(l_2-m+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+11-m} \\
& - \sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2+m-1)(l_2+m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-11-m}\Bigg] \\
& + \Bigg[\frac{4\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m} \\
& + \frac{4\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}\Bigg] \times \\
& \Bigg[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1-m} \\
& + \sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-1-m}\Bigg] \\
& + \Bigg[\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m+1)(l_1+m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m+1} \\
& - \frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m-1)(l_1-m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m+1}\Bigg] \times \\
& \Bigg[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2+m+1)(l_2+m+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1-m-1} \\
& - \sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-m-1)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-1-m-1}\Bigg] \\
& + \Bigg[\xi_i\sqrt{\frac{\pi}{3}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m} \\
& + \xi_i\sqrt{\frac{\pi}{3}}\ \sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}\Bigg] Y_{l_2-m}
\end{aligned}
$$

$$+\left[\sigma\frac{2}{3}\frac{3}{2}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}Y_{l_1 m}\right.$$

$$+\sigma\frac{3}{2}\frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}Y_{l_1-2m}$$

$$\left.+\sigma\frac{3}{2}\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}Y_{l_1+2m}\right]Y_{l_2-m}$$

$$=\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1 l_2+1\, m-1}$$

$$-\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2+m-1)(l_2+m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1 l_2-1\, m-1}$$

$$-\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2-m+1)(l_2-m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1 l_2+1\, m-1}$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1 l_2-1\, m-1}$$

$$+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1 l_2+1\, m}$$

$$+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1 l_2-1\, m}$$

$$+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1 l_2+1\, m}$$

$$+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1 l_2-1\, m}$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1 l_2+1\, m+1}$$

$$-\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-m-1)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1\, l_2-1\, m+1}$$

$$-\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+m+1)(l_2+m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1 l_2+1\, m+1}$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-m-1)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1 l_2-1\, m+1}$$

$$+\frac{1}{2}\xi_i\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}M_{l_1+1\, l_2\, m}$$

$$+\frac{1}{2}\xi_i\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}M_{l_1-1l_2\,m}$$

$$+\sigma\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}M_{l_1\,l_2\,m}$$

$$+\sigma\frac{3\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{2(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}}M_{l_1-2l_2\,m}$$

$$+\sigma\frac{3\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{2(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}M_{l_1+2l_2\,m}. \tag{7.106}$$

4

$$\frac{1}{4}\left(L^{(2)}\right)^2\Bigg(\Bigg(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)$$
$$-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)$$
$$-\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\Bigg)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\Bigg)$$
$$=\left(L^{(2)}\right)^2\Big(-\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\,Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{11}(\vartheta_2,\varphi_2)$$
$$-\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{10}(\vartheta_2,\varphi_2)$$
$$-\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{1-1}(\vartheta_2,\varphi_2)$$
$$-\xi_i\sqrt{\frac{\pi}{12}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)$$
$$-\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{20}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)\Big)$$
$$=\left(L^{(2)}\right)^2\Bigg[-\frac{\pi}{3}\varsigma\Bigg(\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m+1)(l_1-m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m-1}$$
$$-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m-1)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m-1}\Bigg)$$
$$\times\Bigg(\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-m+1)(l_2-m+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+11-m}$$
$$-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2+m-1)(l_2+m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-11-m}\Bigg)$$

$$
\begin{aligned}
&- \frac{2\pi}{3}\varsigma \left(\sqrt{\frac{3}{4\pi}} \sqrt{\frac{(l_1+m+1)\,(l_1-m+1)}{(2l_1+1)\,(2l_1+3)}} Y_{l_1+1m} \right.\\
&\left. + \sqrt{\frac{3}{4\pi}} \sqrt{\frac{(l_1-m)\,(l_1+m)}{(2l_1-1)\,(2l_1+1)}} Y_{l_1-1m} \right)\\
&\times \left(\sqrt{\frac{3}{4\pi}} \sqrt{\frac{(l_2-m+1)\,(l_2+m+1)}{(2l_2+1)\,(2l_2+3)}} Y_{l_2+1-m} \right.\\
&\left. + \sqrt{\frac{3}{4\pi}} \sqrt{\frac{(l_2+m)\,(l_2-m)}{(2l_2-1)\,(2l_2+1)}} Y_{l_2-1-m} \right)\\
&- \frac{\pi}{3}\varsigma \left(\sqrt{\frac{3}{8\pi}} \sqrt{\frac{(l_1+m+1)\,(l_1+m+2)}{(2l_1+1)\,(2l_1+3)}} Y_{l_1+1m+1} \right.\\
&\left. - \sqrt{\frac{3}{8\pi}} \sqrt{\frac{(l_1-m-1)\,(l_1-m)}{(2l_1-1)\,(2l_1+1)}} Y_{l_1-1m+1} \right)\\
&\times \left(\sqrt{\frac{3}{8\pi}} \sqrt{\frac{(l_2+m+1)\,(l_2+m+2)}{(2l_2+1)\,(2l_2+3)}} Y_{l_2+1-m-1} \right.\\
&\left. - \sqrt{\frac{3}{8\pi}} \sqrt{\frac{(l_2-m-1)\,(l_2-m)}{(2l_2-1)\,(2l_2+1)}} Y_{l_2-1-m-1} \right)\\
&- \xi_i \sqrt{\frac{\pi}{12}} \left(\sqrt{\frac{3}{4\pi}} \sqrt{\frac{(l_2-m+1)\,(l_2+m+1)}{(2l_2+1)\,(2l_2+3)}} Y_{l_2+1-m} \right.\\
&\left. + \sqrt{\frac{3}{4\pi}} \sqrt{\frac{(l_2+m)\,(l_2-m)}{(2l_2-1)\,(2l_2+1)}} Y_{l_2-1-m} \right) (Y_{l_1m})\\
&- \sigma \frac{2}{3} \sqrt{\frac{\pi}{20}} \left(\sqrt{\frac{5}{4\pi}} \frac{l_2(l_2+1)-3m^2}{(2l_2-1)(2l_2+3)} Y_{l_2-m} \right.\\
&+ \sqrt{\frac{5}{4\pi}} \frac{3\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{2(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}} Y_{l_2-2-m}\\
&\left. + \sqrt{\frac{5}{4\pi}} \frac{3\sqrt{((l_2+1)^2-m^2)((l_2+2)^2-m^2)}}{2(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}} Y_{l_2+2-m} \right) (Y_{l_1m}) \Bigg]
\end{aligned}
$$

$$
\begin{aligned}
=&\left(L^{(2)}\right)^2\Bigg(-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1l_2+1\,m-1}\\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2+m-1)(l_2+m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1\,l_2-1\,m-1}\\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2-m+1)(l_2-m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1\,l_2+1\,m-1}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1\,l_2-1\,m-1}\\
&-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1l_2+1\,m}\\
&-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1l_2-1\,m}\\
&-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1l_2+1\,m}\\
&-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1\,l_2-1\,m}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1l_2+1\,m+1}\\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-m-1)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1\,l_2-1\,m+1}\\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+m+1)(l_2+m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1l_2+1\,m+1}\\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-m-1)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1l_2-1\,m+1}\\
&-\frac{1}{4}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}M_{l_1\,l_2+1\,m}\\
&-\frac{1}{4}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}M_{l_1\,l_2-1\,m}
\end{aligned}
$$

$$- \sigma \frac{1}{6} \frac{l_2(l_2+1) - 3(-m)^2}{(2l_2-1)(2l_2+3)} M_{l_1\, l_2\, m}$$

$$- \sigma \frac{1}{4} \frac{\sqrt{(l_2^2 - (-m)^2)((l_2-1)^2 - (-m)^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}} M_{l_1\, l_2-2\, m}$$

$$- \sigma \frac{1}{4} \frac{\sqrt{((l_2+1)^2 - (-m)^2)((l_2+2)^2 - (-m)^2)}}{(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}} M_{l_1\, l_2+2\, m} \Bigg)$$

$$= - \frac{1}{8} \varsigma \sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \times$$

$$(l_2+1)((l_2+1)+1) M_{l_1+1 l_2+1\, m-1}$$

$$+ \frac{1}{8} \varsigma \sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2+m-1)(l_2+m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \times$$

$$(l_2-1)((l_2-1)+1) M_{l_1+1\, l_2-1\, m-1}$$

$$+ \frac{1}{8} \varsigma \sqrt{\frac{(l_1+m-1)(l_1+m)(l_2-m+1)(l_2-m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \times$$

$$(l_2+1)((l_2+1)+1) M_{l_1-1\, l_2+1\, m-1}$$

$$- \frac{1}{8} \varsigma \sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} \times$$

$$(l_2-1)((l_2-1)+1) M_{l_1-1\, l_2-1\, m-1}$$

$$- \frac{1}{2} \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \times$$

$$(l_2+1)((l_2+1)+1) M_{l_1+1 l_2+1\, m}$$

$$- \frac{1}{2} \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \times$$

$$(l_2-1)((l_2-1)+1) M_{l_1+1 l_2-1\, m}$$

$$- \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \times$$

$$(l_2+1)((l_2+1)+1) M_{l_1-1 l_2+1\, m}$$

$$
\begin{aligned}
&- \frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)\,(l_1+m)\,(l_2+m)\,(l_2-m)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}}\times\\
&(l_2-1)\,((l_2-1)+1)\,M_{l_1-1\,l_2-1\,m}\\
&- \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)\,(l_1+m+2)\,(l_2+m+1)\,(l_2+m+2)}{(2l_1+1)\,(2l_1+3)\,(2l_2+1)\,(2l_2+3)}}\times\\
&(l_2+1)\,((l_2+1)+1)\,M_{l_1+1 l_2+1\,m+1}\\
&+ \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)\,(l_1+m+2)\,(l_2-m-1)\,(l_2-m)}{(2l_1+1)\,(2l_1+3)\,(2l_2-1)\,(2l_2+1)}}\times\\
&(l_2-1)\,((l_2-1)+1)\,M_{l_1+1\,l_2-1\,m+1}\\
&+ \frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)\,(l_1-m)\,(l_2+m+1)\,(l_2+m+2)}{(2l_1-1)\,(2l_1+1)\,(2l_2+1)\,(2l_2+3)}}\times\\
&(l_2+1)\,((l_2+1)+1)\,M_{l_1-1 l_2+1\,m+1}\\
&- \frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)\,(l_1-m)\,(l_2-m-1)\,(l_2-m)}{(2l_1-1)\,(2l_1+1)\,(2l_2-1)\,(2l_2+1)}}\times\\
&(l_2-1)\,((l_2-1)+1)\,M_{l_1-1 l_2-1\,m+1}\\
&- \frac{1}{4}\xi_i\sqrt{\frac{(l_2-m+1)\,(l_2+m+1)}{(2l_2+1)\,(2l_2+3)}}\times\\
&(l_2+1)\,((l_2+1)+1)\,M_{l_1\,l_2+1\,m}\\
&- \frac{1}{4}\xi_i\sqrt{\frac{(l_2+m)\,(l_2-m)}{(2l_2-1)\,(2l_2+1)}}\times\\
&(l_2-1)\,((l_2-1)+1)\,M_{l_1\,l_2-1\,m}\\
&- \sigma\frac{1}{6}\frac{l_2(l_2+1)-3(-m)^2}{(2l_2-1)(2l_2+3)}l_2\,(l_2+1)\,M_{l_1\,l_2\,m}\\
&- \frac{1}{4}\sigma\frac{\sqrt{(l_2^2-(-m)^2)((l_2-1)^2-(-m)^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\times\\
&(l_2-2)\,((l_2-2)+1)\,M_{l_1\,l_2-2\,m}\\
&- \frac{1}{4}\sigma\frac{\sqrt{((l_2+1)^2-(-m)^2)((l_2+2)^2-(-m)^2)}}{(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}}\times\\
&(l_2+2)\,((l_2+2)+1)\,M_{l_1\,l_2+2\,m}.
\end{aligned}
\tag{7.107}
$$

$$
\begin{aligned}
&\frac{1}{4}\left(\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&+\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)\\
&\left.+\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\right)\left(L^{(2)}\right)^2 Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\left(\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&+\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\xi_i\sqrt{\frac{\pi}{12}}Y_{10}(\vartheta_2,\varphi_2)\\
&\left.+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{20}(\vartheta_2,\varphi_2)\right)\left(L^{(2)}\right)^2 Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\left(\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)+\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&+\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)+\xi_i\sqrt{\frac{\pi}{12}}Y_{10}(\vartheta_2,\varphi_2)\\
&\left.+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{20}(\vartheta_2,\varphi_2)\right)l_2\left(l_2+1\right)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&l_2\left(l_2+1\right)\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{11}(\vartheta_2,\varphi_2)\\
&+l_2\left(l_2+1\right)\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{10}(\vartheta_2,\varphi_2)\\
&+l_2\left(l_2+1\right)\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{1-1}(\vartheta_2,\varphi_2)\\
&+l_2\left(l_2+1\right)\xi_i\sqrt{\frac{\pi}{12}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+l_2\left(l_2+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{20}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\left[l_2\left(l_2+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m-1}\right.\\
&\left.-l_2\left(l_2+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m-1}\right]\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+11-m}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-11-m}\right]
\end{aligned}
$$

$$+\left[l_2\left(l_2+1\right)\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1-m+1\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m}\right.$$

$$\left.+\,l_2\left(l_2+1\right)\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_1-m\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m}\right]\times$$

$$\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2+m+1\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+1-m}\right.$$

$$\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_2+m\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-1-m}\right]$$

$$+\left[l_2\left(l_2+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m+1}\right.$$

$$\left.-\,l_2\left(l_2+1\right)\frac{\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m+1}\right]\times$$

$$\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+1-m-1}\right.$$

$$\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-1-m-1}\right]$$

$$+\left[l_2\left(l_2+1\right)\xi_i\sqrt{\frac{\pi}{12}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2+m+1\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+1-m}Y_{l_1m}\right.$$

$$\left.+\,l_2\left(l_2+1\right)\xi_i\sqrt{\frac{\pi}{12}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{\left(l_2+m\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-1-m}Y_{l_1m}\right]$$

$$+\left[l_2\left(l_2+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\sqrt{\frac{5}{4\pi}}\frac{l_2(l_2+1)-3m^2}{(2l_2-1)(2l_2+3)}Y_{l_2-m}Y_{l_1m}\right.$$

$$+\,l_2\left(l_2+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{2(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}Y_{l_2-2-m}Y_{l_1m}$$

$$\left.+\,l_2\left(l_2+1\right)\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\sqrt{\frac{5}{4\pi}}\frac{3\sqrt{((l_2+1)^2-m^2)((l_2+2)^2-m^2)}}{2(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}}Y_{l_2+2-m}Y_{l_1m}\right]$$

$$=\frac{1}{8}\varsigma\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)\left(2l_2+1\right)\left(2l_2+3\right)}}l_2\left(l_2+1\right)M_{l_1+1l_2+1\,m-1}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_1+1\right)\left(2l_1+3\right)\left(2l_2-1\right)\left(2l_2+1\right)}}l_2\left(l_2+1\right)M_{l_1+1l_2-1\,m-1}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_1-1\right)\left(2l_1+1\right)\left(2l_2+1\right)\left(2l_2+3\right)}}l_2\left(l_2+1\right)M_{l_1-1l_2+1\,m-1}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_2(l_2+1)M_{l_1-1l_2-1m-1}$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}l_2(l_2+1)M_{l_1+1l_2+1m}$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_2(l_2+1)M_{l_1+1l_2-1m}$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}l_2(l_2+1)M_{l_1-1l_2+1m}$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_2(l_2+1)M_{l_1-1l_2-1m}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}l_2(l_2+1)M_{l_1+1l_2+1m+1}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-m-1)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_2(l_2+1)M_{l_1+1l_2-1m+1}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+m+1)(l_2+m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}l_2(l_2+1)M_{l_1-1l_2+1m+1}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-m-1)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_2(l_2+1)M_{l_1-1l_2-1m+1}$$

$$+\frac{1}{4}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}l_2(l_2+1)M_{l_1\,l_2+1\,m}$$

$$+\frac{1}{4}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}l_2(l_2+1)M_{l_1\,l_2-1\,m}$$

$$+\sigma\frac{1}{6}\frac{l_2(l_2+1)-3(-m)^2}{(2l_2-1)(2l_2+3)}l_2(l_2+1)M_{l_1\,l_2\,m}$$

$$+\sigma\frac{1}{4}\frac{\sqrt{(l_2^2-(-m)^2)((l_2-1)^2-(-m)^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}l_2(l_2+1)M_{l_1\,l_2-2\,m}$$

$$+\sigma\frac{1}{4}\frac{\sqrt{((l_2+1)^2-(-m)^2)((l_2+2)^2-(-m)^2)}}{(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}}l_2(l_2+1)M_{l_1\,l_2+2\,m}. \qquad (7.108)$$

6

$$
\begin{aligned}
&\frac{1}{4}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(L^{(2)}\right)^2\left(\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&\quad+\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\quad\left.+\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)+\sigma\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\right)\\
=&Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(\frac{\pi}{3}\varsigma\left(L^{(2)}\right)^2Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&\quad+\frac{2\pi}{3}\varsigma\left(L^{(2)}\right)^2Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\\
&\quad+\frac{\pi}{3}\varsigma\left(L^{(2)}\right)^2Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\quad\left.+\xi_i\sqrt{\frac{\pi}{12}}\left(L^{(2)}\right)^2Y_{10}(\vartheta_2,\varphi_2)+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\left(L^{(2)}\right)^2Y_{20}(\vartheta_2,\varphi_2)\right)\\
=&Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(\frac{\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\left(1\left(1+1\right)\right)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&\quad+\frac{2\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\left(1\left(1+1\right)\right)Y_{10}(\vartheta_2,\varphi_2)\\
&\quad+\frac{\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)\left(1\left(1+1\right)\right)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\quad\left.+\xi_i\sqrt{\frac{\pi}{12}}\left(1\left(1+1\right)\right)Y_{10}(\vartheta_2,\varphi_2)+\sigma\frac{2}{3}\sqrt{\frac{\pi}{20}}\left(2\left(2+1\right)\right)Y_{20}(\vartheta_2,\varphi_2)\right)\\
=&Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\left(\frac{2\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\\
&\quad+\frac{4\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)+\frac{2\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\quad\left.+\xi_i\sqrt{\frac{\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)+\sigma\frac{2}{3}\sqrt{\frac{9\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\right)\\
=&\frac{2\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{11}(\vartheta_2,\varphi_2)\\
&\quad+\frac{4\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{10}(\vartheta_2,\varphi_2)\\
&\quad+\frac{2\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\quad+\xi_i\sqrt{\frac{\pi}{3}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&\quad+\sigma\frac{2}{3}\sqrt{\frac{9\pi}{5}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{20}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)
\end{aligned}
$$

$$
\begin{aligned}
&= \left[\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m+1)(l_1-m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m-1}\right.\\
&\left.-\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m-1)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m-1}\right]\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-m+1)(l_2-m+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+11-m}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2+m-1)(l_2+m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-11-m}\right]\\
&+\left[\frac{4\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m}\right.\\
&\left.+\frac{4\pi}{3}\varsigma\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}\right]\times\\
&\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1-m}\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-1-m}\right]\\
&+\left[\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1+m+1)(l_1+m+2)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m+1}\right.\\
&\left.-\frac{2\pi}{3}\varsigma\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_1-m-1)(l_1-m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m+1}\right]\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2+m+1)(l_2+m+2)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1-m-1}\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l_2-m-1)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-1-m-1}\right]\\
&+\left[\xi_i\sqrt{\frac{\pi}{3}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1-m}\right.\\
&\left.+\xi_i\sqrt{\frac{\pi}{3}}\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-1-m}\right]Y_{l_1m}
\end{aligned}
$$

$$
\begin{aligned}
&+\left[\sigma\frac{2}{3}\frac{3}{2}\frac{l_2(l_2+1)-3m^2}{(2l_2-1)(2l_2+3)}Y_{l_2-m}\right.\\
&+\sigma\frac{3}{2}\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}Y_{l_2-2-m}\\
&\left.+\sigma\frac{3}{2}\frac{\sqrt{((l_2+1)^2-m^2)((l_2+2)^2-m^2)}}{(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}}Y_{l_2+2-m}\right]Y_{l_1m}
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1l_2+1m-1}\\
&-\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2+m-1)(l_2+m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1l_2-1m-1}\\
&-\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2-m+1)(l_2-m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1l_2+1m-1}\\
&+\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m-1)(l_1+m)(l_2+m-1)(l_2+m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1l_2-1m-1}\\
&+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1l_2+1m}\\
&+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1l_2-1m}\\
&+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1l_2+1m}\\
&+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1l_2-1m}\\
&+\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}M_{l_1+1l_2+1m+1}\\
&-\frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2-m-1)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}M_{l_1+1l_2-1m+1}\\
&-\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2+m+1)(l_2+m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}M_{l_1-1l_2+1m+1}\\
&+\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m-1)(l_1-m)(l_2-m-1)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}M_{l_1-1l_2-1m+1}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{2}\xi_i\sqrt{\frac{(l_2-m+1)\,(l_2+m+1)}{(2l_2+1)\,(2l_2+3)}}M_{l_1\,l_2+1\,m}\\
&+\frac{1}{2}\xi_i\sqrt{\frac{(l_2+m)\,(l_2-m)}{(2l_2-1)\,(2l_2+1)}}M_{l_1\,l_2-1\,m}\\
&+\sigma\frac{l_2(l_2+1)-3(-m)^2}{(2l_2-1)(2l_2+3)}M_{l_1\,l_2\,m}\\
&+\sigma\frac{3\sqrt{(l_2^2-(-m)^2)((l_2-1)^2-(-m)^2)}}{2(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}M_{l_1\,l_2-2\,m}\\
&+\sigma\frac{3\sqrt{((l_2+1)^2-(-m)^2)((l_2+2)^2-(-m)^2)}}{2(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}}M_{l_1\,l_2+2\,m}.
\end{aligned}\tag{7.109}
$$

7

$$
\begin{aligned}
&-\frac{1}{2}\left[\left(L^{(1)}\right)^2Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)+\left(L^{(2)}\right)^2Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right]\\
=&-\frac{1}{2}\left(L^{(1)}\right)^2Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)-\frac{1}{2}Y_{l_1m}(\vartheta_1,\varphi_1)\left(L^{(2)}\right)^2Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&-\frac{1}{2}l_1\,(l_1+1)\,Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)-\frac{1}{2}l_2\,(l_2+1)\,Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2).
\end{aligned}\tag{7.110}
$$

8

In this section as well as the following sections, we shall use the following property of the product of two spherical harmonics [2]

$$
(Y_{1\pm1})^{-1}Y_{l\pm m}=\sqrt{\frac{8\pi\,(2l+1)\,(l-m)!}{3\,(l+m)!}}\sum_{L=m-\varepsilon_{lm}}^{l-1}\sqrt{\frac{(2L+1)\,(L+m-1)!}{(L-m+1)!}}Y_{L\pm(m-1)},\tag{7.111}
$$

where $\Delta L=2$. We will also make use of the spherical harmonic

$$
Y_{00}(\vartheta_p,\varphi_p)=\sqrt{\frac{1}{4\pi}}\Rightarrow\sqrt{4\pi}Y_{00}(\vartheta_p,\varphi_p)=1,\ p=1,2.\tag{7.112}
$$

Furthermore, the actions of the angular momentum operators $L_\pm$ and L_Z on a spherical harmonic Y_{lm} are given by

$$
L_\pm Y_{lm}=\sqrt{l\,(l+1)-m\,(m\pm1)}Y_{lm\pm1},\tag{7.113}
$$

$$
L_ZY_{lm}=m.\tag{7.114}
$$

Thus we get

$$
\begin{aligned}
&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(L_Z^{(1)}\left(\mathrm{A}_{1,1,0}^{(1)}\left(\varsigma\right)Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\right.\\
&+\mathrm{A}_{1,1,1}^{(1)}\left(\varsigma\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.\left.+\mathrm{A}_{1,0,0}^{(1)}Y_{10}(\vartheta_1,\varphi_1)+\ \mathrm{A}_{2,0,0}^{(1)}Y_{20}(\vartheta_1,\varphi_1)\right)\right)\left(L_+^{(1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1,1}^{(1)}\right)^{-1}\left(-\frac{8\pi}{3}\varsigma L_Z^{(1)}Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\frac{4\pi}{3}\varsigma L_Z^{(1)}Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&-\xi_i\sqrt{\frac{4\pi}{3}}L_Z^{(1)}Y_{10}(\vartheta_1,\varphi_1)\\
&\left.-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}L_Z^{(1)}Y_{20}(\vartheta_1,\varphi_1)\right)\left(L_+^{(1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1,1}^{(1)}\right)^{-1}\left(-\frac{8\pi}{3}\varsigma\left(0\right)Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\frac{4\pi}{3}\varsigma\left(1\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&-\xi_i\sqrt{\frac{4\pi}{3}}\left(0\right)Y_{10}(\vartheta_1,\varphi_1)\\
&\left.-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\left(0\right)Y_{20}(\vartheta_1,\varphi_1)\right)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}\left(Y_{1,1}^{(1)}\right)^{-1}\times\\
&\left[\left(-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right)\left(Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right.\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(\left(-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(\left(-\frac{4\pi}{3}\varsigma\left[\sqrt{\frac{8\pi(2\left(1\right)+1)(1-1)!}{3(1+1)!}}Y_{0(1-1)}(\vartheta_1,\varphi_1)\right]Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(\left(-\frac{4\pi}{3}\varsigma\left[\sqrt{\frac{8\pi(3)(1)}{3(2)}}Y_{00}(\vartheta_1,\varphi_1)\right]Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(\left(-\frac{4\pi}{3}\varsigma\sqrt{4\pi}Y_{00}Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)\times\\
&(Y_{1-1}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&-\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}Y_{l_1m+1}(\vartheta_1,\varphi_1)\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+1-m-1}(\vartheta_2,\varphi_2)\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-1-m-1}(\vartheta_2,\varphi_2)\right]\\
=&-\frac{i}{4\alpha}\varsigma\sqrt{\frac{l_1\left(l_1+1\right)-m\left(m+1\right)\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}\times\\
&Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2+1-m-1}(\vartheta_2,\varphi_2)\\
&+\frac{i}{4\alpha}\varsigma\sqrt{\frac{l_1\left(l_1+1\right)-m\left(m+1\right)\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\times\\
&Y_{l_1m+1}(\vartheta_1,\varphi_1)Y_{l_2-1-m-1}(\vartheta_2,\varphi_2)\\
=&-\frac{i}{4\alpha}\varsigma\sqrt{\frac{l_1\left(l_1+1\right)-m\left(m+1\right)\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}M_{l_1\,l_2+1\,m+1}\\
&+\frac{i}{4\alpha}\varsigma\sqrt{\frac{l_1\left(l_1+1\right)-m\left(m+1\right)\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}M_{l_1\,l_2-1\,m+1}.
\end{aligned}
\tag{7.115}
$$

9

$$
\begin{aligned}
&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(L_{+}^{(1)}\left(\mathrm{A}_{1,1,0}^{(1)}(\varsigma)\,Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\right.\\
&+\mathrm{A}_{1,1,1}^{(1)}(\varsigma)\,Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.\left.+\mathrm{A}_{1,0,0}^{(1)}Y_{10}(\vartheta_1,\varphi_1)+\ \mathrm{A}_{2,0,0}^{(1)}Y_{20}(\vartheta_1,\varphi_1)\right)\right)\left(L_{Z}^{(1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(L_{+}^{(1)}\left(-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\right.\\
&-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.\left.-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)-\ \sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_1,\varphi_1)\right)\right)\left(L_{Z}^{(1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(-\frac{8\pi}{3}\varsigma\sqrt{1\,(1+1)-0\,(0+1)}Y_{1(0+1)}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\frac{4\pi}{3}\varsigma\sqrt{1\,(1+1)-1\,(1+1)}Y_{1(1+1)}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&-\xi_i\sqrt{\frac{4\pi}{3}}\sqrt{1\,(1+1)-0\,(0+1)}Y_{1(0+1)}(\vartheta_1,\varphi_1)\\
&\left.-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\sqrt{2\,(2+1)-0\,(0+1)}Y_{2(0+1)}(\vartheta_1,\varphi_1)\right)(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(-\frac{8\pi}{3}\varsigma\sqrt{2}Y_{11}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\frac{4\pi}{3}\varsigma\sqrt{0}Y_{12}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\\
&\left.-\xi_i\sqrt{\frac{4\pi}{3}}\sqrt{2}Y_{11}(\vartheta_1,\varphi_1)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\sqrt{6}Y_{21}(\vartheta_1,\varphi_1)\right)(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(1)}\right)^{-1}\left(-\frac{8\sqrt{2}\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\right.\\
&\left.-\xi_i\sqrt{\frac{8\pi}{3}}Y_{11}(\vartheta_1,\varphi_1)-\sigma\sqrt{\frac{32\pi}{15}}Y_{21}(\vartheta_1,\varphi_1)\right)(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left\{-\frac{8\sqrt{2}\pi}{3}\varsigma\left[\sqrt{\frac{8\pi\,(2\,(1)+1)\,(1-1)!}{3\,(1+1)!}}Y_{0(1-1)}(\vartheta_1,\varphi_1)\right]Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\xi_i\sqrt{\frac{8\pi}{3}}\left[\sqrt{\frac{8\pi\,(2\,(1)+1)\,(1-1)!}{3\,(1+1)!}}Y_{0(1-1)}(\vartheta_1,\varphi_1)\right]\\
&\left.-\sigma\sqrt{\frac{32\pi}{15}}\left[\sqrt{\frac{8\pi\,(2\,(2)+1)\,(2-1)!}{3\,(2+1)!}}\sqrt{\frac{(2\,(1)+1)\,(1+1-1)!}{(1-1+1)!}}Y_{1(1-1)}(\vartheta_1,\varphi_1)\right]\right\}\times\\
&(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))
\end{aligned}
$$

$$
\begin{aligned}
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left\{-\frac{8\sqrt{2}\pi}{3}\varsigma\left[\sqrt{\frac{8\pi\,(3)\,(0)!}{3\,(2)!}}Y_{00}(\vartheta_1,\varphi_1)\right]Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\xi_i\sqrt{\frac{8\pi}{3}}\left[\sqrt{\frac{8\pi\,(3)\,(0)!}{3\,(2)!}}Y_{00}(\vartheta_1,\varphi_1)\right]\\
&\left.-\sigma\sqrt{\frac{32\pi}{15}}\left[\sqrt{\frac{8\pi\,(5)\,(1)!}{3\,(3)!}}\sqrt{\frac{(3)\,(1)!}{(1)!}}Y_{10}(\vartheta_1,\varphi_1)\right]\right\}(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left\{-\frac{8\sqrt{2}\pi}{3}\varsigma\left[\sqrt{4\pi}Y_{00}(\vartheta_1,\varphi_1)\right]Y_{10}(\vartheta_2,\varphi_2)\right.\\
&-\xi_i\sqrt{\frac{8\pi}{3}}\left[\sqrt{4\pi}Y_{00}(\vartheta_1,\varphi_1)\right]\\
&\left.-\sigma\sqrt{\frac{32\pi}{15}}\left[\sqrt{\frac{20\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)\right]\right\}(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left\{-\frac{8\sqrt{2}\pi}{3}\varsigma\,Y_{10}(\vartheta_2,\varphi_2)-\xi_i\sqrt{\frac{8\pi}{3}}\right.\\
&\left.-\sigma\sqrt{\frac{32\pi}{15}}\left[\sqrt{\frac{20\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)\right]\right\}(mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\\
=&\frac{i}{4\alpha}m\varsigma\sqrt{\frac{64\pi}{3}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{2\alpha}m\xi_iY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{4\alpha}m\sigma\sqrt{\frac{64\pi}{3}}Y_{10}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\frac{i}{4\alpha}m\varsigma\sqrt{\frac{64\pi}{3}}\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2-m+1)\,(l_2+m+1)}{(2l_2+1)\,(2l_2+3)}}Y_{l_2+1-m}(\vartheta_2,\varphi_2)\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2+m)\,(l_2-m)}{(2l_2-1)\,(2l_2+1)}}Y_{l_2-1-m}(\vartheta_2,\varphi_2)\right]Y_{l_1m}(\vartheta_1,\varphi_1)\\
&+\frac{i}{2\alpha}m\xi_iY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{4\alpha}m\sigma\sqrt{\frac{64\pi}{3}}\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)\,(l_1-m+1)}{(2l_1+1)\,(2l_1+3)}}Y_{l_1+1m}(\vartheta_1,\varphi_1)\right.\\
&\left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)\,(l_1+m)}{(2l_1-1)\,(2l_1+1)}}Y_{l_1-1,m}(\vartheta_1,\varphi_1)\right]Y_{l_2-m}(\vartheta_2,\varphi_2)
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{i}{\alpha}m\varsigma\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2+1-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{\alpha}m\varsigma\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-1-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{2\alpha}m\xi_iY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{\alpha}m\sigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
&+\frac{i}{\alpha}m\sigma\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\frac{i}{\alpha}m\varsigma\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}M_{l_1\,l_2+1\,m}\\
&+\frac{i}{\alpha}m\varsigma\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}M_{l_1\,l_2-1\,m}\\
&+\frac{i}{2\alpha}m\xi_iM_{l_1\,l_2\,m}\\
&+\frac{i}{\alpha}m\sigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}M_{l_1+1\,l_2\,m}\\
&+\frac{i}{\alpha}m\sigma\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}M_{l_1-1\,l_2\,m}.
\end{aligned}
\tag{7.116}
$$

10

$$
\begin{aligned}
&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y^{(1)}_{1-1}\right)^{-1}\left[\left(L^{(1)}_Z\left(\mathrm{A}^{(1)}_{1,1,-1}(\varsigma)\,Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\right)\times\right.\\
&\left(L^{(1)}_-Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(L^{(1)}_-\left(\mathrm{A}^{(1)}_{1,1,-1}(\varsigma)\,Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left.\left(L^{(1)}_ZY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y^{(1)}_{1-1}\right)^{-1}\left[\left(L^{(1)}_Z\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\right)\times\right.\\
&\left(L^{(1)}_-Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(L^{(1)}_-\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\right)\\
&\left.\times\left(L^{(1)}_ZY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1-1}^{(1)}\right)^{-1}\left[\left(-\frac{4\pi}{3}\varsigma L_Z^{(1)} Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left(L_-^{(1)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(-\frac{4\pi}{3}\varsigma L_-^{(1)} Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\\
&\left.\left(L_Z^{(1)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1-1}^{(1)}\right)^{-1}\left[\left(-\frac{4\pi}{3}\varsigma\left(-1\right) Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(-\frac{4\pi}{3}\varsigma\sqrt{1\left(1+1\right)+1\left(-1-1\right)} Y_{1(-1-1)}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\\
&\left.\left(L_Z^{(1)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1-1}^{(1)}\right)^{-1}\left[\left(\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(-\frac{4\pi}{3}\varsigma\sqrt{0} Y_{1(-1-1)}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\\
&\left.\left(L_Z^{(1)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1-1}^{(1)}\right)^{-1}\left[\left(\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left.\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\left(Y_{1-1}^{(1)}\right)^{-1}\left[\left(\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left.\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)} Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\left[\sqrt{\frac{8\pi\left(2\left(1\right)+1\right)\left(1-1\right)!}{3\left(1+1\right)!}} Y_{0-(1-1)}(\vartheta_1,\varphi_1)\right] Y_{11}(\vartheta_2,\varphi_2)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)} Y_{l_1 m-1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\left[\sqrt{\frac{8\pi\left(3\right)\left(0\right)!}{3\left(2\right)!}} Y_{00}(\vartheta_1,\varphi_1)\right] Y_{11}(\vartheta_2,\varphi_2)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)} Y_{l_1 m-1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\left[\sqrt{4\pi}Y_{00}(\vartheta_1,\varphi_1)\right]Y_{11}(\vartheta_2,\varphi_2)\times\\
&\left(\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}Y_{l_1m-1}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}\times\\
&Y_{l_1m-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)Y_{l_2-m}(\vartheta_2,\varphi_2)\\
=&\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}Y_{l_1m-1}(\vartheta_1,\varphi_1)\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}Y_{l_2+11-m}(\vartheta_2,\varphi_2)\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}Y_{l_2-11-m}(\vartheta_2,\varphi_2)\right]\\
=&\frac{i}{4\alpha}\varsigma\sqrt{\frac{l_1\left(l_1+1\right)-m\left(m-1\right)\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}\times\\
&Y_{l_1m-1}(\vartheta_1,\varphi_1)Y_{l_2+11-m}(\vartheta_2,\varphi_2)\\
&-\frac{i}{4\alpha}\varsigma\sqrt{\frac{l_1\left(l_1+1\right)-m\left(m-1\right)\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\times\\
&Y_{l_1m-1}(\vartheta_1,\varphi_1)Y_{l_2-11-m}(\vartheta_2,\varphi_2)\\
=&\frac{i}{4\alpha}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}M_{l_1\,l_2+1\,m-1}\\
&-\frac{i}{4\alpha}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}\sqrt{\frac{\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}M_{l_1\,l_2-1\,m-1}.
\end{aligned}
\tag{7.117}
$$

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$$
\begin{aligned}
&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left(L_Z^{(2)}\left(\mathrm{A}_{1,1,-1}^{(2)}\left(\varsigma\right)Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\right.\\
&+\mathrm{A}_{1,1,0}^{(2)}\left(\varsigma\right)Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)\\
&\left.\left.+\mathrm{A}_{0,1,0}^{(2)}Y_{10}(\vartheta_2,\varphi_2)+\mathrm{A}_{0,2,0}^{(2)}Y_{20}(\vartheta_2,\varphi_2)\right)\right)\times\\
&\left(L_+^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)L_Z^{(2)}Y_{11}(\vartheta_2,\varphi_2)\right.\\
&-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)L_Z^{(2)}Y_{10}(\vartheta_2,\varphi_2)\\
&\left.-\xi_i\sqrt{\frac{4\pi}{3}}L_Z^{(2)}Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}L_Z^{(2)}Y_{20}(\vartheta_2,\varphi_2)\right)\times\\
&\left(L_+^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\,(1)\,Y_{11}(\vartheta_2,\varphi_2)\right.\\
&-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\,(0)\,Y_{10}(\vartheta_2,\varphi_2)\\
&\left.-\xi_i\sqrt{\frac{4\pi}{3}}\,(0)\,Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\,(0)\,Y_{20}(\vartheta_2,\varphi_2)\right)\times\\
&\left(\sqrt{l_2\,(l_2+1)+m\,(-m+1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m+1}(\vartheta_2,\varphi_2)\right)\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right)\times\\
&\left(\sqrt{l_2\,(l_2+1)+m\,(-m+1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m+1}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\left[\sqrt{\frac{8\pi\,(2\,(1)+1)\,(1-1)!}{3\,(1+1)!}}Y_{0-(1-1)}(\vartheta_2,\varphi_2)\right]\times\\
&\left(\sqrt{l_2\,(l_2+1)+m\,(-m+1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m+1}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\left[\sqrt{\frac{8\pi\,(3)\,(0)!}{3\,(2)!}}Y_{00}(\vartheta_2,\varphi_2)\right]\times\\
&\left(\sqrt{l_2\,(l_2+1)+m\,(-m+1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m+1}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\left[\sqrt{4\pi}Y_{00}(\vartheta_2,\varphi_2)\right]\times\\
&\left(\sqrt{l_2\,(l_2+1)+m\,(-m+1)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m+1}(\vartheta_2,\varphi_2)\right)\\
=&-\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_2\,(l_2+1)+m\,(-m+1)}\times\\
&Y_{1-1}(\vartheta_1,\varphi_1)Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m+1}(\vartheta_2,\varphi_2)
\end{aligned}
$$

$$
\begin{aligned}
&= -\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m+1\right)}\times \\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m-1}(\vartheta_1,\varphi_1)\right. \\
&\left. -\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m-1}(\vartheta_1,\varphi_1)\right]Y_{l_2-m+1}(\vartheta_2,\varphi_2) \\
&= -\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m+1\right)}\sqrt{\frac{\left(l_1-m+1\right)\left(l_1-m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}M_{l_1+1\,l_2\,m-1} \\
&+\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m+1\right)}\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}M_{l_1-1\,l_2\,m-1}. \qquad (7.118)
\end{aligned}
$$

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$$
\begin{aligned}
&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left[\left(L_+^{(2)}\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\right.\right. \\
&-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2) \\
&\left.\left.\left.-\xi_i\sqrt{\frac{4\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)-\ \sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\vartheta_2,\varphi_2)\right)\right)\left(L_Z^{(2)}M_{l_1l_2,m}\right)\right] \\
&= -\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left[\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)L_+^{(2)}Y_{11}(\vartheta_2,\varphi_2)\right.\right. \\
&-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)L_+^{(2)}Y_{10}(\vartheta_2,\varphi_2) \\
&\left.-\xi_i\sqrt{\frac{4\pi}{3}}L_+^{(2)}Y_{10}(\vartheta_2,\varphi_2)-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}L_+^{(2)}Y_{20}(\vartheta_2,\varphi_2)\right)\times \\
&\left.\left(L_Z^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right] \\
&= -\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\times \\
&\left[\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\sqrt{(1)\left(1+1\right)-(1)\left(1+1\right)}Y_{11+1}(\vartheta_2,\varphi_2)\right.\right. \\
&-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\sqrt{(1)\left(1+1\right)-(0)\left(0+1\right)}Y_{10+1}(\vartheta_2,\varphi_2) \\
&-\xi_i\sqrt{\frac{4\pi}{3}}\sqrt{(1)\left(1+1\right)-(0)\left(0+1\right)}Y_{10+1}(\vartheta_2,\varphi_2) \\
&\left.-\sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\sqrt{(2)\left(2+1\right)-(0)\left(0+1\right)}Y_{20+1}(\vartheta_2,\varphi_2)\right)\times \\
&\left.(-mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\right]
\end{aligned}
$$

$$
\begin{aligned}
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left[\left(-\frac{4\pi}{3}\varsigma Y_{1-1}(\vartheta_1,\varphi_1)\sqrt{0}Y_{12}(\vartheta_2,\varphi_2)\right.\right.\\
&-\frac{8\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\sqrt{2}Y_{11}(\vartheta_2,\varphi_2)\\
&-\xi_i\sqrt{\frac{4\pi}{3}}\sqrt{2}Y_{11}(\vartheta_2,\varphi_2)\\
&\left.\left.-\ \sigma\frac{4}{3}\sqrt{\frac{\pi}{5}}\sqrt{6}Y_{21}(\vartheta_2,\varphi_2)\right)(-mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\right]\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{11}^{(2)}\right)^{-1}\left[\left(-\frac{8\sqrt{2}\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)Y_{11}(\vartheta_2,\varphi_2)\right.\right.\\
&-\xi_i\sqrt{\frac{8\pi}{3}}Y_{11}(\vartheta_2,\varphi_2)\\
&\left.\left.-\ \sigma\sqrt{\frac{32\pi}{15}}Y_{21}(\vartheta_2,\varphi_2)\right)(-mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\right]\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left[\left(-\frac{8\sqrt{2}\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\left[\sqrt{\frac{8\pi\,(2\,(1)+1)\,(1-1)!}{3\,(1+1)!}}Y_{0(1-1)}(\vartheta_2,\varphi_2)\right]\right.\right.\\
&-\xi_i\sqrt{\frac{8\pi}{3}}\left[\sqrt{\frac{8\pi\,(2\,(1)+1)\,(1-1)!}{3\,(1+1)!}}Y_{0(1-1)}(\vartheta_2,\varphi_2)\right]\\
&\left.-\sigma\sqrt{\frac{32\pi}{15}}\left[\sqrt{\frac{8\pi\,(2\,(2)+1)\,(2-1)!}{3\,(2+1)!}}\sqrt{\frac{(2\,(1)+1)\,(1+1-1)!}{(1-1+1)!}}Y_{1(1-1)}(\vartheta_2,\varphi_2)\right]\right)\times\\
&(-mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))]\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left[\left(-\frac{8\sqrt{2}\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\left[\sqrt{4\pi}Y_{00}(\vartheta_2,\varphi_2)\right]\right.\right.\\
&-\xi_i\sqrt{\frac{8\pi}{3}}\left[\sqrt{4\pi}Y_{00}(\vartheta_2,\varphi_2)\right]\\
&\left.\left.-\ \sigma\sqrt{\frac{32\pi}{15}}\left[\sqrt{\frac{20\pi}{3}}Y_{10}(\vartheta_2,\varphi_2)\right]\right)(-mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))\right]\\
=&-\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left[\left(-\frac{8\sqrt{2}\pi}{3}\varsigma Y_{10}(\vartheta_1,\varphi_1)\ -\xi_i\sqrt{\frac{8\pi}{3}}-\sigma\frac{8\sqrt{2}\pi}{3}Y_{10}(\vartheta_2,\varphi_2)\right)\times\right.\\
&(-mY_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2))]
\end{aligned}
$$

$$
\begin{aligned}
= & -\frac{i}{4\alpha}\sqrt{\frac{64\pi}{3}}\varsigma m Y_{10}(\vartheta_1,\varphi_1)Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2 -m}(\vartheta_2,\varphi_2) \\
& -\frac{i}{2\alpha}\xi_i m Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2 -m}(\vartheta_2,\varphi_2) \\
& -\frac{i}{4\alpha}\sqrt{\frac{64\pi}{3}}\sigma m Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{10}(\vartheta_2,\varphi_2)Y_{l_2 -m}(\vartheta_2,\varphi_2) \\
= & -\frac{i}{4\alpha}\sqrt{\frac{64\pi}{3}}\varsigma m\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}Y_{l_1+1 m}(\vartheta_1,\varphi_1)\right. \\
& \left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}Y_{l_1-1 m}(\vartheta_1,\varphi_1)\right]Y_{l_2 -m}(\vartheta_2,\varphi_2) \\
& -\frac{i}{2\alpha}\xi_i m Y_{l_1 m}(\vartheta_1,\varphi_1)Y_{l_2 -m}(\vartheta_2,\varphi_2) \\
& -\frac{i}{4\alpha}\sqrt{\frac{64\pi}{3}}\sigma m\left[\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}Y_{l_2+1-m}(\vartheta_2,\varphi_2)\right. \\
& \left.+\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}Y_{l_2-1-m}(\vartheta_2,\varphi_2)\right]Y_{l_1 m}(\vartheta_1,\varphi_1) \\
= & -\frac{i}{\alpha}\varsigma m\sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}}M_{l_1+1\, l_2\, m} \\
& -\frac{i}{\alpha}\varsigma m\sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}M_{l_1-1\, l_2\, m} \\
& -\frac{i}{2\alpha}\xi_i m Y_{l_1\, m}(\vartheta_1,\varphi_1)Y_{l_2\, -m}(\vartheta_2,\varphi_2) \\
& -\frac{i}{\alpha}\sigma m\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}M_{l_1\, l_2+1\, m} \\
& -\frac{i}{\alpha}\sigma m\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}M_{l_1\, l_2-1\, m}.
\end{aligned}
\tag{7.119}
$$

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$$
\begin{aligned}
&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1,-1}^{(2)}\right)^{-1}\left[\left(L_Z^{(2)}\left(\mathrm{A}_{1,1,1}^{(2)}\left(\varsigma\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\times\right.\\
&\left(L_-^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(L_-^{(2)}\left(\mathrm{A}_{1,1,1}^{(2)}\left(\varsigma\right)Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right)\right)\\
&\left.\times\left(L_Z^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1,-1}^{(2)}\right)^{-1}\left[\left(-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)L_Z^{(2)}Y_{1-1}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left(L_-^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\\
&-\left(-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)L_-^{(2)}Y_{1-1}(\vartheta_2,\varphi_2)\right)\times\\
&\left.\left(L_Z^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1-1}^{(2)}\right)^{-1}\left[\left(-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)\left(-1\right)Y_{1-1}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left(\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\right)\\
&-\left(-\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)\sqrt{1\left(1+1\right)+1\left(-1-1\right)}Y_{1-1-1}(\vartheta_2,\varphi_2)\right)\times\\
&\left.\left(L_Z^{(2)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1,-1}^{(2)}\right)^{-1}\left[\left(\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left.\left(\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left(Y_{1-1}^{(2)}\right)^{-1}\left[\left(\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)Y_{1-1}(\vartheta_2,\varphi_2)\right)\times\right.\\
&\left.\left(\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left[\left(\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)\left[\sqrt{\frac{8\pi\left(2\left(1\right)+1\right)\left(1-1\right)!}{3\left(1+1\right)!}}Y_{0-(1-1)}(\vartheta_2,\varphi_2)\right]\right)\times\right.\\
&\left.\left(\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\right)\right]\\
=&\frac{i}{4\alpha}\sqrt{\frac{3}{2\pi}}\left[\left(\frac{4\pi}{3}\varsigma Y_{11}(\vartheta_1,\varphi_1)\left[\sqrt{4\pi}Y_{00}(\vartheta_2,\varphi_2)\right]\right)\times\right.\\
&\left.\left(\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}Y_{l_1m}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{i}{4\alpha}\sqrt{\frac{8\pi}{3}}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\times\\
&\left[\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}Y_{l_1+1m+1}(\vartheta_1,\varphi_1)\right.\\
&\left.-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}Y_{l_1-1m+1}(\vartheta_1,\varphi_1)\right]Y_{l_2-m-1}(\vartheta_2,\varphi_2)\\
=&\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}\times\\
&Y_{l_1+1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\\
&-\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\times\\
&Y_{l_1-1m+1}(\vartheta_1,\varphi_1)Y_{l_2-m-1}(\vartheta_2,\varphi_2)\\
=&\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}M_{l_1+1\,l_2\,m+1}\\
&-\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}M_{l_1-1\,l_2\,m+1}. \qquad (7.120)
\end{aligned}
$$

On the next pages we shall evaluate for each function $M_{l_1+i\,l_2+j\,m+k}$ the associated coefficients $d^{l_1\,l_2\,m}_{l_1+i\,l_2+j\,m+k}$ which make up the total differential-recurrence relation.

$\underline{M_{l_1\,l_2\,m}}$

$$
\begin{aligned}
&d^{l_1l_2m}_{l_1l_2m}M_{l_1\,l_2\,m}=\\
&\left[-\sigma\frac{1}{6}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}l_1\left(l_1+1\right)+\sigma\frac{1}{6}\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}l_1\left(l_1+1\right)\right.\\
&+\sigma\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}-\sigma\frac{1}{6}\frac{l_2(l_2+1)-3(-m)^2}{(2l_2-1)(2l_2+3)}l_2\left(l_2+1\right)\\
&+\sigma\frac{1}{6}\frac{l_2(l_2+1)-3(-m)^2}{(2l_2-1)(2l_2+3)}l_2\left(l_2+1\right)+\sigma\frac{l_2(l_2+1)-3(-m)^2}{(2l_2-1)(2l_2+3)}\\
&\left.-\frac{1}{2}l_1\left(l_1+1\right)-\frac{1}{2}l_2\left(l_2+1\right)+\xi_i\frac{i}{2\alpha}m-\xi_i\frac{i}{2\alpha}m\right]M_{l_1\,l_2\,m},
\end{aligned}
$$

$$
d^{l_1l_2m}_{l_1l_2m}=\left[-\frac{1}{2}l_1\left(l_1+1\right)-\frac{1}{2}l_2\left(l_2+1\right)+\sigma\frac{l_1(l_1+1)-3m^2}{(2l_1-1)(2l_1+3)}+\sigma\frac{l_2(l_2+1)-3m^2}{(2l_2-1)(2l_2+3)}\right]. \qquad (7.121)
$$

$\underline{M_{l_1+2\,l_2\,m}}$

$$
\begin{aligned}
&d^{l_1 l_2 m}_{l_1+2 l_2 m} M_{l_1+2 l_2\, m} = \\
&\left[-\frac{1}{4}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\,(l_1+2)\,((l_1+2)+1)\right.\\
&+\frac{1}{4}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}} l_1\,(l_1+1)\\
&\left.+\,\sigma\frac{3\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{2(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\right] M_{l_1+2l_2\,m}\\
=&\left[-\frac{1}{4}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\,(l_1+2)\,(l_1+3)\right.\\
&+\frac{1}{4}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}} l_1\,(l_1+1)\\
&\left.+\,\sigma\frac{3\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{2(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\right] M_{l_1+2l_2\,m}\\
=&\left[-\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}} l_1\right.\\
&-\frac{3}{2}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\\
&\left.+\frac{3}{2}\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}}\right] M_{l_1+2l_2\,m}\\
=&\left[-\sigma\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{(2l_1+3)\sqrt{(2l_1+1)(2l_1+5)}} l_1\right] M_{l_1+2l_2\,m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1+2 l_2 m} = \left[-\sigma\frac{l_1}{2l_1+3}\frac{\sqrt{((l_1+1)^2-m^2)((l_1+2)^2-m^2)}}{\sqrt{(2l_1+1)(2l_1+5)}}\right]. \qquad (7.122)
$$

$\underline{M_{l_1\,l_2+2\,m}}$

$$
\begin{aligned}
& d^{l_1 l_2 m}_{l_1 l_2+2m} M_{l_1\,l_2+2\,m} = \\
& \left[-\sigma \frac{1}{4} \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} (l_2+2)\,((l_2+2)+1) \right. \\
& + \frac{1}{4} \sigma \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} l_2\,(l_2+1) \\
& \left. + \sigma \frac{3\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{2(2l_2+3)\sqrt{(2l_2+1)(2l_2+5)}} \right] M_{l_1\,l_2+2\,m} \\
= & \left[-\sigma \frac{1}{4} \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} (l_2+2)\,(l_2+3) \right. \\
& + \sigma \frac{1}{4} \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} l_2\,(l_2+1) \\
& \left. + \sigma \frac{3}{2} \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} \right] M_{l_1\,l_2+2\,m} \\
= & \left[-\sigma \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} l_2 \right. \\
& - \sigma \frac{3}{2} \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} \\
& \left. + 6 \frac{3}{2} \sigma \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} \right] M_{l_1\,l_2+2\,m} \\
= & \left[-\sigma \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} l_2 \right] M_{l_1\,l_2+2\,m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1 l_2+2m} = \left[-\sigma \frac{l_2}{2l_2+3} \frac{\sqrt{((l_2+1)^2 - m^2)((l_2+2)^2 - m^2)}}{\sqrt{(2l_2+1)(2l_2+5)}} \right]. \tag{7.123}
$$

$\underline{M_{l_1-2\,l_2\,m}}$

$$
\begin{aligned}
& d^{l_1 l_2 m}_{l_1-2 l_2 m} M_{l_1-2\,l_2\,m} = \\
& \left[-\frac{1}{4}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} (l_1-2)\left((l_1-2)+1\right) \right. \\
& + \frac{1}{4}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} l_1 (l_1+1) \\
& \left. + \sigma \frac{3\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{2(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} \right] M_{l_1-2\,l_2\,m} \\
= & \left[-\frac{1}{4}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} (l_1-2)(l_1-1) \right. \\
& + \frac{1}{4}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} l_1 (l_1+1) \\
& \left. + \frac{3}{2}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} \right] M_{l_1-2\,l_2\,m} \\
= & \left[\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} l_1 \right. \\
& - \frac{1}{2}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} \\
& \left. + \frac{3}{2}\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} \right] M_{l_1-2\,l_2\,m} \\
= & \left[\sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} l_1 + \sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{(2l_1-1)\sqrt{(2l_1+1)(2l_1-3)}} \right] M_{l_1-2\,l_2\,m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1-2 l_2 m} = \left[\frac{l_1+1}{(2l_1-1)} \sigma \frac{\sqrt{(l_1^2-m^2)((l_1-1)^2-m^2)}}{\sqrt{(2l_1+1)(2l_1-3)}} \right]. \tag{7.124}
$$

$\underline{M_{l_1\,l_2-2\,m}}$

$$
\begin{aligned}
&d^{l_1 l_2 m}_{l_1 l_2-2m} M_{l_1\,l_2-2\,m} = \\
&\left[-\sigma\frac{1}{4}\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\,(l_2-2)\,((l_2-2)+1)\right. \\
&+\frac{1}{4}\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}l_2\,(l_2+1) \\
&\left.+\,\sigma\frac{3\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{2(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\right]M_{l_1\,l_2-2\,m} \\
=&\left[-\sigma\frac{1}{4}\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\,(l_2-2)\,(l_2-1)\right. \\
&+\frac{1}{4}\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}l_2\,(l_2+1) \\
&\left.+\,\frac{3}{2}\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\right]M_{l_1\,l_2-2\,m} \\
=&\left[\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}l_2\right. \\
&-\frac{1}{2}\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}} \\
&\left.+\,\frac{3}{2}\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\right]M_{l_1\,l_2-2\,m} \\
=&\left[\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-(-m)^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}l_2+\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{(2l_2-1)\sqrt{(2l_2+1)(2l_2-3)}}\right]M_{l_1\,l_2-2\,m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1 l_2-2m} = \left[\frac{l_2+1}{2l_2-1}\sigma\frac{\sqrt{(l_2^2-m^2)((l_2-1)^2-m^2)}}{\sqrt{(2l_2+1)(2l_2-3)}}\right]. \tag{7.125}
$$

$\underline{M_{l_1+1 l_2\, m}}$

$$
\begin{aligned}
& d^{l_1 l_2 m}_{l_1+1 l_2 m} M_{l_1+1 l_2\, m} = \\
& \Bigg[-\frac{1}{4}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} (l_1+1)((l_1+1)+1) \\
& + \frac{1}{4}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} l_1 (l_1+1) \\
& + \frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} + \sigma m \frac{i}{\alpha} \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \\
& - \frac{i}{\alpha} m \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \Bigg] M_{l_1+1 l_2\, m} \\
= & - \Bigg[\frac{1}{4}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} (l_1+1)((l_1+1)+1) \\
& - \frac{1}{4}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} l_1 (l_1+1) \\
& - \frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \\
& - m\sigma \frac{i}{\alpha} \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \\
& + m\varsigma \frac{i}{\alpha} \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \Bigg] M_{l_1+1 l_2\, m} \\
= & - \Bigg[\frac{1}{4}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} (l_1+1)(l_1+2) \\
& - \frac{1}{4}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} l_1 (l_1+1) \\
& - \frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \\
& + \frac{i}{\alpha} m (-\sigma+\varsigma) \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \Bigg] M_{l_1+1 l_2\, m}
\end{aligned}
$$

$$
\begin{aligned}
&= - \left[\frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} l_1 \right. \\
&\quad + \frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \\
&\quad - \frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \\
&\quad \left. - \frac{i}{\alpha} m (\sigma - \varsigma) \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \right] M_{l_1+1 l_2\, m} \\
&= - \left[\frac{1}{2}\xi_i \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} l_1 \right. \\
&\quad \left. - m \frac{i(\sigma-\varsigma)}{\alpha} \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \right] M_{l_1+1 l_2\, m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1+1 l_2 m} = - \left[\left(\frac{\xi_i}{2} l_1 - m \frac{i(\sigma-\varsigma)}{\alpha} \right) \sqrt{\frac{(l_1+m+1)(l_1-m+1)}{(2l_1+1)(2l_1+3)}} \right]. \tag{7.126}
$$

$\underline{M_{l_1 l_2+1\, m}}$

$$
\begin{aligned}
&d^{l_1 l_2 m}_{l_1 l_2+1 m} M_{l_1 l_2+1\, m} = \\
&\left[-\frac{1}{4}\xi_i \sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} (l_2+1)((l_2+1)+1) \right. \\
&+ \frac{1}{4}\xi_i \sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} l_2 (l_2+1) \\
&+ \frac{1}{2}\xi_i \sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} + m\varsigma \frac{i}{\alpha} \sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} \\
&\left. - \frac{i}{\alpha} m\sigma \sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} \right] M_{l_1\, l_2+1\, m}
\end{aligned}
$$

$$
\begin{aligned}
&= -\left[\xi_i \frac{1}{4}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\,(l_2+1)\left((l_2+1)+1\right)\right. \\
&\quad - \frac{1}{4}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}l_2(l_2+1) \\
&\quad - \frac{1}{2}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} - m\varsigma\frac{i}{\alpha}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} \\
&\quad \left. + \frac{i}{\alpha}m\sigma\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\right] M_{l_1\,l_2+1\,m} \\
&= -\left[\xi_i \frac{1}{4}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\,(l_2+1)(l_2+2)\right. \\
&\quad - \frac{1}{4}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}l_2(l_2+1) \\
&\quad - \frac{1}{2}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} \\
&\quad \left. + m\frac{i(-\varsigma+\sigma)}{\alpha}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\right] M_{l_1\,l_2+1\,m}
\end{aligned}
$$

$$
\begin{aligned}
&= -\left[\xi_i \frac{1}{2}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}l_2\right. \\
&\quad + \frac{1}{2}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} \\
&\quad - \frac{1}{2}\xi_i\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}} \\
&\quad \left. + m\frac{i(\sigma-\varsigma)}{2\alpha}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\right] M_{l_1\,l_2+1\,m} \\
&= -\left[\xi_i \frac{1}{2}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}l_2\right. \\
&\quad \left. + m\frac{i(\sigma-\varsigma)}{\alpha}\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\right] M_{l_1\,l_2+1\,m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1 l_2+1 m} = -\left[\left(\xi_i\frac{1}{2}l_2 + m\frac{i(\sigma-\varsigma)}{\alpha}\right)\sqrt{\frac{(l_2-m+1)(l_2+m+1)}{(2l_2+1)(2l_2+3)}}\right]. \qquad (7.127)
$$

$\underline{M_{l_1-1 l_2\, m}}$

$$d^{l_1 l_2 m}_{l_1-1 l_2 m} M_{l_1-1 l_2\, m} =$$

$$\left[-\frac{1}{4}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} (l_1-1)((l_1-1)+1) \right.$$

$$+ \frac{1}{4}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} l_1 (l_1+1) + \frac{1}{2}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}}$$

$$\left. + \sigma m \frac{i}{\alpha} \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} - \frac{i}{\alpha} m \varsigma \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} \right] M_{l_1-1 l_2\, m}$$

$$= \left[-\frac{1}{4}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} (l_1-1)(l_1) + \frac{1}{4}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} l_1 (l_1+1) \right.$$

$$\left. + \frac{1}{2}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} + m \frac{i(\sigma-\varsigma)}{\alpha} \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} \right] M_{l_1-1 l_2\, m}$$

$$= \left[l_1 \frac{1}{2}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} + \frac{1}{2}\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} \right.$$

$$\left. + m \frac{i(\sigma-\varsigma)}{\alpha} \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} \right] M_{l_1-1 l_2\, m}$$

$$= \left[\frac{1}{2}(l_1+1)\xi_i \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} + m \frac{i(\sigma-\varsigma)}{\alpha} \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} \right] M_{l_1-1 l_2\, m},$$

$$d^{l_1 l_2 m}_{l_1-1 l_2 m} = \left[\left(\frac{\xi_i}{2}(l_1+1) + m \frac{i(\sigma-\varsigma)}{\alpha} \right) \sqrt{\frac{(l_1-m)(l_1+m)}{(2l_1-1)(2l_1+1)}} \right]. \tag{7.128}$$

$\underline{M_{l_1\,l_2-1\,m}}$

$$
\begin{aligned}
&d^{l_1 l_2 m}_{l_1 l_2-1 m} M_{l_1\,l_2-1\,m} = \\
&\left[-\frac{1}{4}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}(l_2-1)((l_2-1)+1)\right. \\
&+\frac{1}{4}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}l_2(l_2+1) \\
&+\frac{1}{2}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}+m\varsigma\frac{i}{\alpha}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}} \\
&\left.-\frac{i}{\alpha}m\sigma\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}\right]M_{l_1\,l_2-1\,m} \\
&=\left[-\xi_i\frac{1}{4}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}(l_2-1)(l_2)\right. \\
&+\frac{1}{4}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}l_2(l_2+1) \\
&\left.+\frac{1}{2}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}+m\frac{i(-\sigma+\varsigma)}{\alpha}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}\right]M_{l_1\,l_2-1\,m} \\
&=\left[\frac{1}{2}\xi_i l_2\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}+\frac{1}{2}\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}\right. \\
&\left.-m\frac{i(\sigma-\varsigma)}{\alpha}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}\right]M_{l_1\,l_2-1\,m}
\end{aligned}
$$

$$
=\left[\frac{1}{2}(l_2+1)\xi_i\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}-m\frac{i(\sigma-\varsigma)}{\alpha}\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}\right]M_{l_1\,l_2-1\,m},
$$

$$
d^{l_1 l_2 m}_{l_1 l_2-1 m}=\left[\left(\frac{\xi_i}{2}(l_2+1)-m\frac{i(\sigma-4)}{\alpha}\right)\sqrt{\frac{(l_2+m)(l_2-m)}{(2l_2-1)(2l_2+1)}}\right]. \tag{7.129}
$$

$\underline{M_{l_1+1 l_2+1\, m}}$

$$
\begin{aligned}
&d^{l_1 l_2 m}_{l_1+1 l_2+1\, m} M_{l_1+1 l_2+1\, m} = \\
&\Bigg[-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_1+1)((l_1+1)+1) \\
&+\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_1(l_1+1) \\
&+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_2+1)((l_2+1)+1) \\
&+\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_2(l_2+1) \\
&+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\Bigg] M_{l_1+1 l_2+1\, m} \\
&=\Bigg[-l_1\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+(-m)+1)(l_2-(-m)+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&-\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&-l_2\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&-\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&+\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\Bigg] M_{l_1+1 l_2+1\, m}
\end{aligned}
$$

$$= \left[-l_1 \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \right.$$

$$\left. - \, l_2 \varsigma \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \right] M_{l_1+1 l_2+1\, m},$$

$$d^{l_1 l_2 m}_{l_1+1 l_2+1\, m} = \left[-\varsigma \, (l_1+l_2) \sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-m+1)(l_2+m+1)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \right]. \tag{7.130}$$

$\underline{M_{l_1-1 l_2-1\, m}}$

$$d^{l_1 l_2 m}_{l_1-1 l_2-1\, m} M_{l_1-1 l_2-1\, m} =$$

$$\left[-\frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-(-m))(l_2+(-m))}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} \, (l_1-1)((l_1-1)+1) \right.$$

$$+ \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} l_1 (l_1+1)$$

$$+ \, \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$

$$- \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} \, (l_2-1)((l_2-1)+1)$$

$$+ \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} l_2 (l_2+1)$$

$$\left. + \, \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} \right] M_{l_1-1 l_2-1\, m}$$

$$= \left[-\frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-(-m))(l_2+(-m))}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} \, (l_1-1)(l_1) \right.$$

$$+ \frac{1}{2} \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}} l_1 (l_1+1)$$

$$+ \, \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$

$$- \frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}(l_2-1)(l_2)$$
$$+ \frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_2(l_2+1)$$
$$+ \varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1-1l_2-1\,m}$$
$$= \Bigg[l_1\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$
$$+ l_2\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$
$$+ 2\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1-1l_2-1\,m},$$

$$d^{l_1l_2m}_{l_1-1l_2-1\,m} = \left[\varsigma(l_1+l_2+2)\sqrt{\frac{(l_1-m)(l_1+m)(l_2+m)(l_2-m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\right]. \quad (7.131)$$

$\underline{M_{l_1+1l_2-1\,m}}$

$$d^{l_1l_2m}_{l_1+1l_2-1\,m}M_{l_1+1l_2-1\,m} =$$
$$\Bigg[-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-(-m))(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}(l_1+1)((l_1+1)+1)$$
$$+ \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_1(l_1+1)$$
$$+ \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$
$$- \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}(l_2-1)((l_2-1)+1)$$
$$+ \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_2(l_2+1)$$
$$+ \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1+1l_2-1\,m}$$

$$
\begin{aligned}
&= \Bigg[-\frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-(-m))(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\,(l_1+1)(l_1+2) \\
&\quad + \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\,l_1(l_1+1) \\
&\quad + \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad - \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\,(l_2-1)(l_2) \\
&\quad + \frac{1}{2}\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\,l_2(l_2+1) \\
&\quad + \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1+1 l_2-1\, m} \\
&= \Bigg[-l_1\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2-(-m))(l_2+(-m))}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad - \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad + \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad + l_2\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad + \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1+1 l_2-1\, m} \\
&= \Bigg[-l_1\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad + l_2\varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}} \\
&\quad + \varsigma\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1+1 l_2-1\, m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1+1 l_2-1\, m} = \left[\varsigma\,(l_2-l_1+1)\sqrt{\frac{(l_1+m+1)(l_1-m+1)(l_2+m)(l_2-m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\right]. \tag{7.132}
$$

$\underline{M_{l_1-1 l_2+1\, m}}$

$$d^{l_1 l_2 m}_{l_1-1 l_2+1\, m} M_{l_1-1 l_2+1 m} =$$

$$\Bigg[-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}(l_1-1)((l_1-1)+1)$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} l_1(l_1+1)$$

$$+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}$$

$$-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}(l_2+1)((l_2+1)+1)$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} l_2(l_2+1)$$

$$+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\Bigg] M_{l_1-1 l_2+1 m}$$

$$= \Bigg[-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}(l_1-1)(l_1)$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} l_1(l_1+1)$$

$$+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}$$

$$-\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}(l_2+1)(l_2+2)$$

$$+\frac{1}{2}\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} l_2(l_2+1)$$

$$+\varsigma\sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\Bigg] M_{l_1-1 l_2+1 m}$$

$$
\begin{aligned}
&= \left[l_1 \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \right. \\
&\quad + \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \\
&\quad - l_2 \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \\
&\quad - \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \\
&\quad \left. + \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \right] M_{l_1-1 l_2+1 m} \\
&= \left[l_1 \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \right. \\
&\quad - l_2 \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \\
&\quad \left. + \varsigma \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \right] M_{l_1-1 l_2+1 m},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1-1 l_2+1\, m} = \left[\varsigma \left(l_1 - l_2 + 1\right) \sqrt{\frac{(l_1-m)(l_1+m)(l_2-m+1)(l_2+m+1)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}} \right]. \tag{7.133}
$$

$\underline{M_{l_1+1 l_2+1\, m-1}}$

$$
\begin{aligned}
&d^{l_1 l_2 m}_{l_1+1 l_2+1\, m-1} M_{l_1+1 l_2+1\, m-1} = \\
&\left[-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_1+1)((l_1+1)+1)\right. \\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_1(l_1+1) \\
&+\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_2+1)((l_2+1)+1) \\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_2(l_2+1) \\
&\left.+\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\right] M_{l_1+1 l_2+1\, m-1} \\
&=\left[-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_1+1)(l_1+2)\right. \\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_1(l_1+1) \\
&+\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&-\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_2+1)(l_2+2) \\
&+\frac{1}{8}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_2(l_2+1) \\
&\left.+\frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\right] M_{l_1+1 l_2+1\, m-1}
\end{aligned}
$$

$$= \Bigg[-l_1 \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}$$

$$- \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}$$

$$+ \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}$$

$$- l_2 \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}$$

$$- \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}$$

$$+ \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}\Bigg] M_{l_1+1 l_2+1\, m-1}$$

$$= \Bigg[-l_1 \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}$$

$$- l_2 \frac{1}{4} \varsigma \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}\Bigg] M_{l_1+1 l_2+1\, m-1},$$

$$d^{l_1 l_2 m}_{l_1+1 l_2+1\, m-1} = \left[-\frac{1}{4} \varsigma (l_1 + l_2) \sqrt{\frac{(l_1 - m + 1)(l_1 - m + 2)(l_2 - m + 1)(l_2 - m + 2)}{(2l_1 + 1)(2l_1 + 3)(2l_2 + 1)(2l_2 + 3)}}\right].$$

$\underline{M_{l_1+1 l_2+1\, m+1}}$

$$
\begin{aligned}
& d^{l_1 l_2 m}_{l_1+1 l_2+1\, m+1} M_{l_1+1 l_2+1\, m+1} = \\
& \left[-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_1+1)((l_1+1)+1) \right. \\
& + \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_1(l_1+1) \\
& + \frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
& - \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_2+1)((l_2+1)+1) \\
& + \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_2(l_2+1) \\
& \left. + \frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \right] M_{l_1+1 l_2+1\, m+1} \\
= & \left[-\frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_1+1)(l_1+2) \right. \\
& + \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_1(l_1+1) \\
& + \frac{1}{4}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2-m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
& - \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,(l_2+1)(l_2+2) \\
& + \frac{1}{8}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}}\,l_2(l_2+1) \\
& \left. + \frac{1}{4}\varsigma\sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \right] M_{l_1+1 l_2+1\, m+1}
\end{aligned}
$$

$$
\begin{aligned}
&= \Bigg[-l_1 \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&\quad - \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&\quad + \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&\quad - l_2 \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&\quad - \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&\quad + \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \Bigg] M_{l_1+1 l_2+1\, m+1} \\
&= \Bigg[-l_1 \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \\
&\quad - l_2 \frac{1}{4} \varsigma \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \Bigg] M_{l_1+1 l_2+1\, m+1},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1+1 l_2+1\, m+1} = \left[-\frac{1}{4} \varsigma (l_1+l_2) \sqrt{\frac{(l_1+m+1)(l_1+m+2)(l_2+m+1)(l_2+m+2)}{(2l_1+1)(2l_1+3)(2l_2+1)(2l_2+3)}} \right].
$$

$\underline{M_{l_1+1 l_2-1\, m\pm1}}$

$$d^{l_1 l_2 m}_{l_1+1 l_2+1\, m\pm1} M_{l_1+1 l_2-1\, m\pm1} =$$

$$\left[\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}(l_1+1)((l_1+1)+1)\right.$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_1(l_1+1)$$

$$-\frac{1}{4}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}(l_2-1)((l_2-1)+1)$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_2(l_2+1)$$

$$\left.-\frac{1}{4}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\right]M_{l_1+1 l_2-1\, m\pm1}$$

$$=\left[\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}(l_1+1)(l_1+2)\right.$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_1(l_1+1)$$

$$-\frac{1}{4}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}(l_2-1)(l_2)$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}l_2(l_2+1)$$

$$\left.-\frac{1}{4}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\right]M_{l_1+1 l_2-1\, m\pm1}$$

$$=\left[l_1\frac{1}{4}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\right.$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1\pm m+1)(l_1\pm m+2)(l_2\mp m-1)(l_2\mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$- l_2\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1+1 l_2-1\, m\pm1}$$

$$= \Bigg[l_1\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$- l_2\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}$$

$$- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1+1 l_2-1\, m\pm1},$$

$$d^{l_1 l_2 m}_{l_1+1 l_2+1\, m\pm1} = \left[-\frac{1}{4}\varsigma\,(l_2 - l_1 + 1)\ \sqrt{\frac{(l_1 \pm m+1)(l_1 \pm m+2)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1+1)(2l_1+3)(2l_2-1)(2l_2+1)}}\right]. \tag{7.134}$$

$\underline{M_{l_1-1 l_2+1\, m\pm1}}$

$$d^{l_1 l_2 m}_{l_1-1 l_2+1\, m\pm1} M_{l_1-1 l_2+1\, m\pm1} =$$

$$\Bigg[\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,(l_1-1)\,((l_1-1)+1)$$

$$- \frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,l_1\,(l_1+1)$$

$$- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}$$

$$+ \frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,(l_2+1)\,((l_2+1)+1)$$

$$- \frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,l_2\,(l_2+1)$$

$$- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\Bigg] M_{l_1-1 l_2+1\, m\pm1}$$

$$
\begin{aligned}
&= \left[\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,(l_1-1)(l_1)\right.\\
&\quad - \frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,l_1(l_1+1)\\
&\quad - \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\\
&\quad + \frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,(l_2+1)(l_2+2)\\
&\quad - \frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\,l_2(l_2+1)\\
&\quad \left.- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\right] M_{l_1-1 l_2+1\, m\pm 1}\\
&= \left[-l_1\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\right.\\
&\quad - \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\\
&\quad + l_2\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\\
&\quad + \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\\
&\quad \left.- \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\right] M_{l_1-1 l_2+1\, m\pm 1}\\
&= \left[-l_1\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\right.\\
&\quad - \frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\\
&\quad \left.+ l_2\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\right] M_{l_1-1 l_2+1\, m\pm 1},
\end{aligned}
$$

$$
d^{l_1 l_2 m}_{l_1-1 l_2+1\, m\pm 1} = \left[-\frac{1}{4}\varsigma\,(l_1-l_2+1)\ \sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \pm m+1)(l_2 \pm m+2)}{(2l_1-1)(2l_1+1)(2l_2+1)(2l_2+3)}}\right]. \tag{7.135}
$$

$\underline{M_{l_1-1 l_2-1\, m\pm1}}$

$$d^{l_1 l_2 m}_{l_1-1 l_2-1\, m\pm1} M_{l_1-1 l_2-1\, m\pm1} =$$

$$\Bigg[-\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}(l_1-1)((l_1-1)+1)$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_1(l_1+1)$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}(l_2-1)((l_2-1)+1)$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_2(l_2+1)$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1-1 l_2-1\, m\pm1}$$

$$=\Bigg[-\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}(l_1-1)(l_1)$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_1(l_1+1)$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$

$$-\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}(l_2-1)(l_2)$$

$$+\frac{1}{8}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}l_2(l_2+1)$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\Bigg] M_{l_1-1 l_2-1\, m\pm1}$$

$$=\Bigg[l_1\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$

$$+\frac{1}{4}\varsigma\sqrt{\frac{(l_1 \mp m-1)(l_1 \mp m)(l_2 \mp m-1)(l_2 \mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}$$

$$
l_2\frac{1}{4}\varsigma\sqrt{\frac{(l_1\mp m-1)(l_1\mp m)(l_2\mp m-1)(l_2\mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}
$$

$$
\left.+\ \frac{1}{4}\varsigma\sqrt{\frac{(l_1\mp m-1)(l_1\mp m)(l_2\mp m-1)(l_2\mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\right] M_{l_1-1 l_2-1\, m\pm 1}
$$

$$
=\left[l_1\frac{1}{4}\varsigma\sqrt{\frac{(l_1\mp m-1)(l_1\mp m)(l_2\mp m-1)(l_2\mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\right.
$$

$$
+\, l_2\frac{1}{4}\varsigma\sqrt{\frac{(l_1\mp m-1)(l_1\mp m)(l_2\mp m-1)(l_2\mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}
$$

$$
\left.+\, 2\ \frac{1}{4}\varsigma\sqrt{\frac{(l_1\mp m-1)(l_1\mp m)(l_2\mp m-1)(l_2\mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\right] M_{l_1-1 l_2-1\, m\pm 1},
$$

$$
d^{l_1 l_2 m}_{l_1-1 l_2-1\, m\pm 1}=\left[\frac{1}{4}\varsigma\,(l_1+l_2+2)\ \sqrt{\frac{(l_1\mp m-1)(l_1\mp m)(l_2\mp m-1)(l_2\mp m)}{(2l_1-1)(2l_1+1)(2l_2-1)(2l_2+1)}}\right]. \tag{7.136}
$$

$\underline{M_{l_1+1 l_2\, m-1}}$

$$
d^{l_1 l_2 m}_{l_1+1 l_2\, m-1} M_{l_1+1 l_2\, m-1}=
$$

$$
\left[-\frac{i}{4\alpha}\varsigma\sqrt{l_2(l_2+1)+m(-m+1)}\sqrt{\frac{(l_1-m+1)(l_1-m+2)}{(2l_1+1)(2l_1+3)}}\right] M_{l_1+1 l_2\, m-1}
$$

$$
=\left[-\frac{i}{4\alpha}\varsigma\sqrt{(l_2-m+1)(l_2+m)}\sqrt{\frac{(l_1-m+1)(l_1-m+2)}{(2l_1+1)(2l_1+3)}}\right] M_{l_1+1 l_2\, m-1},
$$

$$
d^{l_1 l_2 m}_{l_1+1 l_2\, m-1}=\left[-\frac{i}{4\alpha}\varsigma\sqrt{\frac{(l_1-m+1)(l_1-m+2)(l_2-m+1)(l_2+m)}{(2l_1+1)(2l_1+3)}}\right]. \tag{7.137}
$$

$\underline{M_{l_1+1 l_2\, m+1}}$

$$d^{l_1 l_2 m}_{l_1+1 l_2\, m+1} M_{l_1+1 l_2\, m+1} =$$
$$\left[\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}\right] M_{l_1+1\, l_2\, m+1}$$
$$=\left[\frac{i}{4\alpha}\varsigma\sqrt{\left(l_2+m+1\right)\left(l_2-m\right)}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}\right] M_{l_1+1\, l_2\, m+1},$$

$$d^{l_1 l_2 m}_{l_1+1 l_2\, m+1} = \left[\frac{i}{4\alpha}\varsigma\sqrt{\frac{\left(l_1+m+1\right)\left(l_1+m+2\right)\left(l_2+m+1\right)\left(l_2-m\right)}{\left(2l_1+1\right)\left(2l_1+3\right)}}\right]. \qquad (7.138)$$

$\underline{M_{l_1 l_2+1\, m+1}}$

$$d^{l_1 l_2 m}_{l_1 l_2+1\, m+1} M_{l_1\, l_2+1\, m+1} =$$
$$\left[-\frac{i}{4\alpha}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}\sqrt{\frac{\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}\right] M_{l_1\, l_2+1\, m+1},$$

$$d^{l_1 l_2 m}_{l_1 l_2+1\, m+1} = \left[-\frac{i\varsigma}{4\alpha}\sqrt{\frac{\left(l_1+m+1\right)\left(l_1-m\right)\left(l_2+m+1\right)\left(l_2+m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}\right]. \qquad (7.139)$$

$\underline{M_{l_1 l_2+1\, m-1}}$

$$d^{l_1 l_2 m}_{l_1 l_2+1\, m-1} M_{l_1\, l_2+1\, m-1} =$$
$$\left[\frac{i}{4\alpha}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2-m+2\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}\right] M_{l_1\, l_2+1\, m-1},$$

$$d^{l_1 l_2 m}_{l_1 l_2+1\, m-1} = \left[\frac{i}{4\alpha}\varsigma\sqrt{\frac{\left(l_2-m+1\right)\left(l_2-m+2\right)\left(l_1-m+1\right)\left(l_1+m\right)}{\left(2l_2+1\right)\left(2l_2+3\right)}}\right]. \qquad (7.140)$$

$\underline{M_{l_1 l_2-1\, m+1}}$

$$d^{l_1 l_2 m}_{l_1 l_2-1\, m+1} M_{l_1\, l_2-1\, m+1} =$$

$$\left[\frac{i}{4\alpha}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m+1\right)}\sqrt{\frac{\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\right] M_{l_1\, l_2-1\, m+1}$$

$$=\left[\frac{i}{4\alpha}\varsigma\sqrt{\left(l_1+m+1\right)\left(l_1-m\right)}\sqrt{\frac{\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\right] M_{l_1\, l_2-1\, m+1},$$

$$d^{l_1 l_2 m}_{l_1 l_2-1\, m+1} = \left[\frac{i}{4\alpha}\varsigma\sqrt{\frac{\left(l_1+m+1\right)\left(l_1-m\right)\left(l_2-m-1\right)\left(l_2-m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\right]. \tag{7.141}$$

$\underline{M_{l_1 l_2-1\, m-1}}$

$$d^{l_1 l_2 m}_{l_1 l_2-1\, m-1} M_{l_1\, l_2-1\, m-1} =$$

$$\left[-\frac{i}{4\alpha}\varsigma\sqrt{l_1\left(l_1+1\right)-m\left(m-1\right)}\sqrt{\frac{\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\right] M_{l_1\, l_2-1\, m-1}$$

$$=\left[-\frac{i}{4\alpha}\varsigma\sqrt{\left(l_1-m+1\right)\left(l_1+m\right)}\sqrt{\frac{\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\right] M_{l_1\, l_2-1\, m-1},$$

$$d^{l_1 l_2 m}_{l_1 l_2-1\, m-1} = \left[-\frac{i}{4\alpha}\varsigma\sqrt{\frac{\left(l_1-m+1\right)\left(l_1+m\right)\left(l_2+m-1\right)\left(l_2+m\right)}{\left(2l_2-1\right)\left(2l_2+1\right)}}\right]. \tag{7.142}$$

$\underline{M_{l_1-1 l_2\, m+1}}$

$$d^{l_1 l_2 m}_{l_1-1\, l_2 m+1} M_{l_1-1\, l_2 m+1} =$$

$$\left[-\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m-1\right)}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\right] M_{l_1-1\, l_2\, m+1}$$

$$=\left[-\frac{i}{4\alpha}\varsigma\sqrt{\left(l_2+m+1\right)\left(l_2-m\right)}\sqrt{\frac{\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\right] M_{l_1-1\, l_2\, m+1},$$

$$d^{l_1 l_2 m}_{l_1-1\, l_2 m+1} = \left[-\frac{i\varsigma}{4\alpha}\sqrt{\frac{\left(l_2+m+1\right)\left(l_2-m\right)\left(l_1-m-1\right)\left(l_1-m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\right]. \tag{7.143}$$

$\underline{M_{l_1-1 l_2\, m-1}}$

$$d^{l_1 l_2 m}_{l_1-1\, l_2 m-1} M_{l_1-1\, l_2 m-1} =$$
$$\left[\frac{i}{4\alpha}\varsigma\sqrt{l_2\left(l_2+1\right)+m\left(-m+1\right)}\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\right] M_{l_1-1\, l_2\, m-1}$$
$$= \left[\frac{i}{4\alpha}\varsigma\sqrt{\left(l_2-m+1\right)\left(l_2+m\right)}\sqrt{\frac{\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\right] M_{l_1-1\, l_2\, m-1},$$

$$d^{l_1 l_2 m}_{l_1-1\, l_2 m-1} = \left[\frac{i\varsigma}{4\alpha}\sqrt{\frac{\left(l_2-m+1\right)\left(l_2+m\right)\left(l_1+m-1\right)\left(l_1+m\right)}{\left(2l_1-1\right)\left(2l_1+1\right)}}\right]. \qquad (7.144)$$

7.E The Matrices $\mathbf{Q}_n$ and $\mathbf{Q}_n^{\pm}$

The matrices $\mathbf{Q}_n,\ \mathbf{Q}_n^{+},\ \mathbf{Q}_n^{-}$ in Eq. (7.17) have the form (see Appendix 7.F for the derivation of $\mathbf{Q}_n,\ \mathbf{Q}_n^{+},\ \mathbf{Q}_n^{-}$)

$$\mathbf{Q}_n^{-} = \begin{pmatrix} \mathbf{V}_{2n-1} & \mathbf{R}_{2n-1} \\ \mathbf{0} & \mathbf{V}_{2n} \end{pmatrix},\ \mathbf{Q}_n = \begin{pmatrix} \mathbf{P}_{2n-1} & \mathbf{S}_{2n-1} \\ \mathbf{R}_{2n} & \mathbf{P}_{2n} \end{pmatrix},\ \mathbf{Q}_n^{+} = \begin{pmatrix} \mathbf{U}_{2n-1} & \mathbf{0} \\ \mathbf{S}_{2n} & \mathbf{U}_{2n} \end{pmatrix}, \qquad (7.145)$$

where

$$\mathbf{P}_m = \begin{pmatrix} \mathbf{p}_{m\,0} & \bar{\mathbf{p}}_{0\,m} & \ddots & \mathbf{0} \\ \bar{\mathbf{p}}_{m-1\,1} & \mathbf{p}_{m-1\,1} & \ddots & \ddots \\ \ddots & \ddots & \ddots & \bar{\mathbf{p}}_{m-1\,1} \\ \mathbf{0} & \ddots & \bar{\mathbf{p}}_{0\,m} & \mathbf{p}_{0\,m} \end{pmatrix},$$

$$\mathbf{R}_m = \begin{pmatrix} \mathbf{r}^*_{0\,m} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{r}_{m-1\,1} & \mathbf{r}^*_{1\,m-1} & \ddots & \ddots \\ \mathbf{0} & \mathbf{r}_{m-2\,2} & \ddots & \mathbf{0} \\ \ddots & \ddots & \ddots & \mathbf{r}^*_{m-1\,1} \\ \mathbf{0} & \ddots & \mathbf{0} & \mathbf{r}_{0\,m} \end{pmatrix},$$

$$\mathbf{S}_m = \begin{pmatrix} \mathbf{s}_{m\,0} & \mathbf{s}^*_{0\,m} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{0} & \mathbf{s}_{m-1\,1} & \mathbf{s}^*_{1\,m-1} & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \mathbf{0} & \mathbf{s}_{0\,m} & \mathbf{s}^*_{m\,0} \end{pmatrix},$$

$$\mathbf{V}_m = \begin{pmatrix} \bar{\mathbf{v}}_{0\,m} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{v}_{m-1\,1} & \bar{\mathbf{v}}_{1\,m-1} & \ddots & \ddots \\ \bar{\mathbf{v}}_{m-2\,2} & \mathbf{v}_{m-2\,2} & \ddots & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{v}}_{m-3\,3} & \ddots & \bar{\mathbf{v}}_{m-2\,2} \\ \ddots & \ddots & \ddots & \mathbf{v}_{1\,m-1} \\ \mathbf{0} & \ddots & \mathbf{0} & \bar{\mathbf{v}}_{0\,m} \end{pmatrix},$$

$$\mathbf{U}_m = \begin{pmatrix} \bar{\mathbf{u}}_{m\,0} & \mathbf{u}_{m\,0} & \bar{\mathbf{u}}_{0\,m} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{u}}_{m-1\,1} & \mathbf{u}_{m-1\,1} & \bar{\mathbf{u}}_{1\,m-1} & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \mathbf{0} & \bar{\mathbf{u}}_{0\,m} & \mathbf{u}_{0\,m} & \bar{\mathbf{u}}_{m\,0} \end{pmatrix},$$

The matrices $\mathbf{p}_{n\,m}, \bar{\mathbf{u}}_{n\,m}, \bar{\mathbf{v}}_{n\,m}$ have the form

$$\mathbf{x}_{n\,m} = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & 0 \\ \ddots & x_{n\,m\,-1} & 0 & \ddots & \ddots \\ \ddots & 0 & x_{n\,m\,0} & 0 & \ddots \\ \ddots & \ddots & 0 & x_{n\,m\,1} & \ddots \\ 0 & \ddots & \ddots & \ddots & \ddots \end{pmatrix}_{(2r+1)\times(2r_x+1)}, \tag{7.146}$$

and the matrices $\bar{\mathbf{p}}_{n\,m}, \mathbf{s}_{n\,m}, \mathbf{r}_{n\,m}, \mathbf{u}_{n\,m}, \mathbf{v}_{n\,m}$ have the form

$$\mathbf{x}_{n\,m} = \begin{pmatrix} \ddots & \ddots & \ddots & \ddots & 0 \\ \ddots & x_{n\,m\,-1} & x^+_{n\,m\,-1} & 0 & \ddots \\ \ddots & x^-_{n\,m\,0} & x_{n\,m\,0} & x^+_{n\,m\,0} & \ddots \\ \ddots & 0 & x^-_{n\,m\,1} & x_{n\,m\,1} & \ddots \\ 0 & \ddots & \ddots & \ddots & \ddots \end{pmatrix}_{(2r+1)\times(2r_x+1)}. \tag{7.147}$$

Here $\mathbf{x}$ denotes one of the submatrices $\mathbf{p}_{n\,m}, \bar{\mathbf{p}}_{n\,m}, \mathbf{s}_{n\,m}, \mathbf{r}_{n\,m}, \mathbf{u}_{n\,m}, \bar{\mathbf{u}}_{n\,m}, \mathbf{v}_{n\,m}, \bar{\mathbf{v}}_{n\,m}$. All the submatrices have the same number of rows, namely, $2r+1$, where $r = \min[n, m]$.

The number of columns also can be found as $2r_x + 1$, however each submatrix now has its own number r_x, namely

$$
\begin{aligned}
r_p &= \min[n, m], & r_{\bar{p}} &= \min[n+1, m-1],\\
r_s &= \min[n+1, m], & r_r &= \min[n, m-1],\\
r_v &= \min[n-1, m-1], & r_u &= \min[n+1, m+1],\\
r_{\bar{v}} &= \min[n, m-2], & r_{\bar{u}} &= \min[n+2, m].
\end{aligned}
$$

The initial value vectors $\mathbf{C}_n(0)$ in Eq. (7.18) are calculated in the following manner. We introduce the vector

$$
\mathbf{F}_n^i = \begin{pmatrix} \mathbf{f}^i_{2n-1\,0} \\ \mathbf{f}^i_{2n-1\,1} \\ \vdots \\ \mathbf{f}^i_{0\,2n-1} \\ \mathbf{f}^i_{2n\,0} \\ \mathbf{f}^i_{2n-1\,1} \\ \vdots \\ \mathbf{f}^\gamma_{0\,2n} \end{pmatrix}, \quad \mathbf{f}^\gamma_{n,m} = \begin{pmatrix} M^i_{n\,m-r} \\ M^i_{n\,m-r+1} \\ \vdots \\ M^i_{n\,m\,r} \end{pmatrix}, \tag{7.148}
$$

where $r = \min[n, m]$ and the index $i = \mathrm{I}, \mathrm{II}$ corresponds to the fields $\mathbf{H}_Z^{\mathrm{I}}$ and $\mathbf{H}_Z^{\mathrm{II}}$. Therefore we may transform Eq. (7.15) to the three term super-matrix recursion formula

$$
\mathbf{Q}_n^- \mathbf{F}_{n-1}^i + \mathbf{Q}_n \mathbf{F}_n^i + \mathbf{Q}_n^+ \mathbf{F}_{n+1}^i = \mathbf{0}. \tag{7.149}
$$

The solution of this equation is rendered by the matrix product [2]

$$
\mathbf{F}_n^i = \boldsymbol{\Delta}_n^i(0)\,\mathbf{Q}_n^- \mathbf{F}_{n-1}^i = \frac{1}{4\pi} \boldsymbol{\Delta}_n^i(0)\,\mathbf{Q}_n^- \boldsymbol{\Delta}_{n-1}^i(0)\,\mathbf{Q}_n^- \ldots \boldsymbol{\Delta}_1^i(0)\,\mathbf{Q}_1^-. \tag{7.150}
$$

Here, we have used $\mathbf{F}_0^i = 1/(4\pi)$. Thus, we can write the initial vectors $\mathbf{C}_n(0)$ as

$$
\mathbf{C}_n(0) = \mathbf{F}_n^{\mathrm{I}} - \mathbf{F}_n^{\mathrm{II}}. \tag{7.151}
$$

For more details on the derivation of Eq. (7.151) see Appendix 7.G.

7.F Derivation of the Matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^{\pm}$ and their Submatrices

Recall that the differential-recurrence relation for the observables, namely, the relaxation functions $c_{l_1\,l_2\,m}(t) = \langle M_{l_1\,l_2\,m}\rangle(t) - \langle M_{l_1\,l_2\,m}\rangle_{\mathrm{II}}$ of the two-spin system is given by

$$\tau_N \dot{c}_{l_1\,l_2\,m} = \sum_{i=-2}^{2}\sum_{j=-2}^{2}\sum_{k=-1}^{1} d_{l_1+i\,l_2+j\,m+k}^{l_1\,l_2\,m} c_{l_1+i\,l_2+j\,m+k}, \tag{7.152}$$

where the angular brackets $\langle\rangle(t)$ denote ensemble averaging over the sharp values and $\langle\rangle_i, i = \mathrm{I}, \mathrm{II}$ denotes the equilibrium ensemble averages corresponding to the initial (I) and final states (II) of the two-spin system, evaluated from

$$\langle M_{l_1\,l_2\,m}\rangle_i = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} M_{l_1\,l_2\,m} W_i(\vartheta_1,\varphi_1,\vartheta_2,\varphi_2)\sin\vartheta_2\sin\vartheta_1 d\vartheta_2 d\vartheta_1 d\varphi_2 d\varphi_1. \tag{7.153}$$

In writing Eq. (7.152) we have also used the fact that the equilibrium averages $\langle M_{l_1\,l_2\,m}\rangle_i$ satisfy the time-independent recurrence relation

$$\sum_{i=-2}^{2}\sum_{j=-2}^{2}\sum_{k=-1}^{1} d_{l_1+i\,l_2+j\,m+k}^{l_1\,l_2\,m} \langle M_{l_1+i\,l_2+j\,m+k}\rangle_i = 0. \tag{7.154}$$

As stated earlier, the hierarchy of recurrence relations Eq. (7.152) for the relaxation functions $c_{l_1\,l_2\,m}(t)$ must be solved subject to the initial conditions $c_{l_1\,l_2\,m}(0) = \langle M_{l_1\,l_2\,m}\rangle_{\mathrm{I}} - \langle M_{l_1\,l_2\,m}\rangle_{\mathrm{II}}$. To achieve this, we shall write Eq. (7.152) as a tractable tridiagonal vector recurrence relation. Consider the one-sided pentadiagonal recurrence relation

$$\tau_N \dot{\mathbf{c}}_n = \mathbf{V}_n\mathbf{c}_{n-2} + \mathbf{R}_n\mathbf{c}_{n-1} + \mathbf{P}_n\mathbf{c}_n + \mathbf{S}_n\mathbf{c}_{n+1} + \mathbf{U}_n\mathbf{c}_{n+2}, \tag{7.155}$$

and then write it down for even and odd indices n

$$\tau_N \dot{\mathbf{c}}_{2n-1} = \mathbf{V}_{2n-1}\mathbf{c}_{2n-3} + \mathbf{R}_{2n-1}\mathbf{c}_{2n-2} + \mathbf{P}_{2n-1}\mathbf{c}_{2n-1} + \mathbf{S}_{2n-1}\mathbf{c}_{2n} + \mathbf{U}_{2n-1}\mathbf{c}_{2n+1}, \tag{7.156}$$

$$\tau_N \dot{\mathbf{c}}_{2n} = \mathbf{V}_{2n}\mathbf{c}_{2n-2} + \mathbf{R}_{2n}\mathbf{c}_{2n-1} + \mathbf{P}_{2n}\mathbf{c}_{2n} + \mathbf{S}_{2n}\mathbf{c}_{2n+1} + \mathbf{U}_{2n}\mathbf{c}_{2n+2}, \tag{7.157}$$

where

$$\mathbf{c}_{2n} = \begin{pmatrix} c_{2n,0,0} \\ c_{(2n-1),1,-1} \\ c_{(2n-1),1,0} \\ c_{(2n-1),1,1} \\ c_{(2n-2),2,-2} \\ c_{(2n-2),2,-1} \\ c_{(2n-2),2,0} \\ c_{(2n-2),2,1} \\ c_{(2n-2),2,2} \\ \vdots \\ c_{0,2n,0} \end{pmatrix}, \ \mathbf{c}_{2n-1} = \begin{pmatrix} c_{(2n-1),0,0} \\ c_{(2n-2),1,-1} \\ c_{(2n-2),1,0} \\ c_{(2n-2),1,1} \\ c_{(2n-3),2,-2} \\ c_{(2n-3),2,-1} \\ c_{(2n-3),2,0} \\ c_{(2n-3),2,1} \\ c_{(2n-3),2,2} \\ \vdots \\ c_{0,(2n-1),0} \end{pmatrix}, \ \mathbf{c}_{2n-2} = \begin{pmatrix} c_{(2n-2),0,0} \\ c_{(2n-3),1,-1} \\ c_{(2n-3),1,0} \\ c_{(2n-3),1,1} \\ c_{(2n-4),2,-2} \\ c_{(2n-4),2,-1} \\ c_{(2n-4),2,0} \\ c_{(2n-4),2,1} \\ c_{(2n-4),2,2} \\ \vdots \\ c_{0,(2n-2),0} \end{pmatrix},$$

$$\mathbf{c}_{2n-3} = \begin{pmatrix} c_{(2n-3),0,0} \\ c_{(2n-4),1,-1} \\ c_{(2n-4),1,0} \\ c_{(2n-4),1,1} \\ c_{(2n-5),2,-2} \\ c_{(2n-5),2,-1} \\ c_{(2n-5),2,0} \\ c_{(2n-5),2,1} \\ c_{(2n-5),2,2} \\ \vdots \\ c_{0,(2n-3),0} \end{pmatrix}, \ \mathbf{c}_{2n+1} = \begin{pmatrix} c_{(2n+1),0,0} \\ c_{2n,1,-1} \\ c_{2n,1,0} \\ c_{2n,1,1} \\ c_{(2n-1),2,-2} \\ c_{(2n-1),2,-1} \\ c_{(2n-1),2,0} \\ c_{(2n-1),2,1} \\ c_{(2n-1),2,2} \\ \vdots \\ c_{0,(2n+1),0} \end{pmatrix}, \ \mathbf{c}_{2n+2} = \begin{pmatrix} c_{(2n+2),0,0} \\ c_{(2n+1),1,-1} \\ c_{(2n+1),1,0} \\ c_{(2n+1),1,1} \\ c_{2n,2,-2} \\ c_{2n,2,-1} \\ c_{2n,2,0} \\ c_{2n,2,1} \\ c_{2n,2,2} \\ \vdots \\ c_{0,(2n+2),0} \end{pmatrix}. \tag{7.158}$$

The elements of the matrices $\mathbf{V}_{2n}, \mathbf{R}_{2n}, \mathbf{P}_{2n}, \mathbf{S}_{2n}, \mathbf{U}_{2n}$ can be determined from equations (7.152), (7.156) and (7.157). We start by introducing the column vectors

$$\mathbf{C}_n = \begin{pmatrix} \mathbf{c}_{2n-1} \\ \mathbf{c}_{2n} \end{pmatrix} = \begin{pmatrix} \mathbf{c}_{2n-1\,0} \\ \mathbf{c}_{2n-2\,1} \\ \vdots \\ \mathbf{c}_{0\,2n-1} \\ \mathbf{c}_{2n\,0} \\ \mathbf{c}_{2n-1\,1} \\ \vdots \\ \mathbf{c}_{0\,2n} \end{pmatrix}, \ \mathbf{c}_{n\,m}(t) = \begin{pmatrix} c_{n\,m\,-r} \\ c_{n\,m\,-r+1} \\ \vdots \\ c_{n\,m\,r} \end{pmatrix}, \tag{7.159}$$

where ($r = \min[n, m]$). Using Eq. (7.159) we can write Eqs. (7.156) and (7.157) into a tractable tridiagonal vector recurrence relation viz.,

$$\begin{pmatrix} \tau_N \dot{\mathbf{c}}_{2n-1} \\ \tau_N \dot{\mathbf{c}}_{2n} \end{pmatrix} = \begin{pmatrix} \mathbf{V}_{2n-1} & \mathbf{R}_{2n-1} \\ \mathbf{0} & \mathbf{V}_{2n} \end{pmatrix} \begin{pmatrix} \mathbf{c}_{2n-3} \\ \mathbf{c}_{2n-2} \end{pmatrix} + \begin{pmatrix} \mathbf{P}_{2n-1} & \mathbf{S}_{2n-1} \\ \mathbf{R}_{2n} & \mathbf{P}_{2n} \end{pmatrix} \begin{pmatrix} \mathbf{c}_{2n-1} \\ \mathbf{c}_{2n} \end{pmatrix}$$
$$+ \begin{pmatrix} \mathbf{U}_{2n-1} & \mathbf{0} \\ \mathbf{S}_{2n} & \mathbf{U}_{2n} \end{pmatrix} \begin{pmatrix} \mathbf{c}_{2n+1} \\ \mathbf{c}_{2n+2} \end{pmatrix}, \tag{7.160}$$

which can be more compactly written as

$$\tau_N \dot{\mathbf{C}}_n = \mathbf{Q}_n^- \mathbf{C}_{n-1} + \mathbf{Q}_n \, \mathbf{C}_n + \mathbf{Q}_n^+ \mathbf{C}_{n+1}, \tag{7.161}$$

where

$$\mathbf{Q}_n^- = \begin{pmatrix} \mathbf{V}_{2n-1} & \mathbf{R}_{2n-1} \\ \mathbf{0} & \mathbf{V}_{2n} \end{pmatrix}, \ \mathbf{Q}_n = \begin{pmatrix} \mathbf{P}_{2n-1} & \mathbf{S}_{2n-1} \\ \mathbf{R}_{2n} & \mathbf{P}_{2n} \end{pmatrix}, \ \mathbf{Q}_n^+ = \begin{pmatrix} \mathbf{U}_{2n-1} & \mathbf{0} \\ \mathbf{S}_{2n} & \mathbf{U}_{2n} \end{pmatrix}. \tag{7.162}$$

The non-zero coefficients in the right hand side of Eq. (7.152) are listed in Appendix 7.C. We seek now to derive the submatrices $\mathbf{V}_{2n}, \mathbf{R}_{2n}, \mathbf{P}_{2n}, \mathbf{S}_{2n}, \mathbf{U}_{2n}$ in order to demonstrate their general structure for all values of $2n$ and $2n-1$ in the tractable tridiagonal vector recurrence relation in Eq. (7.160), which will thus allow for its implementation in Wolfram Mathematica code. To do this, we shall determine the non-zero elements of the matrices $\mathbf{V}_{2n}, \mathbf{R}_{2n}, \mathbf{P}_{2n}, \mathbf{S}_{2n}, \mathbf{U}_{2n}$ from Eq. (7.152). Then using Eqs. (7.157), and (7.158), we shall determine their positions in the matrices $\mathbf{V}_{2n}, \mathbf{R}_{2n}, \mathbf{P}_{2n}, \mathbf{S}_{2n}, \mathbf{U}_{2n}$ and then generalise their structures for all values of n. From Eq. (7.157) we have

$$\tau_N \dot{\mathbf{c}}_{2n} = \begin{pmatrix} \tau_N \dot{c}_{2n,0,0} \\ \tau_N \dot{c}_{(2n-1),1,-1} \\ \tau_N \dot{c}_{(2n-1),1,0} \\ \tau_N \dot{c}_{(2n-1),1,1} \\ \tau_N \dot{c}_{(2n-2),2,-2} \\ \tau_N \dot{c}_{(2n-2),2,-1} \\ \tau_N \dot{c}_{(2n-2),2,0} \\ \tau_N \dot{c}_{(2n-2),2,1} \\ \tau_N \dot{c}_{(2n-2),2,2} \\ \vdots \\ \tau_N \dot{c}_{0,2n,0} \end{pmatrix}. \tag{7.163}$$

From this we can determine from Eq. (7.152) and the list of the non-zero coefficients in Appendix 7.C the following:

$\underline{l_1 = 2n,\ l_2 = 0,\ m = 0}$

$$\begin{aligned}
&\tau_N \dot{c}_{2n\,0\,0} = \\
&d^{2n\,0\,0}_{2n\,0\,0} c_{2n\,0\,0} + d^{2n\,0\,0}_{2n-1\,1\,-1} c_{2n-1\,1\,-1} + d^{2n\,0\,0}_{2n-1\,1\,0} c_{2n-1\,1\,0} \\
&+ d^{2n\,0\,0}_{2n-1\,1\,1} c_{2n-1\,1\,1} + d^{2n\,0\,0}_{2n-1\,0\,0} c_{2n-1\,0\,0} + d^{2n\,0\,0}_{2n+1\,0\,0} c_{2n+1\,0\,0} + d^{2n\,0\,0}_{2n\,1\,-1} c_{2n\,1\,-1} \\
&+ d^{2n\,0\,0}_{2n\,1\,0} c_{2n\,1\,0} + d^{2n\,0\,0}_{2n\,1\,1} c_{2n\,1\,1} + d^{2n\,0\,0}_{2n+2\,0\,0} c_{2n+2\,0\,0} + d^{2n\,0\,0}_{2n+1\,1\,-1} c_{2n+1\,1\,-1} \\
&+ d^{2n\,0\,0}_{2n+1\,1\,0} c_{2n+1\,1\,0} + d^{2n\,0\,0}_{2n+1\,1\,1} c_{2n+1\,1\,1} + d^{2n\,0\,0}_{2n\,2\,0} c_{2n\,2\,0} + d^{2n\,0\,0}_{2n-2\,0\,0} c_{2n-2\,0\,0}.
\end{aligned} \tag{7.164}$$

$\underline{l_1 = 2n-1,\ l_2 = 1,\ m = -1}$

$$\tau_N \dot{c}_{2n-1\,1\,-1} =$$
$$d^{2n-1\,1\,-1}_{2n\,0\,0} c_{2n\,0\,0} + d^{2n-1\,1\,-1}_{2n-1\,1\,-1} c_{2n-1\,1\,-1} + d^{2n-1\,1\,-1}_{2n-2\,2\,-2} c_{2n-2\,2\,-2}$$
$$+d^{2n-1\,1\,-1}_{2n-2\,2\,-1} c_{2n-2\,2\,-1} + d^{2n-1\,1\,-1}_{2n-2\,2\,0} c_{2n-2\,2\,0} + d^{2n-1\,1\,-1}_{2n-1\,0\,0} c_{2n-1\,0\,0} + d^{2n-1\,1\,-1}_{2n-2\,1\,-1} c_{2n-2\,1\,-1}$$
$$+d^{2n-1\,1\,-1}_{2n-2\,1\,0} c_{2n-2\,1\,0} + d^{2n-1\,1\,-1}_{2n\,1\,-1} c_{2n\,1\,-1} + d^{2n-1\,1\,-1}_{2n\,1\,0} c_{2n\,1\,0} + d^{2n-1\,1\,-1}_{2n-1\,2\,-2} c_{2n-1\,2\,-2}$$
$$+d^{2n-1\,1\,-1}_{2n-1\,2\,-1} c_{2n-1\,2\,-1} + d^{2n-1\,1\,-1}_{2n-1\,2\,0} c_{2n-1\,2\,0} + d^{2n-1\,1\,-1}_{2n+1\,1\,-1} c_{2n+1\,1\,-1} + d^{2n-1\,1\,-1}_{2n\,2\,-2} c_{2n\,2\,-2}$$
$$+d^{2n-1\,1\,-1}_{2n\,2\,-1} c_{2n\,2\,-1} + d^{2n-1\,1\,-1}_{2n\,2\,0} c_{2n\,2\,0} + d^{2n-1\,1\,-1}_{2n-1\,3\,-1} c_{2n-1\,3\,-1} + d^{2n-1\,1\,-1}_{2n-2\,0\,0} c_{2n-2\,0\,0}$$
$$+d^{2n-1\,1\,-1}_{2n-3\,1\,-1} c_{2n-3\,1\,-1}. \tag{7.165}$$

$\underline{l_1 = 2n-1,\ l_2 = 1,\ m = 0}$

$$\tau_N \dot{c}_{2n-1\,1\,0} =$$
$$d^{2n-1\,1\,0}_{2n\,0\,0} c_{2n\,0\,0} + d^{2n-1\,1\,0}_{2n-1\,1\,0} c_{2n-1\,1\,0} + d^{2n-1\,1\,0}_{2n-2\,2\,-1} c_{2n-2\,2\,-1}$$
$$+d^{2n-1\,1\,0}_{2n-2\,2\,0} c_{2n-2\,2\,0} + d^{2n-1\,1\,0}_{2n-2\,2\,1} c_{2n-2\,2\,1} + d^{2n-1\,1\,0}_{2n-1\,0\,0} c_{2n\,0\,0} + d^{2n-1\,1\,0}_{2n-2\,1\,-1} c_{2n-2\,1\,-1}$$
$$+d^{2n-1\,1\,0}_{2n-2\,1\,0} c_{2n-2\,1\,0} + d^{2n-1\,1\,0}_{2n-2\,1\,1} c_{2n-2\,1\,1} + d^{2n-1\,1\,0}_{2n\,1\,-1} c_{2n\,1\,-1} + d^{2n-1\,1\,0}_{2n\,1\,0} c_{2n\,1\,0}$$
$$+d^{2n-1\,1\,0}_{2n\,1\,1} c_{2n\,1\,1} + d^{2n-1\,1\,0}_{2n-1\,2\,-1} c_{2n-1\,2\,-1} + d^{2n-1\,1\,0}_{2n-1\,2\,0} c_{2n-1\,2\,0} + d^{2n-1\,1\,0}_{2n-1\,2\,1} c_{2n-1\,2\,1}$$
$$+d^{2n-1\,1\,0}_{2n+1\,1\,0} c_{2n+1\,1\,0} + d^{2n-1\,1\,0}_{2n\,2\,-1} c_{2n\,2\,-1} + d^{2n-1\,1\,0}_{2n\,2\,0} c_{2n\,2\,0} + d^{2n-1\,1\,0}_{2n\,2\,1} c_{2n\,2\,1}$$
$$+d^{2n-1\,1\,0}_{2n-1\,3\,0} c_{2n-1\,3\,0} + d^{2n-1\,1\,0}_{2n-2\,0\,0} c_{2n-2\,0\,0} + d^{2n-1\,1\,0}_{2n-3\,1\,0} c_{2n-3\,1\,0}. \tag{7.166}$$

$\underline{l_1 = 2n-1,\ l_2 = 1,\ m = 1}$

$$\tau_N \dot{c}_{2n-1\,1\,1} =$$
$$d^{2n-1\,1\,1}_{2n\,0\,0} c_{2n\,0\,0} + d^{2n-1\,1\,1}_{2n-1\,1\,1} c_{2n-1\,1\,1} + d^{2n-1\,1\,1}_{2n-2\,2\,0} c_{2n-2\,2\,0}$$
$$+d^{2n-1\,1\,1}_{2n-2\,2\,1} c_{2n-2\,2\,1} + d^{2n-1\,1\,1}_{2n-2\,2\,2} c_{2n-2\,2\,2} + d^{2n-1\,1\,1}_{2n-1\,0\,0} c_{2n\,0\,0} + d^{2n-1\,1\,1}_{2n-2\,1\,0} c_{2n-2\,1\,0}$$
$$+d^{2n-1\,1\,1}_{2n-2\,1\,1} c_{2n-2\,1\,1} + d^{2n-1\,1\,1}_{2n\,1\,0} c_{2n\,1\,0} + d^{2n-1\,1\,1}_{2n\,1\,1} c_{2n\,1\,1} + d^{2n-1\,1\,1}_{2n-1\,2\,0} c_{2n-1\,2\,0}$$
$$+d^{2n-1\,1\,1}_{2n-1\,2\,1} c_{2n-1\,2\,1} + d^{2n-1\,1\,1}_{2n-1\,2\,2} c_{2n-1\,2\,2} + d^{2n-1\,1\,1}_{2n+1\,1\,1} c_{2n+1\,1\,1} + d^{2n-1\,1\,1}_{2n\,2\,0} c_{2n\,2\,0}$$
$$+d^{2n-1\,1\,1}_{2n\,2\,1} c_{2n\,2\,1} + d^{2n-1\,1\,1}_{2n\,2\,2} c_{2n\,2\,2} + d^{2n-1\,1\,1}_{2n-1\,3\,1} c_{2n-1\,3\,1} + d^{2n-1\,1\,1}_{2n-2\,0\,0} c_{2n-2\,0\,0}$$
$$+d^{2n-1\,1\,1}_{2n-3\,1\,1} c_{2n-3\,1\,1}. \tag{7.167}$$

$\underline{l_1 = 2n-2,\ l_2 = 2,\ m = -2}$

$$
\begin{aligned}
&\tau_N \dot{c}_{2n-2\,2\,-2} = \\
&d^{2n-2\,2\,-2}_{2n-1\,1\,-1} c_{2n-1\,1\,-1} + d^{2n-2\,2\,-2}_{2n-2\,2\,-2} c_{2n-2\,2\,-2} + d^{2n-2\,2\,-2}_{2n-3\,3\,-3} c_{2n-3\,3\,-3} \\
&+ d^{2n-2\,2\,-2}_{2n-3\,3\,-2} c_{2n-3\,3\,-2} + d^{2n-2\,2\,-2}_{2n-3\,3\,-1} c_{2n-3\,3\,-1} + d^{2n-2\,2\,-2}_{2n-2\,1\,-1} c_{2n-2\,1\,-1} + d^{2n-2\,2\,-2}_{2n-3\,2\,-2} c_{2n-3\,2\,-2} \\
&+ d^{2n-2\,2\,-2}_{2n-3\,2\,-1} c_{2n-3\,2\,-1} + d^{2n-2\,2\,-2}_{2n-1\,2\,-2} c_{2n-1\,2\,-2} + d^{2n-2\,2\,-2}_{2n-1\,2\,-1} c_{2n-1\,2\,-1} + d^{2n-2\,2\,-2}_{2n-2\,3\,-3} c_{2n-3\,3\,-3} \\
&+ d^{2n-2\,2\,-2}_{2n-2\,3\,-2} c_{2n-3\,3\,-2} + d^{2n-2\,2\,-2}_{2n-2\,3\,-1} c_{2n-3\,3\,-1} + d^{2n-2\,2\,-2}_{2n\,2\,-2} c_{2n\,2\,-2} + d^{2n-2\,2\,-2}_{2n-1\,3\,-3} c_{2n-1\,3\,-3} \\
&+ d^{2n-2\,2\,-2}_{2n-1\,3\,-2} c_{2n-1\,3\,-2} + d^{2n-2\,2\,-2}_{2n-1\,3\,-1} c_{2n-1\,3\,-1} + d^{2n-2\,2\,-2}_{2n-2\,4\,-2} c_{2n-2\,4\,-2} + d^{2n-2\,2\,-2}_{2n-3\,1\,-1} c_{2n-3\,1\,-1} \\
&+ d^{2n-2\,2\,-2}_{2n-4\,2\,-2} c_{2n-4\,2\,-2}.
\end{aligned}
\tag{7.168}
$$

$\underline{l_1 = 2n-2,\ l_2 = 2,\ m = -1}$

$$
\begin{aligned}
&\tau_N \dot{c}_{2n-2\,2\,-1} = \\
&d^{2n-2\,2\,-1}_{2n-1\,1\,-1} c_{2n-1\,1\,-1} + d^{2n-2\,2\,-1}_{2n-1\,1\,0} c_{2n-1\,1\,0} + d^{2n-2\,2\,-1}_{2n-2\,2\,-1} c_{2n-2\,2\,-1} \\
&+ d^{2n-2\,2\,-1}_{2n-3\,3\,-2} c_{2n-3\,3\,-2} + d^{2n-2\,2\,-1}_{2n-3\,3\,-1} c_{2n-3\,3\,-1} + d^{2n-2\,2\,-1}_{2n-3\,3\,0} c_{2n-3\,3\,0} + d^{2n-2\,2\,-1}_{2n-2\,1\,-1} c_{2n-2\,1\,-1} \\
&+ d^{2n-2\,2\,-1}_{2n-2\,1\,0} c_{2n-2\,1\,0} + d^{2n-2\,2\,-1}_{2n-3\,2\,-2} c_{2n-3\,2\,-2} + d^{2n-2\,2\,-1}_{2n-3\,2\,-1} c_{2n-3\,2\,-1} + d^{2n-2\,2\,-1}_{2n-3\,2\,0} c_{2n-3\,2\,0} \\
&+ d^{2n-2\,2\,-1}_{2n-1\,2\,-2} c_{2n-1\,2\,-2} + d^{2n-2\,2\,-1}_{2n-1\,2\,-1} c_{2n-1\,2\,-1} + d^{2n-2\,2\,-1}_{2n-1\,2\,0} c_{2n-1\,2\,0} + d^{2n-2\,2\,-1}_{2n-2\,3\,-2} c_{2n-2\,3\,-2} \\
&+ d^{2n-2\,2\,-1}_{2n-2\,3\,-1} c_{2n-2\,3\,-1} + d^{2n-2\,2\,-1}_{2n-2\,3\,0} c_{2n-2\,3\,0} + d^{2n-2\,2\,-1}_{2n\,2\,-1} c_{2n\,2\,-1} + d^{2n-2\,2\,-1}_{2n-1\,3\,-2} c_{2n-1\,3\,-2} \\
&+ d^{2n-2\,2\,-1}_{2n-1\,3\,-1} c_{2n-1\,3\,-1} + d^{2n-2\,2\,-1}_{2n-1\,3\,0} c_{2n-1\,3\,0} + d^{2n-2\,2\,-1}_{2n-2\,4\,-1} c_{2n-2\,4\,-1} + d^{2n-2\,2\,-1}_{2n-3\,1\,-1} c_{2n-3\,1\,-1} \\
&+ d^{2n-2\,2\,-1}_{2n-3\,1\,0} c_{2n-3\,1\,0} + d^{2n-2\,2\,-1}_{2n-4\,2\,-1} c_{2n-4\,2\,-1}.
\end{aligned}
\tag{7.169}
$$

$\underline{l_1 = 2n-2,\ l_2 = 2,\ m = 0}$

$$
\begin{aligned}
&\tau_N \dot{c}_{2n-2\,2\,0} = \\
&d^{2n-2\,2\,0}_{2n-1\,1\,-1} c_{2n-1\,1\,-1} + d^{2n-2\,2\,0}_{2n-1\,1\,0} c_{2n-1\,1\,0} + d^{2n-2\,2\,0}_{2n-1\,1\,1} c_{2n-1\,1\,1} \\
&+ d^{2n-2\,2\,0}_{2n-2\,2\,0} c_{2n-2\,2\,0} + d^{2n-2\,2\,0}_{2n-3\,3\,-1} c_{2n-3\,3\,-1} + d^{2n-2\,2\,0}_{2n-3\,3\,0} c_{2n-3\,3\,0} + d^{2n-2\,2\,0}_{2n-3\,3\,1} c_{2n-3\,3\,1} \\
&+ d^{2n-2\,2\,0}_{2n-2\,1\,-1} c_{2n-2\,1\,-1} + d^{2n-2\,2\,0}_{2n-2\,1\,0} c_{2n-2\,1\,0} + d^{2n-2\,2\,0}_{2n-2\,1\,1} c_{2n-2\,1\,1} + d^{2n-2\,2\,0}_{2n-3\,2\,-1} c_{2n-3\,2\,-1} \\
&+ d^{2n-2\,2\,0}_{2n-3\,2\,0} c_{2n-3\,2\,0} + d^{2n-2\,2\,0}_{2n-3\,2\,1} c_{2n-3\,2\,1} + d^{2n-2\,2\,0}_{2n-1\,2\,-1} c_{2n-1\,2\,-1} + d^{2n-2\,2\,0}_{2n-1\,2\,0} c_{2n-1\,2\,0} \\
&+ d^{2n-2\,2\,0}_{2n-1\,2\,1} c_{2n-1\,2\,1} + d^{2n-2\,2\,0}_{2n-2\,3\,-1} c_{2n-2\,3\,-1} + d^{2n-2\,2\,0}_{2n-2\,3\,0} c_{2n-2\,3\,0} + d^{2n-2\,2\,0}_{2n-2\,3\,1} c_{2n-3\,3\,1} \\
&+ d^{2n-2\,2\,0}_{2n\,2\,0} c_{2n\,2\,0} + d^{2n-2\,2\,0}_{2n-1\,3\,-1} c_{2n-1\,3\,-1} + d^{2n-2\,2\,0}_{2n-1\,3\,0} c_{2n-1\,3\,0} + d^{2n-2\,2\,0}_{2n-1\,3\,1} c_{2n-1\,3\,1} \\
&+ d^{2n-2\,2\,0}_{2n-2\,4\,0} c_{2n-2\,4\,0} + d^{2n-2\,2\,0}_{2n-2\,0\,0} c_{2n-2\,0\,0} + d^{2n-2\,2\,0}_{2n-3\,1\,-1} c_{2n-3\,1\,-1} + d^{2n-2\,2\,0}_{2n-3\,1\,0} c_{2n-3\,1\,0} \\
&+ d^{2n-2\,2\,0}_{2n-3\,1\,1} c_{2n-3\,1\,1} + d^{2n-2\,2\,0}_{2n-4\,2\,0} c_{2n-4\,2\,0}.
\end{aligned}
\tag{7.170}
$$

$\underline{l_1 = 2n-2,\ l_2 = 2,\ m = 1}$

$$
\begin{aligned}
&\tau_N \dot{c}_{2n-2\,2\,1} = \\
&d^{2n-2\,2\,1}_{2n-1\,1\,0} c_{2n-1\,1\,0} + d^{2n-2\,2\,1}_{2n-1\,1\,1} c_{2n-1\,1\,1} + d^{2n-2\,2\,1}_{2n-2\,2\,1} c_{2n-2\,2\,1} \\
&+ d^{2n-2\,2\,1}_{2n-3\,3\,0} c_{2n-3\,3\,0} + d^{2n-2\,2\,1}_{2n-3\,3\,1} c_{2n-3\,3\,1} + d^{2n-2\,2\,1}_{2n-3\,3\,2} c_{2n-3\,3\,2} + d^{2n-2\,2\,1}_{2n-2\,1\,0} c_{2n-2\,1\,0} \\
&+ d^{2n-2\,2\,1}_{2n-2\,1\,1} c_{2n-2\,1\,1} + d^{2n-2\,2\,1}_{2n-3\,2\,0} c_{2n-3\,2\,0} + d^{2n-2\,2\,1}_{2n-3\,2\,1} c_{2n-3\,2\,1} + d^{2n-2\,2\,1}_{2n-3\,2\,2} c_{2n-3\,2\,2} \\
&+ d^{2n-2\,2\,1}_{2n-1\,2\,0} c_{2n-1\,2\,0} + d^{2n-2\,2\,1}_{2n-1\,2\,1} c_{2n-1\,2\,1} + d^{2n-2\,2\,1}_{2n-1\,2\,2} c_{2n-1\,2\,2} + d^{2n-2\,2\,1}_{2n-2\,3\,2} \\
&+ d^{2n-2\,2\,1}_{2n\,2\,1} c_{2n\,2\,1} + d^{2n-2\,2\,1}_{2n-1\,3\,0} c_{2n-1\,3\,0} + d^{2n-2\,2\,1}_{2n-1\,3\,1} c_{2n-1\,3\,1} + d^{2n-2\,2\,1}_{2n-1\,3\,2} c_{2n-1\,3\,2} \\
&+ d^{2n-2\,2\,1}_{2n-2\,4\,1} c_{2n-2\,4\,1} + d^{2n-2\,2\,1}_{2n-3\,1\,0} c_{2n-3\,1\,0} + d^{2n-2\,2\,1}_{2n-3\,1\,1} c_{2n-3\,1\,1} + d^{2n-2\,2\,1}_{2n-4\,2\,1} c_{2n-4\,2\,1}.
\end{aligned}
\tag{7.171}
$$

$\underline{l_1 = 2n-2,\ l_2 = 2,\ m = 2}$

$$\begin{aligned}
&\tau_N \dot{c}_{2n-2\,2\,2} = \\
&d^{2n-2\,2\,2}_{2n-1\,1\,1} c_{2n-1\,1\,1} + d^{2n-2\,2\,2}_{2n-2\,2\,2} c_{2n-2\,2\,2} + d^{2n-2\,2\,2}_{2n-3\,3\,1} c_{2n-3\,3\,1} \\
&+ d^{2n-2\,2\,2}_{2n-3\,3\,2} c_{2n-3\,3\,2} + d^{2n-2\,2\,2}_{2n-3\,3\,3} c_{2n-3\,3\,3} + d^{2n-2\,2\,2}_{2n-2\,1\,1} c_{2n-2\,1\,1} + d^{2n-2\,2\,2}_{2n-3\,2\,1} c_{2n-3\,2\,1} \\
&+ d^{2n-2\,2\,2}_{2n-3\,2\,2} c_{2n-3\,2\,2} + d^{2n-2\,2\,2}_{2n-1\,2\,1} c_{2n-1\,2\,1} + d^{2n-2\,2\,2}_{2n-1\,2\,2} c_{2n-1\,2\,2} + d^{2n-2\,2\,2}_{2n-2\,3\,1} c_{2n-2\,3\,1} \\
&+ d^{2n-2\,2\,2}_{2n-2\,3\,2} c_{2n-2\,3\,2} + d^{2n-2\,2\,2}_{2n-2\,3\,3} c_{2n-2\,3\,3} + d^{2n-2\,2\,2}_{2n\,2\,2} c_{2n\,2\,2} + d^{2n-2\,2\,2}_{2n-1\,3\,1} c_{2n-1\,3\,1} \\
&+ d^{2n-2\,2\,2}_{2n-1\,3\,2} c_{2n-1\,3\,2} + d^{2n-2\,2\,2}_{2n-1\,3\,3} c_{2n-1\,3\,3} + d^{2n-2\,2\,2}_{2n-2\,4\,2} c_{2n-2\,4\,2} + d^{2n-2\,2\,2}_{2n-3\,1\,1} c_{2n-3\,1\,1} \\
&+ d^{2n-2\,2\,2}_{2n-4\,2\,2} c_{2n-4\,2\,2}.
\end{aligned} \tag{7.172}$$

$\underline{l_1 = 0,\ l_2 = 2n,\ m = 0}$

$$\begin{aligned}
&\tau_N \dot{c}_{0\,2n\,0} = \\
&d^{0\,2n\,0}_{1\,2n-1\,-1} c_{1\,2n-1\,-1} + d^{0\,2n\,0}_{1\,2n-1\,0} c_{1\,2n-1\,0} + d^{0\,2n\,0}_{1\,2n-1\,1} c_{1\,2n-1\,1} \\
&+ d^{0\,2n\,0}_{0\,2n\,0} c_{0\,2n\,0} + d^{0\,2n\,0}_{0\,2n-1\,0} c_{0\,2n-1\,0} + d^{0\,2n\,0}_{0\,2n+1\,0} c_{0\,2n+1\,0} + d^{0\,2n\,0}_{1\,2n\,-1} c_{1\,2n\,-1} \\
&+ d^{0\,2n\,0}_{1\,2n\,0} c_{1\,2n\,0} + d^{0\,2n\,0}_{1\,2n\,1} c_{1\,2n\,1} + d^{0\,2n\,0}_{0\,2n+2\,0} c_{0\,2n+2\,0} + d^{0\,2n\,0}_{1\,2n+1\,1} c_{1\,2n+1\,1} \\
&+ d^{0\,2n\,0}_{1\,2n+1\,0} c_{1\,2n+1\,0} + d^{0\,2n\,0}_{1\,2n+1\,-1} c_{1\,2n+1\,-1} + d^{0\,2n\,0}_{2\,2n\,0} c_{2\,2n\,0} + d^{0\,2n\,0}_{0\,2n-2\,0} c_{0\,2n-2\,0}.
\end{aligned} \tag{7.173}$$

$\underline{l_1 = 1,\ l_2 = 2n-1,\ m = 1}$

$$\begin{aligned}
&\tau_N \dot{c}_{1\,2n-1\,1} = \\
&d^{1\,2n-1\,1}_{0\,2n\,0} c_{0\,2n\,0} + d^{1\,2n-1\,1}_{1\,2n-1\,1} c_{1\,2n-1\,1} + d^{1\,2n-1\,1}_{2\,2n-2\,0} c_{2\,2n-2\,0} \\
&+ d^{1\,2n-1\,1}_{2\,2n-2\,1} c_{2\,2n-2\,1} + d^{1\,2n-1\,1}_{2\,2n-2\,2} c_{2\,2n-2\,2} + d^{1\,2n-1\,1}_{0\,2n-1\,0} c_{0\,2n-1\,0} + d^{1\,2n-1\,1}_{1\,2n-2\,0} c_{0\,2n-2\,0} \\
&+ d^{1\,2n-1\,1}_{1\,2n-2\,1} c_{0\,2n-2\,1} + d^{1\,2n-1\,1}_{1\,2n\,0} c_{1\,2n\,0} + d^{1\,2n-1\,1}_{1\,2n\,1} c_{1\,2n\,1} + d^{1\,2n-1\,1}_{2\,2n-1\,0} c_{2\,2n-1\,0} \\
&+ d^{1\,2n-1\,1}_{2\,2n-1\,1} c_{2\,2n-1\,1} + d^{1\,2n-1\,1}_{2\,2n-1\,2} c_{2\,2n-1\,2} + d^{1\,2n-1\,1}_{1\,2n+1\,1} c_{1\,2n+1\,1} + d^{1\,2n-1\,1}_{2\,2n\,2} c_{2\,2n\,2} \\
&+ d^{1\,2n-1\,1}_{2\,2n\,1} c_{2\,2n\,1} + d^{1\,2n-1\,1}_{2\,2n\,0} c_{2\,2n\,0} + d^{1\,2n-1\,1}_{3\,2n-1\,1} c_{3\,2n-1\,1} + d^{1\,2n-1\,1}_{0\,2n-2\,0} c_{0\,2n-2\,0} \\
&+ d^{1\,2n-1\,1}_{1\,2n-3\,1} c_{1\,2n-3\,1}.
\end{aligned} \tag{7.174}$$

$\underline{l_1 = 1,\ l_2 = 2n-1,\ m = 0}$

$$
\begin{aligned}
&\tau_N \dot{c}_{1\,2n-1\,0} = \\
&d^{1\,2n-1\,0}_{0\,2n\,0} c_{0\,2n\,0} + d^{1\,2n-1\,0}_{1\,2n-1\,0} c_{1\,2n-1\,0} + d^{1\,2n-1\,0}_{2\,2n-2\,0} c_{2\,2n-2\,-1} \\
&+ d^{1\,2n-1\,0}_{2\,2n-2\,0} c_{2\,2n-2\,0} + d^{1\,2n-1\,0}_{2\,2n-2\,1} c_{2\,2n-2\,1} + d^{1\,2n-1\,0}_{0\,2n-1\,0} c_{0\,2n-1\,0} + d^{1\,2n-1\,0}_{1\,2n-2\,-1} c_{0\,2n-2\,-1} \\
&+ d^{1\,2n-1\,0}_{1\,2n-2\,0} c_{0\,2n-2\,0} + d^{1\,2n-1\,0}_{1\,2n-2\,1} c_{0\,2n-2\,1} + d^{1\,2n-1\,0}_{1\,2n\,-1} c_{1\,2n\,-1} + d^{1\,2n-1\,0}_{1\,2n\,0} c_{1\,2n\,0} \\
&+ d^{1\,2n-1\,0}_{1\,2n\,1} c_{1\,2n\,1} + d^{1\,2n-1\,0}_{2\,2n-1\,-1} c_{2\,2n-1\,-1} + d^{1\,2n-1\,0}_{2\,2n-1\,0} c_{2\,2n-1\,0} + d^{1\,2n-1\,0}_{2\,2n-1\,1} c_{2\,2n-1\,1} \\
&+ d^{1\,2n-1\,0}_{1\,2n+1\,0} c_{1\,2n+1\,0} + d^{1\,2n-1\,0}_{2\,2n\,1} c_{2\,2n\,1} + d^{1\,2n-1\,0}_{2\,2n\,0} c_{2\,2n\,0} + d^{1\,2n-1\,0}_{2\,2n\,-1} c_{2\,2n\,-1} \\
&+ d^{1\,2n-1\,0}_{3\,2n-1\,0} c_{3\,2n-1\,0} + d^{1\,2n-1\,0}_{0\,2n-2\,0} c_{0\,2n-2\,0} + d^{1\,2n-1\,0}_{1\,2n-3\,0} c_{1\,2n-3\,0}.
\end{aligned}
\tag{7.175}
$$

$\underline{l_1 = 1,\ l_2 = 2n-1,\ m = -1}$

$$
\begin{aligned}
&\tau_N \dot{c}_{1\,2n-1\,-1} = \\
&d^{1\,2n-1\,-1}_{0\,2n\,0} c_{0\,2n\,0} + d^{1\,2n-1\,-1}_{1\,2n-1\,-1} c_{1\,2n-1\,-1} + d^{1\,2n-1\,-1}_{2\,2n-2\,-2} c_{2\,2n-2\,-2} \\
&+ d^{1\,2n-1\,-1}_{2\,2n-2\,-1} c_{2\,2n-2\,-1} + d^{1\,2n-1\,-1}_{2\,2n-2\,0} c_{2\,2n-2\,0} + d^{1\,2n-1\,-1}_{0\,2n-1\,0} c_{0\,2n-1\,0} + d^{1\,2n-1\,-1}_{1\,2n-2\,-1} c_{0\,2n-2\,-1} \\
&+ d^{1\,2n-1\,-1}_{1\,2n-2\,0} c_{0\,2n-2\,0} + d^{1\,2n-1\,-1}_{1\,2n\,-1} c_{1\,2n\,-1} + d^{1\,2n-1\,-1}_{1\,2n\,0} c_{1\,2n\,0} + d^{1\,2n-1\,-1}_{2\,2n-1\,-2} c_{2\,2n-1\,-2} \\
&+ d^{1\,2n-1\,-1}_{2\,2n-1\,-1} c_{2\,2n-1\,-1} + d^{1\,2n-1\,-1}_{2\,2n-1\,0} c_{2\,2n-1\,0} + d^{1\,2n-1\,-1}_{1\,2n+1\,-1} c_{1\,2n+1\,-1} + d^{1\,2n-1\,-1}_{2\,2n\,0} c_{2\,2n\,0} \\
&+ d^{1\,2n-1\,-1}_{2\,2n\,-1} c_{2\,2n\,-1} + d^{1\,2n-1\,-1}_{2\,2n\,-2} c_{2\,2n\,-2} + d^{1\,2n-1\,-1}_{3\,2n-1\,-1} c_{3\,2n-1\,-1} + d^{1\,2n-1\,-1}_{0\,2n-2\,0} c_{0\,2n-2\,0} \\
&+ d^{1\,2n-1\,-1}_{1\,2n-3\,-1} c_{1\,2n-3\,-1}.
\end{aligned}
\tag{7.176}
$$

From Eq. (7.157) we have

$$\tau_N \dot{\mathbf{c}}_{2n} = \begin{pmatrix} \tau_N \dot{c}_{2n,0,0} \\ \tau_N \dot{c}_{(2n-1),1,-1} \\ \tau_N \dot{c}_{(2n-1),1,0} \\ \tau_N \dot{c}_{(2n-1),1,1} \\ \tau_N \dot{c}_{(2n-2),2,-2} \\ \tau_N \dot{c}_{(2n-2),2,-1} \\ \tau_N \dot{c}_{(2n-2),2,0} \\ \tau_N \dot{c}_{(2n-2),2,1} \\ \tau_N \dot{c}_{(2n-2),2,2} \\ \vdots \\ \tau_N \dot{c}_{0,2n,0} \end{pmatrix} = \mathbf{V}_{2n}\mathbf{c}_{2n-2} + \mathbf{R}_{2n}\mathbf{c}_{2n-1} + \mathbf{P}_{2n}\mathbf{c}_{2n} + \mathbf{S}_{2n}\mathbf{c}_{2n+1} + \mathbf{U}_{2n}\mathbf{c}_{2n+2}, \tag{7.177}$$

where from Eq. (7.158) and Eqs. (7.164) - (7.176), we have

$$
\mathbf{V}_{2n} = \left(\begin{array}{cccccccccccccc}
d^{2n\,0\,0}_{2n-2\,0\,0} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & 0 \\
d^{2n-1\,1\,-1}_{2n-2\,0\,0} & d^{2n-1\,1\,-1}_{2n-3\,1\,-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
d^{2n-1\,1\,0}_{2n-2\,0\,0} & 0 & d^{2n-1\,1\,0}_{2n-3\,1\,0} & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
d^{2n-1\,1\,1}_{2n-2\,0\,0} & 0 & 0 & d^{2n-1\,1\,1}_{2n-3\,1\,1} & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & d^{2n-2\,2\,-2}_{2n-3\,1\,-1} & 0 & 0 & d^{2n-2\,2\,-2}_{2n-4\,2\,-2} & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & d^{2n-2\,2\,-1}_{2n-3\,1\,-1} & d^{2n-2\,2\,-1}_{2n-3\,1\,0} & 0 & 0 & d^{2n-2\,2\,-1}_{2n-4\,2\,-1} & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
d^{2n-2\,2\,0}_{2n-2\,0\,0} & d^{2n-2\,2\,0}_{2n-3\,1\,-1} & d^{2n-2\,2\,0}_{2n-3\,1\,0} & d^{2n-2\,2\,0}_{2n-3\,1\,1} & 0 & 0 & d^{2n-2\,2\,0}_{2n-4\,2\,0} & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & d^{2n-2\,2\,1}_{2n-3\,1\,0} & d^{2n-2\,2\,1}_{2n-3\,1\,1} & 0 & 0 & 0 & d^{2n-2\,2\,1}_{2n-4\,2\,1} & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & d^{2n-2\,2\,2}_{2n-3\,1\,1} & 0 & 0 & 0 & 0 & d^{2n-2\,2\,2}_{2n-4\,2\,2} & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & d^{1\,2n-1\,-1}_{1\,2n-3\,-1} & 0 & 0 & d^{1\,2n-1\,-1}_{0\,2n-2\,0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & d^{1\,2n-1\,0}_{1\,2n-3\,0} & 0 & d^{1\,2n-1\,0}_{0\,2n-2\,0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & d^{1\,2n-1\,1}_{1\,2n-3\,1} & d^{1\,2n-1\,1}_{0\,2n-2\,0} \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & d^{0\,2n\,0}_{0\,2n-2\,0}
\end{array}\right), \tag{7.179}
$$

which in the notation of Appendix 7.B can be written as

$$
\mathbf{V}_{2n} = \left(\begin{array}{cccccccccccccc}
\bar{v}_{0\,2n\,0} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & 0 \\
v^{+}_{2n-1\,1\,-1} & \bar{v}_{1\,2n-1\,-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
v_{2n-1\,1\,0} & 0 & \bar{v}_{1\,2n-1\,0} & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
v^{-}_{2n-1\,1\,1} & 0 & 0 & \bar{v}_{1\,2n-1\,1} & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & v^{+}_{2n-2\,2\,-2} & 0 & 0 & \bar{v}_{2\,2n-2\,-2} & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & v_{2n-2\,2\,-1} & v^{+}_{2n-2\,2\,-1} & 0 & 0 & \bar{v}_{2\,2n-2\,-1} & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
\bar{v}_{2n-2\,2\,0} & v^{-}_{2n-2\,2\,0} & v_{2n-2\,2\,0} & v^{+}_{2n-2\,2\,0} & 0 & 0 & \bar{v}_{2\,2n-2\,0} & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & v^{-}_{2n-2\,2\,1} & v_{2n-2\,2\,1} & 0 & 0 & 0 & \bar{v}_{2\,2n-2\,1} & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & v^{-}_{2n-2\,2\,2} & 0 & 0 & 0 & 0 & \bar{v}_{2\,2n-2\,2} & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \bar{v}_{1\,2n-1\,-1} & 0 & 0 & v^{+}_{1\,2n-1\,-1} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & \bar{v}_{1\,2n-1\,0} & 0 & v_{1\,2n-1\,0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & \bar{v}_{1\,2n-1\,1} & v^{-}_{1\,2n-1\,1} \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & \bar{v}_{0\,2n\,0}
\end{array}\right), \tag{7.180}
$$

or

$$\mathbf{V}_{2n}\mathbf{c}_{2n-2} = \begin{pmatrix} \bar{\mathbf{v}}_{0\,2n} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{v}_{2n-1\,1} & \bar{\mathbf{v}}_{1\,2n-1} & \ddots & \ddots \\ \bar{\mathbf{v}}_{2n-2\,2} & \mathbf{v}_{2n-2\,2} & \ddots & \mathbf{0} \\ \mathbf{0} & \ddots & \ddots & \bar{\mathbf{v}}_{2n-2\,2} \\ \ddots & \ddots & \ddots & \mathbf{v}_{1\,2n-1} \\ \mathbf{0} & \ddots & \mathbf{0} & \bar{\mathbf{v}}_{0\,2n} \end{pmatrix}, \tag{7.181}$$

where for example

$$\bar{\mathbf{v}}_{0\,2n} = (\bar{v}_{0\,2n\,0})\,,\ \mathbf{v}_{2n-1\,1} = \begin{pmatrix} v^{+}_{2n-1\,1\,-1} \\ v_{2n-1\,1\,0} \\ v^{-}_{2n-1\,1\,1} \end{pmatrix},\ \bar{\mathbf{v}}_{2n-2\,2} = \begin{pmatrix} 0 \\ 0 \\ \bar{v}_{2n-2\,2\,0} \\ 0 \\ 0 \end{pmatrix},\ \bar{\mathbf{v}}_{1\,2n-1} = \begin{pmatrix} \bar{v}_{1\,2n-1\,-1} & 0 & 0 \\ 0 & \bar{v}_{1\,2n-1\,0} & 0 \\ 0 & 0 & \bar{v}_{1\,2n-1\,1} \end{pmatrix},\ \mathbf{v}_{2n-2\,2} = \begin{pmatrix} v^{+}_{2n-2\,2\,-2} & 0 & 0 \\ v_{2n-2\,2\,-1} & v^{+}_{2n-2\,2\,-1} & 0 \\ v^{-}_{2n-2\,2\,0} & v_{2n-2\,2\,0} & v^{+}_{2n-2\,2\,0} \\ 0 & v^{-}_{2n-2\,2\,1} & v_{2n-2\,2\,1} \\ 0 & 0 & v^{-}_{2n-2\,2\,2} \end{pmatrix}, \tag{7.182}$$

$$
\mathbf{R}_{2n} = \begin{pmatrix}
d^{2n\,0\,0}_{2n-1\,0\,0} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & 0 \\
d^{2n-1\,1\,-1}_{2n-1\,0\,0} & d^{2n-1\,1\,-1}_{2n-2\,1\,-1} & d^{2n-1\,1\,-1}_{2n-2\,1\,0} & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
d^{2n-1\,1\,0}_{2n-1\,0\,0} & d^{2n-1\,1\,0}_{2n-2\,1\,-1} & d^{2n-1\,1\,0}_{2n-2\,1\,0} & d^{2n-1\,1\,0}_{2n-2\,1\,1} & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
d^{2n-1\,1\,1}_{2n-1\,0\,0} & 0 & d^{2n-1\,1\,1}_{2n-2\,1\,0} & d^{2n-1\,1\,1}_{2n-2\,1\,1} & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & d^{2n-2\,2\,-2}_{2n-2\,1\,-1} & 0 & 0 & d^{2n-2\,2\,-2}_{2n-3\,2\,-2} & d^{2n-2\,2\,-2}_{2n-3\,2\,-1} & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & d^{2n-2\,2\,-1}_{2n-2\,1\,-1} & d^{2n-2\,2\,-1}_{2n-2\,1\,0} & 0 & d^{2n-2\,2\,-1}_{2n-3\,2\,-2} & d^{2n-2\,2\,-1}_{2n-3\,2\,-1} & d^{2n-2\,2\,-1}_{2n-3\,2\,0} & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & d^{2n-2\,2\,0}_{2n-2\,1\,-1} & d^{2n-2\,2\,0}_{2n-2\,1\,0} & d^{2n-2\,2\,0}_{2n-2\,1\,1} & 0 & d^{2n-2\,2\,0}_{2n-3\,2\,-1} & d^{2n-2\,2\,0}_{2n-3\,2\,0} & d^{2n-2\,2\,0}_{2n-3\,2\,1} & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & d^{2n-2\,2\,1}_{2n-2\,1\,0} & d^{2n-2\,2\,1}_{2n-2\,1\,1} & 0 & 0 & d^{2n-2\,2\,1}_{2n-3\,2\,0} & d^{2n-2\,2\,1}_{2n-3\,2\,1} & d^{2n-2\,2\,1}_{2n-3\,2\,2} & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & d^{2n-2\,2\,2}_{2n-2\,1\,1} & 0 & 0 & 0 & d^{2n-2\,2\,2}_{2n-3\,2\,1} & d^{2n-2\,2\,2}_{2n-3\,2\,2} & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & d^{1\,2n-1\,-1}_{1\,2n-2\,-1} & d^{1\,2n-1\,-1}_{1\,2n-2\,0} & 0 & d^{1\,2n-1\,-1}_{0\,2n-1\,0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & d^{1\,2n-1\,0}_{1\,2n-2\,-1} & d^{1\,2n-1\,0}_{1\,2n-2\,0} & d^{1\,2n-1\,0}_{1\,2n-2\,1} & d^{1\,2n-1\,0}_{0\,2n-1\,0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & d^{1\,2n-1\,1}_{1\,2n-2\,0} & d^{1\,2n-1\,1}_{1\,2n-2\,1} & d^{1\,2n-1\,1}_{0\,2n-1\,0} \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & d^{0\,2n\,0}_{0\,2n-1\,0}
\end{pmatrix}, \tag{7.183}
$$

which in the notation of Appendix 7.B can be written as

$$
\mathbf{R}_{2n} = \begin{pmatrix}
(r_{0\,2n\,0})^* & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & 0 \\
r^+_{2n-1\,1\,-1} & (r_{1\,2n-1\,-1})^* & (r^+_{1\,2n-1\,-1})^* & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
r_{2n-1\,1\,0} & (r^-_{1\,2n-1\,0})^* & (r_{1\,2n-1\,0})^* & (r^+_{1\,2n-1\,0})^* & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
r^-_{2n-1\,1\,1} & 0 & (r^-_{1\,2n-1\,1})^* & (r_{1\,2n-1\,1})^* & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & r^+_{2n-2\,2\,-2} & 0 & 0 & (r_{2\,2n-2\,-2})^* & (r^+_{2\,2n-2\,-2})^* & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & r_{2n-2\,2\,-1} & r^+_{2n-2\,2\,-1} & 0 & (r^-_{2\,2n-2\,-1})^* & (r_{2\,2n-2\,-1})^* & (r^+_{2\,2n-2\,-1})^* & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & r^-_{2n-2\,2\,0} & r_{2n-2\,2\,0} & r^+_{2n-2\,2\,0} & 0 & (r^-_{2\,2n-2\,0})^* & (r_{2\,2n-2\,0})^* & (r^+_{2\,2n-2\,0})^* & 0 & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & r^-_{2n-2\,2\,1} & r_{2n-2\,2\,1} & 0 & 0 & (r^-_{2\,2n-2\,1})^* & (r_{2\,2n-2\,1})^* & (r^+_{2\,2n-2\,1})^* & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & r^-_{2n-2\,2\,2} & 0 & 0 & 0 & (r^-_{2\,2n-2\,2})^* & (r_{2\,2n-2\,2})^* & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & r_{1\,2n-1\,-1} & r^+_{1\,2n-1\,-1} & 0 & (r^+_{2n-1\,1\,-1})^* \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & r^-_{1\,2n-1\,0} & r_{1\,2n-1\,0} & r^+_{1\,2n-1\,0} & (r_{2n-1\,1\,0})^* \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & r^-_{1\,2n-1\,1} & r_{1\,2n-1\,1} & (r^-_{2n-1\,1\,1})^* \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & r_{0\,2n\,0}
\end{pmatrix}, \tag{7.184}
$$

or

$$\mathbf{R}_{2n} = \begin{pmatrix} \mathbf{r}^*_{0\,2n} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{0} \\ \mathbf{r}_{2n-1\,1} & \mathbf{r}^*_{1\,2n-1} & \mathbf{0} & \mathbf{0} & \ddots & \ddots \\ \mathbf{0} & \mathbf{r}_{2n-2\,2} & \mathbf{r}^*_{2\,2n-2} & \mathbf{0} & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \mathbf{r}_{1\,2n-1} & \mathbf{r}^*_{2n-1\,1} \\ \mathbf{0} & \ddots & \ddots & \ddots & \mathbf{0} & \mathbf{r}_{0\,2n} \end{pmatrix}, \tag{7.185}$$

where for example

$$\mathbf{r}^*_{0\,2n} = \left((r_{0\,2n\,0})^*\right), \quad \mathbf{r}_{2n-1\,1} = \begin{pmatrix} r^+_{2n-1\,1\,-1} \\ r_{2n-1\,1\,0} \\ r^-_{2n-1\,1\,1} \end{pmatrix}, \quad \mathbf{r}^*_{1\,2n-1} = \begin{pmatrix} \left(r_{1\,2n-1\,-1}\right)^* & \left(r^+_{1\,2n-1\,-1}\right)^* & 0 \\ \left(r^-_{1\,2n-1\,0}\right)^* & \left(r_{1\,2n-1\,0}\right)^* & \left(r^+_{1\,2n-1\,0}\right)^* \\ 0 & \left(r^-_{1\,2n-1\,1}\right)^* & \left(r_{1\,2n-1\,1}\right)^* \end{pmatrix},$$

$$\mathbf{r}_{2n-2\,2} = \begin{pmatrix} r^+_{2n-2\,2\,-2} & 0 & 0 \\ r_{2n-2\,2\,-1} & r^+_{2n-2\,2\,-1} & 0 \\ r^-_{2n-2\,2\,0} & r_{2n-2\,2\,0} & r^+_{2n-2\,2\,0} \\ 0 & r^-_{2n-2\,2\,1} & r_{2n-2\,2\,1} \\ 0 & 0 & r^-_{2n-2\,2\,2} \end{pmatrix}, \quad \mathbf{r}^*_{2\,2n-2} = \begin{pmatrix} \left(r_{2\,2n-2\,-2}\right)^* & \left(r^+_{2\,2n-2\,-2}\right)^* & 0 & 0 & 0 \\ \left(r^-_{2\,2n-2\,-1}\right)^* & \left(r_{2\,2n-2\,-1}\right)^* & \left(r^+_{2\,2n-2\,-1}\right)^* & 0 & 0 \\ 0 & \left(r^-_{2\,2n-2\,0}\right)^* & \left(r_{2\,2n-2\,0}\right)^* & \left(r^+_{2\,2n-2\,0}\right)^* & 0 \\ 0 & 0 & \left(r^-_{2\,2n-2\,1}\right)^* & \left(r_{2\,2n-2\,1}\right)^* & \left(r^+_{2\,2n-2\,1}\right)^* \\ 0 & 0 & 0 & \left(r^-_{2\,2n-2\,2}\right)^* & \left(r_{2\,2n-2\,2}\right)^* \end{pmatrix}, \tag{7.186}$$

$$
\mathbf{P}_{2n} = \begin{pmatrix}
d^{2n00}_{2n00} & d^{2n00}_{2n-11-1} & d^{2n00}_{2n-110} & d^{2n00}_{2n-111} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & 0 \\
d^{2n-11-1}_{2n00} & d^{2n-11-1}_{2n-11-1} & 0 & 0 & d^{2n-11-1}_{2n-22-2} & d^{2n-11-1}_{2n-22-1} & d^{2n-11-1}_{2n-220} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \\
d^{2n-110}_{2n00} & 0 & d^{2n-110}_{2n-110} & 0 & 0 & d^{2n-110}_{2n-22-1} & d^{2n-110}_{2n-220} & d^{2n-110}_{2n-221} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \\
d^{2n-111}_{2n00} & 0 & 0 & d^{2n-111}_{2n-111} & 0 & 0 & d^{2n-111}_{2n-220} & d^{2n-111}_{2n-221} & d^{2n-111}_{2n-222} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \\
0 & d^{2n-22-2}_{2n-11-1} & 0 & 0 & d^{2n-22-2}_{2n-22-2} & 0 & 0 & 0 & 0 & d^{2n-22-2}_{2n-33-3} & d^{2n-22-2}_{2n-33-2} & d^{2n-22-2}_{2n-33-1} & 0 & 0 & 0 & 0 & \ddots & \ddots \\
0 & d^{2n-22-1}_{2n-11-1} & d^{2n-22-1}_{2n-110} & 0 & 0 & d^{2n-22-1}_{2n-22-1} & 0 & 0 & 0 & 0 & d^{2n-22-1}_{2n-33-2} & d^{2n-22-1}_{2n-33-1} & d^{2n-22-1}_{2n-330} & 0 & 0 & 0 & \ddots & \ddots \\
0 & d^{2n-220}_{2n-11-1} & d^{2n-220}_{2n-110} & d^{2n-220}_{2n-111} & 0 & 0 & d^{2n-220}_{2n-220} & 0 & 0 & 0 & 0 & d^{2n-220}_{2n-33-1} & d^{2n-220}_{2n-330} & d^{2n-220}_{2n-331} & 0 & 0 & \ddots & \ddots \\
0 & 0 & d^{2n-221}_{2n-110} & d^{2n-221}_{2n-111} & 0 & 0 & 0 & d^{2n-221}_{2n-221} & 0 & 0 & 0 & 0 & d^{2n-221}_{2n-330} & d^{2n-221}_{2n-331} & d^{2n-221}_{2n-332} & 0 & \ddots & \ddots \\
0 & 0 & 0 & d^{2n-222}_{2n-111} & 0 & 0 & 0 & 0 & d^{2n-222}_{2n-222} & 0 & 0 & 0 & 0 & d^{2n-222}_{2n-331} & d^{2n-222}_{2n-332} & d^{2n-222}_{2n-333} & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & d^{12n-1-1}_{22n-2-2} & d^{12n-1-1}_{22n-2-1} & d^{12n-1-1}_{22n-20} & 0 & 0 & d^{12n-1-1}_{12n-1-1} & 0 & 0 & d^{12n-1-1}_{02n0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & d^{12n-10}_{22n-2-1} & d^{12n-10}_{22n-20} & d^{12n-10}_{22n-21} & 0 & 0 & d^{12n-10}_{12n-10} & 0 & d^{12n-10}_{02n0} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & d^{12n-11}_{22n-20} & d^{12n-11}_{22n-21} & d^{12n-11}_{22n-22} & 0 & 0 & d^{12n-11}_{12n-11} & d^{12n-11}_{02n0} \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & d^{02n0}_{12n-1-1} & d^{02n0}_{12n-10} & d^{02n0}_{12n-11} & d^{02n0}_{02n0}
\end{pmatrix}, \qquad (7.187)
$$

which in the notation of Appendix 7.B can be written as

$$
\mathbf{P}_{2n} = \begin{pmatrix}
p_{2n00} & \bar{p}^{-}_{02n0} & \bar{p}_{02n0} & \bar{p}^{+}_{02n0} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & 0 \\
\bar{p}^{+}_{2n-11-1} & p_{2n-11-1} & 0 & 0 & \bar{p}^{-}_{12n-1-1} & \bar{p}_{12n-1-1} & \bar{p}^{+}_{12n-1-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \\
s\bar{p}_{2n-110} & 0 & p_{2n-110} & 0 & 0 & \bar{p}^{-}_{12n-10} & \bar{p}_{12n-10} & \bar{p}^{+}_{12n-10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \\
\bar{p}^{-}_{2n-111} & 0 & 0 & p_{2n-111} & 0 & 0 & \bar{p}^{-}_{12n-11} & \bar{p}_{12n-11} & \bar{p}^{+}_{12n-11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots \\
0 & \bar{p}^{+}_{2n-22-2} & 0 & 0 & p_{2n-22-2} & 0 & 0 & 0 & 0 & \bar{p}^{-}_{22n-2-2} & \bar{p}_{22n-2-2} & \bar{p}^{+}_{22n-2-2} & 0 & 0 & 0 & 0 & \ddots & \ddots \\
0 & \bar{p}_{2n-22-1} & \bar{p}^{+}_{2n-22-1} & 0 & 0 & p_{2n-22-1} & 0 & 0 & 0 & 0 & \bar{p}^{-}_{22n-2-1} & \bar{p}_{22n-2-1} & \bar{p}^{+}_{22n-2-1} & 0 & 0 & 0 & \ddots & \ddots \\
0 & \bar{p}^{-}_{2n-220} & \bar{p}_{2n-220} & \bar{p}^{+}_{2n-220} & 0 & 0 & p_{2n-220} & 0 & 0 & 0 & 0 & \bar{p}^{-}_{22n-20} & \bar{p}_{22n-20} & \bar{p}^{+}_{22n-20} & 0 & 0 & \ddots & \ddots \\
0 & 0 & \bar{p}^{-}_{2n-221} & \bar{p}_{2n-221} & 0 & 0 & 0 & p_{2n-221} & 0 & 0 & 0 & 0 & \bar{p}^{-}_{22n-21} & \bar{p}_{22n-21} & \bar{p}^{+}_{22n-21} & 0 & \ddots & \ddots \\
0 & 0 & 0 & \bar{p}^{-}_{2n-222} & 0 & 0 & 0 & 0 & p_{2n-222} & 0 & 0 & 0 & 0 & \bar{p}^{-}_{22n-22} & \bar{p}_{22n-22} & \bar{p}^{+}_{22n-22} & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \bar{p}^{-}_{12n-1-1} & \bar{p}_{12n-1-1} & \bar{p}^{+}_{12n-1-1} & 0 & 0 & p_{12n-1-1} & 0 & 0 & \bar{p}^{+}_{2n-11-1} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & \bar{p}^{-}_{12n-10} & \bar{p}_{12n-10} & \bar{p}^{+}_{12n-10} & 0 & 0 & p_{12n-10} & 0 & \bar{p}_{2n-110} \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & \bar{p}^{-}_{12n-11} & \bar{p}_{12n-11} & \bar{p}^{+}_{12n-11} & 0 & 0 & p_{12n-11} & \bar{p}^{-}_{2n-111} \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & \bar{p}^{-}_{02n0} & \bar{p}_{02n0} & \bar{p}^{+}_{02n0} & p_{02n0}
\end{pmatrix}, \qquad (7.188)
$$

or

$$\mathbf{P}_{2n} = \begin{pmatrix} \mathbf{p}_{2n\,0} & \bar{\mathbf{p}}_{0\,2n} & \mathbf{0} & \mathbf{0} & \ddots & \ddots & \mathbf{0} \\ \bar{\mathbf{p}}_{2n-1\,1} & \mathbf{p}_{2n-1\,1} & \bar{\mathbf{p}}_{1\,2n-1} & \mathbf{0} & \ddots & \ddots & \ddots \\ \mathbf{0} & \bar{\mathbf{p}}_{2n-2\,2} & \mathbf{p}_{2n-2\,2} & \bar{\mathbf{p}}_{2\,2n-2} & \ddots & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\ \ddots & \ddots & \ddots & \ddots & \bar{\mathbf{p}}_{1\,2n-1} & \mathbf{p}_{1\,2n-1} & \bar{\mathbf{p}}_{2n-1\,1} \\ \mathbf{0} & \ddots & \ddots & \ddots & \mathbf{0} & \bar{\mathbf{p}}_{0\,2n} & \mathbf{p}_{0\,2n} \end{pmatrix}, \tag{7.189}$$

where for example

$$\mathbf{p}_{2n\,0} = (p_{2n\,0\,0}), \quad \bar{\mathbf{p}}_{2n-1\,1} = \begin{pmatrix} \bar{p}^{+}_{2n-1\,1\,-1} \\ \bar{p}_{2n-1\,1\,0} \\ \bar{p}^{-}_{2n-1\,1\,1} \end{pmatrix}, \quad \bar{\mathbf{p}}_{0\,2n} = \begin{pmatrix} \bar{p}^{-}_{0\,2n\,0} & \bar{p}_{0\,2n\,0} & \bar{p}^{+}_{0\,2n\,0} \end{pmatrix}, \quad \mathbf{p}_{2n-1\,1} = \begin{pmatrix} p_{2n-1\,1\,-1} & 0 & 0 \\ 0 & p_{2n-1\,1\,0} & 0 \\ 0 & 0 & p_{2n-1\,1\,1} \end{pmatrix},$$

$$\bar{\mathbf{p}}_{2n-2\,2} = \begin{pmatrix} \bar{p}^{+}_{2n-2\,2\,-2} & 0 & 0 \\ \bar{p}_{2n-2\,2\,-1} & \bar{p}^{+}_{2n-2\,2\,-1} & 0 \\ \bar{p}^{-}_{2n-2\,2\,0} & \bar{p}_{2n-2\,2\,0} & \bar{p}^{+}_{2n-2\,2\,0} \\ 0 & \bar{p}^{-}_{2n-2\,2\,1} & \bar{p}_{2n-2\,2\,1} \\ 0 & 0 & \bar{p}^{-}_{2n-2\,2\,2} \end{pmatrix}, \quad \bar{\mathbf{p}}_{1\,2n-1} = \begin{pmatrix} \bar{p}^{-}_{1\,2n-1\,-1} & \bar{p}_{1\,2n-1\,-1} & \bar{p}^{+}_{1\,2n-1\,-1} & 0 & 0 \\ 0 & \bar{p}^{-}_{1\,2n-1\,0} & \bar{p}_{1\,2n-1\,0} & \bar{p}^{+}_{1\,2n-1\,0} & 0 \\ 0 & 0 & \bar{p}^{-}_{1\,2n-1\,1} & \bar{p}_{1\,2n-1\,1} & \bar{p}^{+}_{1\,2n-1\,1} \end{pmatrix}, \quad \mathbf{p}_{2n-2\,2} = \begin{pmatrix} p_{2n-2\,2\,-2} & 0 & 0 & 0 & 0 \\ 0 & p_{2n-2\,2\,-1} & 0 & 0 & 0 \\ 0 & 0 & p_{2n-2\,2\,0} & 0 & 0 \\ 0 & 0 & 0 & p_{2n-2\,2\,1} & 0 \\ 0 & 0 & 0 & 0 & p_{2n-2\,2\,2} \end{pmatrix},$$

$$\bar{\mathbf{p}}_{2\,2n-2} = \begin{pmatrix} \bar{p}^{-}_{2\,2n-2\,-2} & \bar{p}_{2\,2n-2\,-2} & \bar{p}^{+}_{2\,2n-2\,-2} & 0 & 0 & 0 & 0 \\ 0 & \bar{p}^{-}_{2\,2n-2\,-1} & \bar{p}_{2\,2n-2\,-1} & \bar{p}^{+}_{2\,2n-2\,-1} & 0 & 0 & 0 \\ 0 & 0 & \bar{p}^{-}_{2\,2n-2\,0} & \bar{p}_{2\,2n-2\,0} & \bar{p}^{+}_{2\,2n-2\,0} & 0 & 0 \\ 0 & 0 & 0 & \bar{p}^{-}_{2\,2n-2\,1} & \bar{p}_{2\,2n-2\,1} & \bar{p}^{+}_{2\,2n-2\,1} & 0 \\ 0 & 0 & 0 & 0 & \bar{p}^{-}_{2\,2n-2\,2} & \bar{p}_{2\,2n-2\,2} & \bar{p}^{+}_{2\,2n-2\,2} \end{pmatrix}, \tag{7.190}$$

$$
\mathbf{S}_{2n} = \begin{pmatrix}
d^{2n\,0\,0}_{2n+1\,0\,0} & d^{2n\,0\,0}_{2n\,1\,-1} & d^{2n\,0\,0}_{2n\,1\,0} & d^{2n\,0\,0}_{2n\,1\,1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 \\
0 & d^{2n-1\,1\,-1}_{2n\,1\,-1} & d^{2n-1\,1\,-1}_{2n\,1\,0} & 0 & d^{2n-1\,1\,-1}_{2n-1\,2\,-2} & d^{2n-1\,1\,-1}_{2n-1\,2\,-1} & d^{2n-1\,1\,-1}_{2n-1\,2\,0} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & d^{2n-1\,1\,0}_{2n\,1\,-1} & d^{2n-1\,1\,0}_{2n\,1\,0} & d^{2n-1\,1\,0}_{2n\,1\,1} & 0 & d^{2n-1\,1\,0}_{2n-1\,2\,-1} & d^{2n-1\,1\,0}_{2n-1\,2\,0} & d^{2n-1\,1\,0}_{2n-1\,2\,1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & d^{2n-1\,1\,1}_{2n\,1\,0} & d^{2n-1\,1\,1}_{2n\,1\,1} & 0 & 0 & d^{2n-1\,1\,1}_{2n-1\,2\,0} & d^{2n-1\,1\,1}_{2n-1\,2\,1} & d^{2n-1\,1\,1}_{2n-1\,2\,2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & d^{2n-2\,2\,-2}_{2n-1\,2\,-2} & d^{2n-2\,2\,-2}_{2n-1\,2\,-1} & 0 & 0 & 0 & d^{2n-2\,2\,-2}_{2n-2\,3\,-3} & d^{2n-2\,2\,-2}_{2n-2\,3\,-2} & d^{2n-2\,2\,-2}_{2n-2\,3\,-1} & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & d^{2n-2\,2\,-1}_{2n-1\,2\,-2} & d^{2n-2\,2\,-1}_{2n-1\,2\,-1} & d^{2n-2\,2\,-1}_{2n-1\,2\,0} & 0 & 0 & 0 & d^{2n-2\,2\,-1}_{2n-2\,3\,-2} & d^{2n-2\,2\,-1}_{2n-2\,3\,-1} & d^{2n-2\,2\,-1}_{2n-2\,3\,0} & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & d^{2n-2\,2\,0}_{2n-1\,2\,-1} & d^{2n-2\,2\,0}_{2n-1\,2\,0} & d^{2n-2\,2\,0}_{2n-1\,2\,1} & 0 & 0 & 0 & d^{2n-2\,2\,0}_{2n-2\,3\,-1} & d^{2n-2\,2\,0}_{2n-2\,3\,0} & d^{2n-2\,2\,0}_{2n-2\,3\,1} & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & d^{2n-2\,2\,1}_{2n-1\,2\,0} & d^{2n-2\,2\,1}_{2n-1\,2\,1} & d^{2n-2\,2\,1}_{2n-1\,2\,2} & 0 & 0 & 0 & d^{2n-2\,2\,1}_{2n-2\,3\,0} & d^{2n-2\,2\,1}_{2n-2\,3\,1} & d^{2n-2\,2\,1}_{2n-2\,3\,2} & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-2\,2\,2}_{2n-1\,2\,1} & d^{2n-2\,2\,2}_{2n-1\,2\,2} & 0 & 0 & 0 & 0 & d^{2n-2\,2\,2}_{2n-2\,3\,1} & d^{2n-2\,2\,2}_{2n-2\,3\,2} & d^{2n-2\,2\,2}_{2n-2\,3\,3} & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & d^{1\,2n-1\,-1}_{2\,2n-1\,-2} & d^{1\,2n-1\,-1}_{2\,2n-1\,-1} & d^{1\,2n-1\,-1}_{2\,2n-1\,0} & 0 & 0 & d^{1\,2n-1\,-1}_{1\,2n\,-1} & d^{1\,2n-1\,-1}_{1\,2n\,0} & 0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & d^{1\,2n-1\,0}_{2\,2n-1\,-1} & d^{1\,2n-1\,0}_{2\,2n-1\,0} & d^{1\,2n-1\,0}_{2\,2n-1\,1} & 0 & d^{1\,2n-1\,0}_{1\,2n\,-1} & d^{1\,2n-1\,0}_{1\,2n\,0} & d^{1\,2n-1\,0}_{1\,2n\,1} & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & d^{1\,2n-1\,1}_{2\,2n-1\,0} & d^{1\,2n-1\,1}_{2\,2n-1\,1} & d^{1\,2n-1\,1}_{2\,2n-1\,2} & 0 & d^{1\,2n-1\,1}_{1\,2n\,0} & d^{1\,2n-1\,1}_{1\,2n\,1} & 0 \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & d^{0\,2n\,0}_{1\,2n\,-1} & d^{0\,2n\,0}_{1\,2n\,0} & d^{0\,2n\,0}_{1\,2n\,1} & d^{0\,2n\,0}_{0\,2n+1\,0}
\end{pmatrix}, \quad (7.191)
$$

which in the notation of Appendix 7.B can be written as

$$
\mathbf{S}_{2n} = \begin{pmatrix}
s_{2n\,0\,0} & (s^-_{0\,2n\,0})^* & (s_{0\,2n\,0})^* & (s^+_{0\,2n\,0})^* & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 \\
0 & s_{2n-1\,1\,-1} & s^+_{2n-1\,1\,-1} & 0 & (s^-_{1\,2n-1\,-1})^* & (s_{1\,2n-1\,-1})^* & (s^+_{1\,2n-1\,-1})^* & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & s^-_{2n-1\,1\,0} & s_{2n-1\,1\,0} & s^+_{2n-1\,1\,0} & 0 & (s^-_{1\,2n-1\,0})^* & (s_{1\,2n-1\,0})^* & (s^+_{1\,2n-1\,0})^* & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & s^-_{2n-1\,1\,1} & s_{2n-1\,1\,1} & 0 & 0 & (s^-_{1\,2n-1\,1})^* & (s_{1\,2n-1\,1})^* & (s^+_{1\,2n-1\,1})^* & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & s_{2n-2\,2\,-2} & s^+_{2n-2\,2\,-2} & 0 & 0 & 0 & (s^-_{2\,2n-2\,-2})^* & (s_{2\,2n-2\,-2})^* & (s^+_{2\,2n-2\,-2})^* & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & s^-_{2n-2\,2\,-1} & s_{2n-2\,2\,-1} & s^+_{2n-2\,2\,-1} & 0 & 0 & 0 & (s^-_{2\,2n-2\,-1})^* & (s_{2\,2n-2\,-1})^* & (s^+_{2\,2n-2\,-1})^* & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & s^-_{2n-2\,2\,0} & s_{2n-2\,2\,0} & s^+_{2n-2\,2\,0} & 0 & 0 & 0 & (s^-_{2\,2n-2\,0})^* & (s_{2\,2n-2\,0})^* & (s^+_{2\,2n-2\,0})^* & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & s^-_{2n-2\,2\,1} & s_{2n-2\,2\,1} & s^+_{2n-2\,2\,1} & 0 & 0 & 0 & (s^-_{2\,2n-2\,1})^* & (s_{2\,2n-2\,1})^* & (s^+_{2\,2n-2\,1})^* & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & s^-_{2n-2\,2\,2} & s_{2n-2\,2\,2} & 0 & 0 & 0 & 0 & (s^-_{2\,2n-2\,2})^* & (s_{2\,2n-2\,2})^* & (s^+_{2\,2n-2\,2})^* & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & s^-_{1\,2n-1\,-1} & s_{1\,2n-1\,-1} & s^+_{1\,2n-1\,-1} & 0 & 0 & (s_{2n-1\,1\,-1})^* & (s^+_{2n-1\,1\,-1})^* & 0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & s^-_{1\,2n-1\,0} & s_{1\,2n-1\,0} & s^+_{1\,2n-1\,0} & 0 & (s^-_{2n-1\,1\,0})^* & (s_{2n-1\,1\,0})^* & (s^+_{2n-1\,1\,0})^* & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & s^-_{1\,2n-1\,1} & s_{1\,2n-1\,1} & s^+_{1\,2n-1\,1} & 0 & (s^-_{2n-1\,1\,1})^* & (s_{2n-1\,1\,1})^* & 0 \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & s^-_{0\,2n\,0} & s_{0\,2n\,0} & s^+_{0\,2n\,0} & (s_{2n\,0\,0})^*
\end{pmatrix}, \quad (7.192)
$$

or

$$
\mathbf{S}_{2n} = \begin{pmatrix}
\mathbf{s}_{2n\,0} & \mathbf{s}^*_{0\,2n} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{0} \\
\mathbf{0} & \mathbf{s}_{2n-1\,1} & \mathbf{s}^*_{1\,2n-1} & \mathbf{0} & \ddots & \ddots \\
\mathbf{0} & \mathbf{0} & \mathbf{s}_{2n-2\,2} & \mathbf{s}^*_{2\,2n-2} & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\
\mathbf{0} & \ddots & \ddots & \mathbf{0} & \mathbf{s}_{0\,2n} & \mathbf{s}^*_{2n\,0}
\end{pmatrix}, \quad (7.193)
$$

where for example

$$\mathbf{s}_{2n\,0} = \left(s_{2n\,0\,0}\right),$$

$$\mathbf{s}^*_{0\,2n} = \begin{pmatrix} \left(s^-_{0\,2n\,0}\right)^* & \left(s_{0\,2n\,0}\right)^* & \left(s^+_{0\,2n\,0}\right)^* \end{pmatrix},$$

$$\mathbf{s}_{2n-1\,1} = \begin{pmatrix} s_{2n-1\,1\,-1} & s^+_{2n-1\,1\,-1} & 0 \\ s^-_{2n-1\,1\,0} & s_{2n-1\,1\,0} & s^+_{2n-1\,1\,0} \\ 0 & s^-_{2n-1\,1\,1} & s_{2n-1\,1\,1} \end{pmatrix},$$

$$\mathbf{s}^*_{1\,2n-1} = \begin{pmatrix} \left(s^-_{1\,2n-1\,-1}\right)^* & \left(s_{1\,2n-1\,-1}\right)^* & \left(s^+_{1\,2n-1\,-1}\right)^* & 0 & 0 \\ 0 & \left(s^-_{1\,2n-1\,0}\right)^* & \left(s_{1\,2n-1\,0}\right)^* & \left(s^+_{1\,2n-1\,0}\right)^* & 0 \\ 0 & 0 & \left(s^-_{1\,2n-1\,1}\right)^* & \left(s_{1\,2n-1\,1}\right)^* & \left(s^+_{1\,2n-1\,1}\right)^* \end{pmatrix},$$

$$\mathbf{s}_{2n-2\,2} = \begin{pmatrix} s_{2n-2\,2\,-2} & s^+_{2n-2\,2\,-2} & 0 & 0 & 0 \\ s^-_{2n-2\,2\,-1} & s_{2n-2\,2\,-1} & s^+_{2n-2\,2\,-1} & 0 & 0 \\ 0 & s^-_{2n-2\,2\,0} & s_{2n-2\,2\,0} & s^+_{2n-2\,2\,0} & 0 \\ 0 & 0 & s^-_{2n-2\,2\,1} & s_{2n-2\,2\,1} & s^+_{2n-2\,2\,1} \\ 0 & 0 & 0 & s^-_{2n-2\,2\,2} & s_{2n-2\,2\,2} \end{pmatrix},$$

$$\mathbf{s}^*_{2\,2n-2} = \begin{pmatrix} \left(s^-_{2\,2n-2\,-2}\right)^* & \left(s_{2\,2n-2\,-2}\right)^* & \left(s^+_{2\,2n-2\,-2}\right)^* & 0 & 0 & 0 & 0 \\ 0 & \left(s^-_{2\,2n-2\,-1}\right)^* & \left(s_{2\,2n-2\,-1}\right)^* & \left(s^+_{2\,2n-2\,-1}\right)^* & 0 & 0 & 0 \\ 0 & 0 & \left(s^-_{2\,2n-2\,0}\right)^* & \left(s_{2\,2n-2\,0}\right)^* & \left(s^+_{2\,2n-2\,0}\right)^* & 0 & 0 \\ 0 & 0 & 0 & \left(s^-_{2\,2n-2\,1}\right)^* & \left(s_{2\,2n-2\,1}\right)^* & \left(s^+_{2\,2n-2\,1}\right)^* & 0 \\ 0 & 0 & 0 & 0 & \left(s^-_{2\,2n-2\,2}\right)^* & \left(s_{2\,2n-2\,2}\right)^* & \left(s^+_{2\,2n-2\,2}\right)^* \end{pmatrix}, \tag{7.194}$$

and

$$
\mathbf{U}_{2n} = \left(\begin{array}{cccccccccccccccccccccccccccccccccccccc}
d^{2n00}_{2n+200} & d^{2n00}_{2n+11-1} & d^{2n00}_{2n+110} & d^{2n00}_{2n+111} & 0 & 0 & d^{2n00}_{2n20} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 \\
0 & d^{2n-11-1}_{2n+11-1} & 0 & 0 & d^{2n-11-1}_{2n2-2} & d^{2n-11-1}_{2n2-1} & d^{2n-11-1}_{2n20} & 0 & 0 & 0 & 0 & d^{2n-11-1}_{2n-13-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & d^{2n-110}_{2n+110} & 0 & 0 & d^{2n-110}_{2n2-1} & d^{2n-110}_{2n20} & d^{2n-110}_{2n21} & 0 & 0 & 0 & 0 & d^{2n-110}_{2n-130} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & d^{2n-111}_{2n+111} & 0 & 0 & d^{2n-111}_{2n20} & d^{2n-111}_{2n21} & d^{2n-111}_{2n22} & 0 & 0 & 0 & 0 & d^{2n-111}_{2n-131} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & d^{2n-22-2}_{2n2-2} & 0 & 0 & 0 & 0 & d^{2n-22-2}_{2n-13-3} & d^{2n-22-2}_{2n-13-2} & d^{2n-22-2}_{2n-13-1} & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-22-2}_{2n-24-2} & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & d^{2n-22-1}_{2n2-1} & 0 & 0 & 0 & 0 & d^{2n-22-1}_{2n-13-2} & d^{2n-22-1}_{2n-13-1} & d^{2n-22-1}_{2n-130} & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-22-1}_{2n-24-1} & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & d^{2n-220}_{2n20} & 0 & 0 & 0 & 0 & d^{2n-220}_{2n-13-1} & d^{2n-220}_{2n-130} & d^{2n-220}_{2n-131} & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-220}_{2n-240} & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-221}_{2n21} & 0 & 0 & 0 & 0 & d^{2n-221}_{2n-130} & d^{2n-221}_{2n-131} & d^{2n-221}_{2n-132} & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-221}_{2n-241} & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-222}_{2n22} & 0 & 0 & 0 & 0 & d^{2n-222}_{2n-131} & d^{2n-222}_{2n-132} & d^{2n-222}_{2n-133} & 0 & 0 & 0 & 0 & 0 & 0 & d^{2n-222}_{2n-242} & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & d^{12n-1-1}_{320n-1-1} & 0 & 0 & 0 & 0 & d^{12n-1-1}_{22n-2} & d^{12n-1-1}_{22n-1} & d^{12n-1-1}_{22n0} & 0 & 0 & d^{12n-1-1}_{12n+1-1} & 0 & 0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & d^{12n-10}_{32n-10} & 0 & 0 & 0 & 0 & d^{12n-10}_{22n-1} & d^{12n-10}_{22n0} & d^{12n-10}_{22n1} & 0 & 0 & d^{12n-10}_{12n+10} & 0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & d^{12n-11}_{32n-11} & 0 & 0 & 0 & 0 & d^{12n-11}_{22n0} & d^{12n-11}_{22n1} & d^{12n-11}_{22n2} & 0 & 0 & d^{12n-11}_{12n+11} & 0 \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & 0 & 0 & d^{02n0}_{22n0} & 0 & 0 & d^{02n0}_{12n+1-1} & d^{02n0}_{12n+10} & d^{02n0}_{12n+11} & d^{02n0}_{02n+20}
\end{array}\right), \quad (7.195)
$$

which in the notation of Appendix 7.B can be written as

$$
\mathbf{U}_{2n} = \left(\begin{array}{cccccccccccccccccccccccccccccccccccccc}
\bar{u}_{2n00} & u^-_{2n00} & u_{2n00} & u^+_{2n00} & 0 & 0 & \bar{u}_{02n0} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 \\
0 & \bar{u}_{2n-11-1} & 0 & 0 & u^-_{2n-11-1} & u_{2n-11-1} & u^+_{2n-11-1} & 0 & 0 & 0 & 0 & \bar{u}_{12n-1-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & \bar{u}_{2n-110} & 0 & 0 & u^-_{2n-110} & u_{2n-110} & u^+_{2n-110} & 0 & 0 & 0 & 0 & \bar{u}_{12n-10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & \bar{u}_{2n-111} & 0 & 0 & u^-_{2n-111} & u_{2n-111} & u^+_{2n-111} & 0 & 0 & 0 & 0 & \bar{u}_{12n-11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & \bar{u}_{2n-22-2} & 0 & 0 & 0 & 0 & u^-_{2n-22-2} & u_{2n-22-2} & u^+_{2n-22-2} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{22n-2-2} & 0 & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & \bar{u}_{2n-22-1} & 0 & 0 & 0 & 0 & u^-_{2n-22-1} & u_{2n-22-1} & u^+_{2n-22-1} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{22n-2-1} & 0 & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{2n-220} & 0 & 0 & 0 & 0 & u^-_{2n-220} & u_{2n-220} & u^+_{2n-220} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{22n-20} & 0 & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{2n-221} & 0 & 0 & 0 & 0 & u^-_{2n-221} & u_{2n-221} & u^+_{2n-221} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{22n-21} & 0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{2n-222} & 0 & 0 & 0 & 0 & u^-_{2n-222} & u_{2n-222} & u^+_{2n-222} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{22n-22} & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \bar{u}_{12n-1-1} & 0 & 0 & 0 & 0 & u^-_{12n-1-1} & u_{12n-1-1} & u^+_{12n-1-1} & 0 & 0 & \bar{u}_{2n-11-1} & 0 & 0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & \bar{u}_{12n-10} & 0 & 0 & 0 & 0 & u^-_{12n-10} & u_{12n-10} & u^+_{12n-10} & 0 & 0 & \bar{u}_{2n-110} & 0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & \bar{u}_{12n-11} & 0 & 0 & 0 & 0 & u^-_{12n-11} & u_{12n-11} & u^+_{12n-11} & 0 & 0 & \bar{u}_{2n-111} & 0 \\
0 & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{02n0} & 0 & 0 & u^-_{02n0} & u_{02n0} & u^+_{02n0} & \bar{u}_{2n00}
\end{array}\right), \quad (7.196)
$$

or

$$
\mathbf{U}_{2n} = \begin{pmatrix}
\bar{\mathbf{u}}_{2n\,0} & \mathbf{u}_{2n\,0} & \bar{\mathbf{u}}_{0\,2n} & \mathbf{0} & \mathbf{0} & \ddots & \mathbf{0} \\
\mathbf{0} & \bar{\mathbf{u}}_{2n-1\,1} & \mathbf{u}_{2n-1\,1} & \bar{\mathbf{u}}_{1\,2n-1} & \mathbf{0} & \ddots & \ddots \\
\mathbf{0} & \mathbf{0} & \bar{\mathbf{u}}_{2n-2\,2} & \mathbf{u}_{2n-2\,2} & \bar{\mathbf{u}}_{2\,2n-2} & \ddots & \ddots \\
\ddots & \ddots & \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\
\mathbf{0} & \ddots & \ddots & \ddots & \bar{\mathbf{u}}_{0\,2n} & \mathbf{u}_{0\,2n} & \bar{\mathbf{u}}_{2n\,0}
\end{pmatrix}, \quad (7.197)
$$

where for example

$$
\begin{aligned}
\bar{\mathbf{u}}_{2n\,0} &= (\bar{u}_{2n\,0\,0})\,,\\
\mathbf{u}_{2n\,0} &= \begin{pmatrix} u^-_{2n\,0\,0} & u_{2n\,0\,0} & u^+_{2n\,0\,0} \end{pmatrix},\\
\bar{\mathbf{u}}_{2n-1\,1} &= \begin{pmatrix} \bar{u}_{2n-1\,1\,-1} & 0 & 0 \\ 0 & \bar{u}_{2n-1\,1\,0} & 0 \\ 0 & 0 & \bar{u}_{2n-1\,1\,1} \end{pmatrix},\\
\bar{\mathbf{u}}_{0\,2n} &= \begin{pmatrix} 0 & 0 & \bar{u}_{0\,2n\,0} & 0 & 0 \end{pmatrix},\\
\mathbf{u}_{2n-1\,1} &= \begin{pmatrix} u^-_{2n-1\,1\,-1} & u_{2n-1\,1\,-1} & u^+_{2n-1\,1\,-1} & 0 & 0 \\ 0 & u^-_{2n-1\,1\,0} & u_{2n-1\,1\,0} & u^+_{2n-1\,1\,0} & 0 \\ 0 & 0 & u^-_{2n-1\,1\,1} & u_{2n-1\,1\,1} & u^+_{2n-1\,1\,1} \end{pmatrix},\\
\bar{\mathbf{u}}_{2n-2\,2} &= \begin{pmatrix} \bar{u}_{2n-2\,2\,-2} & 0 & 0 & 0 & 0 \\ 0 & \bar{u}_{2n-2\,2\,-1} & 0 & 0 & 0 \\ 0 & 0 & \bar{u}_{2n-2\,2\,0} & 0 & 0 \\ 0 & 0 & 0 & \bar{u}_{2n-2\,2\,1} & 0 \\ 0 & 0 & 0 & 0 & \bar{u}_{2n-2\,2\,2} \end{pmatrix},\\
\bar{\mathbf{u}}_{1\,2n-1} &= \begin{pmatrix} 0 & 0 & \bar{u}_{1\,2n-1\,-1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{u}_{1\,2n-1\,0} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{u}_{1\,2n-1\,1} & 0 & 0 \end{pmatrix},\\
\mathbf{u}_{2n-2\,2} &= \begin{pmatrix} u^-_{2n-2\,2\,-2} & u_{2n-2\,2\,-2} & u^+_{2n-2\,2\,-2} & 0 & 0 & 0 & 0 \\ 0 & u^-_{2n-2\,2\,-1} & u_{2n-2\,2\,-1} & u^+_{2n-2\,2\,-1} & 0 & 0 & 0 \\ 0 & 0 & u^-_{2n-2\,2\,0} & u_{2n-2\,2\,0} & u^+_{2n-2\,2\,0} & 0 & 0 \\ 0 & 0 & 0 & u^-_{2n-2\,2\,1} & u_{2n-2\,2\,1} & u^+_{2n-2\,2\,1} & 0 \\ 0 & 0 & 0 & 0 & u^-_{2n-2\,2\,2} & u_{2n-2\,2\,2} & u^+_{2n-2\,2\,2} \end{pmatrix},\\
\bar{\mathbf{u}}_{2\,2n-2} &= \begin{pmatrix} 0 & 0 & \bar{u}_{2\,2n-2\,-2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{u}_{2\,2n-2\,-1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{u}_{2\,2n-2\,0} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{u}_{2\,2n-2\,1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \bar{u}_{2\,2n-2\,2} & 0 & 0 \end{pmatrix}.
\end{aligned}
\tag{7.198}
$$

7.G Calculation of the Initial Value Vectors $\mathbf{C}_n(0)$

Recall that the equilibrium averages $\langle M_{l_1\,l_2\,m}\rangle_i$ satisfy the time-independent recurrence relation

$$\tau_N \left\langle \dot{M}_{l_1\,l_2\,m} \right\rangle_i = \sum_{i,j=-2}^{2} \sum_{k=-1}^{1} d_{l_1+i\,l_2+j\,m+k}^{l_1\,l_2\,m} \langle M_{l_1+i\,l_2+j\,m+k}\rangle_i = 0. \tag{7.199}$$

We introduce the vector

$$\mathbf{F}_n^i = \begin{pmatrix} \mathbf{f}_{2n-1\,0}^i \\ \mathbf{f}_{2n-2\,1}^i \\ \vdots \\ \mathbf{f}_{0\,2n-1}^i \\ \mathbf{f}_{2n\,0}^i \\ \mathbf{f}_{2n-1\,1}^i \\ \vdots \\ \mathbf{f}_{0\,2n}^i \end{pmatrix}, \mathbf{f}_{n,m}^i = \begin{pmatrix} M_{n\,m\,-r}^i \\ M_{n\,m\,-r+1}^i \\ \vdots \\ M_{n\,m\,r}^i \end{pmatrix}, \tag{7.200}$$

where $r = \min[n, m]$ and the index i = I, II corresponds to the fields $\mathbf{H}_Z^{\mathrm{I}}$ and $\mathbf{H}_Z^{\mathrm{II}}$. We may thus transform Eq. (7.199) to the three term supermatrix recursion formula

$$\tau_N \frac{d}{dt}\mathbf{F}_n^i = \mathbf{Q}_n^- \mathbf{F}_{n-1}^i + \mathbf{Q}_n \mathbf{F}_n^i + \mathbf{Q}_n^+ \mathbf{F}_{n+1}^i = \mathbf{0}. \tag{7.201}$$

We seek the solution of Eq. (7.201) as

$$\mathbf{F}_n^i = \mathbf{T}_n^i \mathbf{F}_{n-1}^i, \tag{7.202}$$

where $\mathbf{T}_n^i$ is a transformation matrix. Using Eq. (7.202) we may rewrite Eq. (7.201) as

$$\mathbf{Q}_n^- \mathbf{F}_{n-1}^i + \mathbf{Q}_n \mathbf{T}_n^i \mathbf{F}_{n-1}^i + \mathbf{Q}_n^+ \mathbf{T}_{n+1}^i \mathbf{T}_n^i \mathbf{F}_{n-1}^i = \mathbf{0}, \tag{7.203}$$

which can be rewritten as

$$\left[\mathbf{Q}_n^- + \mathbf{Q}_n \mathbf{T}_n^i + \mathbf{Q}_n^+ \mathbf{T}_{n+1}^i \mathbf{T}_n^i\right] \mathbf{F}_{n-1}^i = \mathbf{0}. \tag{7.204}$$

$$\Rightarrow \left[\mathbf{Q}_n^- + \mathbf{Q}_n \mathbf{T}_n^i + \mathbf{Q}_n^+ \mathbf{T}_{n+1}^i \mathbf{T}_n^i\right] = \mathbf{0}. \tag{7.205}$$

$$\Rightarrow \mathbf{Q}_n^- = \left[-\mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{T}_{n+1}^i\right] \mathbf{T}_n^i. \tag{7.206}$$

Multiplying both sides of Eq. (7.206) by $\left[-\mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{T}_{n+1}^i\right]^{-1}$ we get

$$\left[-\mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{T}_{n+1}^i\right]^{-1} \mathbf{Q}_n^- = \mathbf{T}_n^i. \tag{7.207}$$

Recall from Eq. (4.42) that

$$\mathbf{S}_n(s) = \left[s\tau_N \mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{n+1}(s)\right]^{-1} \mathbf{Q}_n^- = \mathbf{\Delta}_n(s) \mathbf{Q}_n^-, \tag{7.208}$$

where $\mathbf{\Delta}_n(s)$ is given by

$$\begin{aligned} \mathbf{\Delta}_n(s) =& \left[s\tau_N \mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{n+1}(s)\right]^{-1} \\ =& \left[s\tau_N \mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{\Delta}_{n+1}(s) \mathbf{Q}_{n+1}^-\right]^{-1}, \end{aligned} \tag{7.209}$$

since

$$\mathbf{S}_{n+1}(s) = \mathbf{\Delta}_{n+1}(s) \mathbf{Q}_{n+1}^-. \tag{7.210}$$

With $s = 0$ in Eq. (7.208) we have

$$\mathbf{S}_n(0) = \left[-\mathbf{Q}_n - \mathbf{Q}_n^+ \mathbf{S}_{n+1}(0)\right]^{-1} \mathbf{Q}_n^- = \mathbf{\Delta}_n(0) \mathbf{Q}_n^-. \tag{7.211}$$

By comparing Eqs. (7.207) and (7.211) we can see that

$$\mathbf{T}_n^i = \mathbf{S}_n(0) = \mathbf{\Delta}_n(0) \mathbf{Q}_n^-. \tag{7.212}$$

Substituting Eq. (7.212) into Eq. (7.202) we get

$$\mathbf{F}_n^i = \mathbf{\Delta}_n(0)\mathbf{Q}_n^- \mathbf{F}_{n-1}^i. \tag{7.213}$$

Let $n = 0$ in Eq. (7.200)

$$\begin{aligned}\mathbf{F}_0^i &= \left(\mathbf{f}_{0\,0}^i\right) \\ &= \left(M_{0\,0\,0}^i\right) \\ &= \left(Y_{0\,0}(\vartheta_1, \varphi_1) Y_{0\,0}(\vartheta_2, \varphi_2)\right) \\ &= \left(\sqrt{\frac{1}{4\pi}}\sqrt{\frac{1}{4\pi}}\right) \\ &= \left(\frac{1}{4\pi}\right). \end{aligned} \tag{7.214}$$

Using Eq. (7.214) we can rewrite Eq. (7.213) as

$$\mathbf{F}_n^i = \mathbf{\Delta}_n(0)\mathbf{Q}_n^- \mathbf{F}_{n-1}^i = \mathbf{\Delta}_n^i(0)\,\mathbf{Q}_n^- \mathbf{\Delta}_{n-1}^i(0)\,\mathbf{Q}_n^- \ldots \mathbf{\Delta}_1^i(0)\,\mathbf{Q}_1^- \frac{1}{4\pi}, \tag{7.215}$$

Thus, we can write the initial vectors $\mathbf{C}_n(0)$ as

$$\mathbf{C}_n(0) = \mathbf{F}_n^{\mathrm{I}} - \mathbf{F}_n^{\mathrm{II}}. \tag{7.216}$$

7.H The Effective Relaxation Time $\tau_{\mathbf{ef}}$

We suppose that a weak external magnetic field, having been applied to the system in the infinite past, $t \to -\infty$, is suddenly switched off at time $t = 0$. We study the relaxation of a pair of macrospins, including the effect of dipole-dipole interaction, starting from an initial equilibrium state at $t = 0$. The effective relaxation time is defined as

$$\tau_{\mathrm{ef}} = -\frac{f(0)}{\dot{f}(0)}, \tag{7.217}$$

where the relaxation function, $f(t)$ is given by

$$f(t) = \langle\cos\vartheta_1\rangle(t) + \langle\cos\vartheta_2\rangle(t) - \langle\cos\vartheta_1\rangle_0 - \langle\cos\vartheta_2\rangle_0. \tag{7.218}$$

The initial value $f(0)$ is given by

$$f(0) = \langle \cos\vartheta_1 \rangle_\xi + \langle \cos\vartheta_2 \rangle_\xi - \langle \cos\vartheta_1 \rangle_0 - \langle \cos\vartheta_2 \rangle_0, \tag{7.219}$$

where $\langle \cos\vartheta_p \rangle_\xi$ and $\langle \cos\vartheta_p \rangle_0$ are the equilibrium ensemble averages corresponding to the Boltzmann distribution functions with the external field

$$W_\xi = Z_\xi^{-1} e^{\left[\sum\limits_p (\sigma \cos^2\vartheta_p + \xi\cos\vartheta_p) - \varsigma\cos\Xi\right]}, \tag{7.220}$$

and without the external field

$$W_0 = Z_0^{-1} e^{\left[\sum\limits_p \sigma \cos^2\vartheta_p + \varsigma\cos\Xi\right]}, \tag{7.221}$$

respectively. Here $\cos\Xi$ is by spherical trigonometry

$$\cos\Xi = 2\cos\vartheta_1\cos\vartheta_2 - \sin\vartheta_1\sin\vartheta_2\cos(\varphi_1 - \varphi_2). \tag{7.222}$$

Using Eq. (7.217) we may write

$$\frac{\tau_\mathrm{N}}{\tau_\mathrm{ef}} = -\tau_\mathrm{N}\frac{\dot{f}(0)}{f(0)}. \tag{7.223}$$

We consider the case of switching off the small permanent magnetic field (theory of linear response) at time $t = 0$. We have from the Landau-Lifshitz-Gilbert equation (see Eq. (2.404) in [34])

$$\sum_p \left[\tau_\mathrm{N}\frac{d}{dt}\langle\cos\vartheta_p\rangle(t) + \langle\cos\vartheta_p\rangle(t)\right] = \sum_p \left[\left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle(t) + \left\langle\frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle(t)\right], \tag{7.224}$$

where $E = -\sum_p \sigma \cos^2\vartheta_p - \varsigma \cos\Xi$. Using Eq. (7.224), we may write

$$\begin{aligned}
&\sum_p \left[\tau_{\mathrm{N}} \frac{d}{dt}\left(\langle\cos\vartheta_p\rangle(t) - \langle\cos\vartheta_p\rangle_0\right) + \langle\cos\vartheta_p\rangle(t) - \langle\cos\vartheta_p\rangle_0\right] \\
=&\sum_p \left[\left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle(t) - \left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_0 + \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle(t) - \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle_0\right].
\end{aligned} \tag{7.225}$$

Using Eqs. (7.218) and (7.225) we have

$$\begin{aligned}
\tau_N \dot{f}(t) =& \sum_p \tau_N \frac{d}{dt}\left[\langle\cos\vartheta_p\rangle(t) - \langle\cos\vartheta_p\rangle_0\right] \\
=& \sum_p \left[-\langle\cos\vartheta_p\rangle(t) + \langle\cos\vartheta_p\rangle_0 + \left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle(t)\right. \\
&\left. - \left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_0 + \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle(t) - \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle_0\right].
\end{aligned} \tag{7.226}$$

By taking $t = 0$ in Eq. (7.226) and noting that $\partial_{\varphi_1} E = -\partial_{\varphi_2} E$, we can substitute Eqs. (7.226) and (7.219) into Eq. (7.223) to get

$$\begin{aligned}
\frac{\tau_{\mathrm{N}}}{\tau_{\mathrm{ef}}} = -\frac{\tau_{\mathrm{N}}\dot{f}(0)}{f(0)} =& \frac{\sum_p \left[\langle\cos\vartheta_p\rangle_\xi - \langle\cos\vartheta_p\rangle_0 - \left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_\xi + \left\langle \frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_0\right]}{\sum_p \left(\langle\cos\vartheta_p\rangle_\xi - \langle\cos\vartheta_p\rangle_0\right)} \\
&+ \frac{\sum_p \left[-\left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle_\xi + \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_p}\right\rangle_0\right]}{\sum_p \left(\langle\cos\vartheta_p\rangle_\xi - \langle\cos\vartheta_p\rangle_0\right)} \\
=& \frac{\langle\cos\vartheta_1\rangle_\xi - \langle\cos\vartheta_1\rangle_0 + \langle\cos\vartheta_2\rangle_\xi - \langle\cos\vartheta_2\rangle_0}{\sum_p \left(\langle\cos\vartheta_p\rangle_\xi - \langle\cos\vartheta_p\rangle_0\right)} \\
&+ \frac{-\left\langle \frac{\sin\vartheta_1}{2}\frac{\partial E}{\partial\vartheta_1}\right\rangle_\xi + \left\langle \frac{\sin\vartheta_1}{2}\frac{\partial E}{\partial\vartheta_1}\right\rangle_0 - \left\langle \frac{\sin\vartheta_2}{2}\frac{\partial E}{\partial\vartheta_2}\right\rangle_\xi + \left\langle \frac{\sin\vartheta_2}{2}\frac{\partial E}{\partial\vartheta_2}\right\rangle_0}{\sum_p \left(\langle\cos\vartheta_p\rangle_\xi - \langle\cos\vartheta_p\rangle_0\right)} \\
&+ \frac{-\left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_1}\right\rangle_\xi + \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_1}\right\rangle_0 - \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_2}\right\rangle_\xi + \left\langle \frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_2}\right\rangle_0}{\sum_p \left(\langle\cos\vartheta_p\rangle_\xi - \langle\cos\vartheta_p\rangle_0\right)}
\end{aligned}$$

$$
\begin{aligned}
=&\frac{\langle\cos\vartheta_1\rangle_\xi-\langle\cos\vartheta_1\rangle_0+\langle\cos\vartheta_2\rangle_\xi-\langle\cos\vartheta_2\rangle_0}{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0\right)}\\
&+\frac{-\left\langle\frac{\sin\vartheta_1}{2}\frac{\partial E}{\partial\vartheta_1}\right\rangle_\xi+\left\langle\frac{\sin\vartheta_1}{2}\frac{\partial E}{\partial\vartheta_1}\right\rangle_0-\left\langle\frac{\sin\vartheta_2}{2}\frac{\partial E}{\partial\vartheta_2}\right\rangle_\xi+\left\langle\frac{\sin\vartheta_2}{2}\frac{\partial E}{\partial\vartheta_2}\right\rangle_0}{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0\right)}\\
&+\frac{-\left\langle\frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_1}\right\rangle_\xi+\left\langle\frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_1}\right\rangle_0+\left\langle\frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_1}\right\rangle_\xi-\left\langle\frac{1}{2\alpha}\frac{\partial E}{\partial\varphi_1}\right\rangle_0}{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0\right)}
\end{aligned}
$$

$$
\begin{aligned}
=&\frac{\langle\cos\vartheta_1\rangle_\xi-\langle\cos\vartheta_1\rangle_0+\langle\cos\vartheta_2\rangle_\xi-\langle\cos\vartheta_2\rangle_0}{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0\right)}\\
&+\frac{-\left\langle\frac{\sin\vartheta_1}{2}\frac{\partial E}{\partial\vartheta_1}\right\rangle_\xi+\left\langle\frac{\sin\vartheta_1}{2}\frac{\partial E}{\partial\vartheta_1}\right\rangle_0-\left\langle\frac{\sin\vartheta_2}{2}\frac{\partial E}{\partial\vartheta_2}\right\rangle_\xi+\left\langle\frac{\sin\vartheta_2}{2}\frac{\partial E}{\partial\vartheta_2}\right\rangle_0}{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0\right)}
\end{aligned}
$$

$$
=\frac{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0-\left\langle\frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_\xi+\left\langle\frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_0\right)}{\sum_p\left(\langle\cos\vartheta_p\rangle_\xi-\langle\cos\vartheta_p\rangle_0\right)}. \tag{7.227}
$$

For an arbitrary function A we have

$$
\begin{aligned}
&\langle A\rangle_\xi-\langle A\rangle_0\\
=&\langle A-\langle A\rangle_0\rangle_\xi\\
=&\frac{1}{Z_\xi}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left(\sum_p\left(\sigma\cos^2\vartheta_p+\xi\cos\vartheta_p\right)+\varsigma\cos\Xi\right)}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2\\
=&\frac{1}{Z_\xi}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}e^{\left[\xi\left(\cos\vartheta_1+\cos\vartheta_2\right)\right]}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2.
\end{aligned}
\tag{7.228}
$$

Since the external field parameter $\xi \ll 1$, we can approximate $\exp\left[\xi\left(\cos\vartheta_1+\cos\vartheta_2\right)\right]$ using the Taylor series expansion as

$$
e^{\left[\xi\left(\cos\vartheta_1+\cos\vartheta_2\right)\right]}\approx 1+\xi\left(\cos\vartheta_1+\cos\vartheta_2\right). \tag{7.229}
$$

Substituting Eq. (7.229) into Eq. (7.228) we obtain

$$
\begin{aligned}
&\langle A\rangle_\xi - \langle A\rangle_0 \\
\approx&\frac{1}{Z_\xi}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\left[1+\xi\left(\cos\vartheta_1+\cos\vartheta_2\right)\right]\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
=&\frac{1}{Z_\xi}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
&+\xi\frac{1}{Z_\xi}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\left(\cos\vartheta_1+\cos\vartheta_2\right)\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2.
\end{aligned}
\tag{7.230}
$$

Note that

$$
Z_0=\int_0^\pi\int_0^\pi e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2,
\tag{7.231}
$$

and

$$
\begin{aligned}
Z_\xi=&\int_0^\pi\int_0^\pi e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}e^{\left[\xi\left(\cos\vartheta_1+\cos\vartheta_2\right)\right]}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
\approx&\int_0^\pi\int_0^\pi e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\left[1+\xi\left(\cos\vartheta_1+\cos\vartheta_2\right)\right]\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
\approx&\int_0^\pi\int_0^\pi e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2,
\end{aligned}
\tag{7.232}
$$

since $\xi \ll 1$. Since from Eq. (7.232) we find that $Z_\xi \approx Z_0$ (through comparison of Eqs. (7.231) and (7.232)), Eq. (7.230) can be written as

$$
\begin{aligned}
\langle A\rangle_\xi - \langle A\rangle_0 \approx&\frac{1}{Z_0}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
&+\xi\frac{1}{Z_0}\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]e^{\left[\sum_p\left(\sigma\cos^2\vartheta_p\right)+\varsigma\cos\Xi\right]}\left(\cos\vartheta_1+\cos\vartheta_2\right)\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2. \\
=&\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]W_0\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
&+\xi\int_0^\pi\int_0^\pi\left[A-\langle A\rangle_0\right]\left(\cos\vartheta_1+\cos\vartheta_2\right)W_0\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2. \\
=&\langle A-\langle A\rangle_0\rangle_0+\xi\langle\left(A-\langle A\rangle_0\right)\left(\cos\vartheta_1+\cos\vartheta_2\right)\rangle_0.
\end{aligned}
\tag{7.233}
$$

Note that $\langle A - \langle A \rangle_0 \rangle_0 = \langle A \rangle_0 - \langle A \rangle_0 = 0$. Thus

$$\begin{aligned}\langle A \rangle_\xi - \langle A \rangle_0 \approx & \xi \langle (A - \langle A \rangle_0) (\cos\vartheta_1 + \cos\vartheta_2) \rangle_0 \\ = & \xi \langle A (\cos\vartheta_1 + \cos\vartheta_2) - \langle A \rangle_0 (\cos\vartheta_1 + \cos\vartheta_2) \rangle_0 \\ = & \xi \langle A (\cos\vartheta_1 + \cos\vartheta_2) \rangle_0 - \xi \langle A \rangle_0 \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0 . \end{aligned} \tag{7.234}$$

By using Eq. (7.234) we have for the denominator in Eq. (7.227)

$$\begin{aligned} & \sum_p \left[\langle \cos\vartheta_p \rangle_\xi - \langle \cos\vartheta_p \rangle_0 \right] \\ = & \sum_p \left[\xi \langle \cos\vartheta_p (\cos\vartheta_1 + \cos\vartheta_2) \rangle_0 - \xi \langle \cos\vartheta_p \rangle_0 \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0 \right] \\ = & \xi \left(\left\langle (\cos\vartheta_1 + \cos\vartheta_2)^2 \right\rangle_0 - \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0^2 \right) . \end{aligned} \tag{7.235}$$

Moreover we have (see numerator of Eq. (7.227))

$$\begin{aligned} & \left\langle \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_\xi - \left\langle \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_0 \\ = & \xi \left(\left\langle (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_0 - \left\langle \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_0 \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0 \right) . \end{aligned} \tag{7.236}$$

Eq. (7.227) may now be written as

$$\begin{aligned} \frac{\tau_{\mathrm{N}}}{\tau_{\mathrm{ef}}} = & \frac{\left\langle (\cos\vartheta_1 + \cos\vartheta_2)^2 \right\rangle_0 - \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0^2}{\left\langle (\cos\vartheta_1 + \cos\vartheta_2)^2 \right\rangle_0 - \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0^2} \\ & - \frac{\sum_p \left\langle (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_0 - \sum_p \left\langle \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_0 \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0}{\left\langle (\cos\vartheta_1 + \cos\vartheta_2)^2 \right\rangle_0 - \langle \cos\vartheta_1 + \cos\vartheta_2 \rangle_0^2} . \end{aligned} \tag{7.237}$$

The Maxwell-Boltzmann distribution W_0 is given by

$$W_0 = \frac{e^{-E}}{Z_0} . \tag{7.238}$$

Differentiating W_0 with respect to ϑ_p we have

$$\begin{aligned}\frac{\partial W_0}{\partial \vartheta_p} =& \frac{\partial}{\partial \vartheta_p}\left[\frac{e^{-E}}{Z_0}\right] \\ =& \frac{1}{Z_0}\left[e^{-E}\left(-\frac{\partial E}{\partial \vartheta_p}\right)\right] \\ =& - W_0 \frac{\partial E}{\partial \vartheta_p}. \end{aligned} \tag{7.239}$$

Using Eq. (7.239) and integrating by parts, we have

$$\begin{aligned}
&\sum_p \left\langle (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} \right\rangle_0 \\
=& \sum_p \int_0^\pi \int_0^\pi (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin\vartheta_p}{2} \frac{\partial E}{\partial \vartheta_p} W_0 \sin\vartheta_1 \sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
=& -\sum_p \int_0^\pi \int_0^\pi (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin\vartheta_p}{2} \frac{\partial W_0}{\partial \vartheta_p} \sin\vartheta_1 \sin\vartheta_2 d\vartheta_1 d\vartheta_2 \\
=& -\int_0^\pi \left[\int_0^\pi (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin^2\vartheta_1}{2} \frac{\partial W_0}{\partial \vartheta_1} d\vartheta_1\right] \sin\vartheta_2 d\vartheta_2 \\
&- \int_0^\pi \left[\int_0^\pi (\cos\vartheta_1 + \cos\vartheta_2) \frac{\sin^2\vartheta_2}{2} \frac{\partial W_0}{\partial \vartheta_2} d\vartheta_2\right] \sin\vartheta_1 d\vartheta_1 \\
=& -\frac{1}{2}\int_0^\pi (\cos\vartheta_1 + \cos\vartheta_2)\sin^2\vartheta_1 W_0\Big|_{\vartheta_1=0}^{\pi} \sin\vartheta_2 d\vartheta_2 \\
&+ \frac{1}{2}\int_0^\pi \int_0^\pi W_0 \frac{d}{d\vartheta_1}\left[(\cos\vartheta_1 + \cos\vartheta_2)\sin^2\vartheta_1\right] d\vartheta_1 \sin\vartheta_2 d\vartheta_2 \\
&- \frac{1}{2}\int_0^\pi (\cos\vartheta_1 + \cos\vartheta_2)\sin^2\vartheta_2 W_0\Big|_{\vartheta_2=0}^{\pi} \sin\vartheta_1 d\vartheta_1 \\
&+ \frac{1}{2}\int_0^\pi \int_0^\pi W_0 \frac{d}{d\vartheta_2}\left[(\cos\vartheta_1 + \cos\vartheta_2)\sin^2\vartheta_2\right] d\vartheta_2 \sin\vartheta_1 d\vartheta_1 \\
=& \frac{1}{2}\int_0^\pi \int_0^\pi W_0 \frac{d}{d\vartheta_1}\left[(\cos\vartheta_1 + \cos\vartheta_2)\sin^2\vartheta_1\right] d\vartheta_1 \sin\vartheta_2 d\vartheta_2 \\
&+ \frac{1}{2}\int_0^\pi \int_0^\pi W_0 \frac{d}{d\vartheta_2}\left[(\cos\vartheta_1 + \cos\vartheta_2)\sin^2\vartheta_2\right] d\vartheta_2 \sin\vartheta_1 d\vartheta_1 \\
=& \frac{1}{2}\int_0^\pi \int_0^\pi W_0 \left[(-\sin\vartheta_1)\sin^2\vartheta_1 + (\cos\vartheta_1 + \cos\vartheta_2)\, 2\sin\vartheta_1\cos\vartheta_1\right] d\vartheta_1 \sin\vartheta_2 d\vartheta_2 \\
&+ \frac{1}{2}\int_0^\pi \int_0^\pi W_0 \left[(-\sin\vartheta_2)\sin^2\vartheta_2 + (\cos\vartheta_1 + \cos\vartheta_2)\, 2\sin\vartheta_2\cos\vartheta_2\right] d\vartheta_2 \sin\vartheta_1 d\vartheta_1
\end{aligned}$$

$$
\begin{aligned}
=&\frac{1}{2}\int_0^\pi\int_0^\pi W_0\left[-\sin^2\vartheta_1+(\cos\vartheta_1+\cos\vartheta_2)\,2\cos\vartheta_1\right]\sin\vartheta_1\sin\vartheta_2 d\vartheta_1 d\vartheta_2\\
&+\frac{1}{2}\int_0^\pi\int_0^\pi W_0\left[-\sin^2\vartheta_2+(\cos\vartheta_1+\cos\vartheta_2)\,2\cos\vartheta_2\right]\sin\vartheta_2\sin\vartheta_1 d\vartheta_2 d\vartheta_1\\
=&\frac{1}{2}\left\langle-\sin^2\vartheta_1+2\cos^2\vartheta_1+2\cos\vartheta_1\cos\vartheta_2\right\rangle_0\\
&+\frac{1}{2}\left\langle-\sin^2\vartheta_2+2\cos^2\vartheta_2+2\cos\vartheta_1\cos\vartheta_2\right\rangle_0\\
=&\frac{1}{2}\left\langle-\sin^2\vartheta_1-\sin^2\vartheta_2+2\cos^2\vartheta_1+4\cos\vartheta_1\cos\vartheta_2+2\cos^2\vartheta_2\right\rangle_0\\
=&\frac{1}{2}\left\langle-\sin^2\vartheta_1-\sin^2\vartheta_2+2(\cos\vartheta_1+\cos\vartheta_2)^2\right\rangle_0\\
=&-\frac{1}{2}\left\langle\sin^2\vartheta_1+\sin^2\vartheta_2\right\rangle_0+\left\langle(\cos\vartheta_1+\cos\vartheta_2)^2\right\rangle_0.
\end{aligned}
\tag{7.240}
$$

In a similar manner we obtain

$$
\begin{aligned}
&\sum_p\left\langle\frac{\sin\vartheta_p}{2}\frac{\partial E}{\partial\vartheta_p}\right\rangle_0=-\sum_p\int_0^\pi\int_0^\pi\frac{\sin\vartheta_p}{2}\frac{\partial W_0}{\partial\vartheta_p}\sin\vartheta_1 d\vartheta_1\sin\vartheta_2 d\vartheta_2\\
=&-\frac{1}{2}\int_0^\pi\sin^2\vartheta_1 W_0\Big|_{\vartheta_1=0}^{\pi}\sin\vartheta_2 d\vartheta_2+\frac{1}{2}Z_0^{-1}\int_0^\pi\int_0^\pi W_0\frac{d}{d\vartheta}\left(\sin^2\vartheta_1\right)d\vartheta_1\sin\vartheta_2 d\vartheta_2\\
&-\frac{1}{2}\int_0^\pi\sin^2\vartheta_2 W_0\Big|_{\vartheta_2=0}^{\pi}\sin\vartheta_1 d\vartheta_1+\frac{1}{2}Z_0^{-1}\int_0^\pi\int_0^\pi W_0\frac{d}{d\vartheta}\left(\sin^2\vartheta_2\right)d\vartheta_2\sin\vartheta_1 d\vartheta_1\\
=&\langle\cos\vartheta_1+\cos\vartheta_2\rangle_0.
\end{aligned}
\tag{7.241}
$$

Substituting Eqs. (7.240) and (7.241) into Eq. (7.237) we obtain

$$
\frac{\tau_{\mathrm{N}}}{\tau_{\mathrm{ef}}}=\frac{\frac{1}{2}\left\langle\sin^2\vartheta_1+\sin^2\vartheta_2\right\rangle_0}{\left\langle(\cos\vartheta_1+\cos\vartheta_2)^2\right\rangle_0-\langle\cos\vartheta_1+\cos\vartheta_2\rangle_0^2}.
\tag{7.242}
$$

The effective relaxation time τ_{ef} is thus given by

$$
\tau_{\mathrm{ef}}=2\tau_{\mathrm{N}}\frac{\left\langle(\cos\vartheta_1+\cos\vartheta_2)^2\right\rangle_0-\langle\cos\vartheta_1+\cos\vartheta_2\rangle_0^2}{\left\langle\sin^2\vartheta_1+\sin^2\vartheta_2\right\rangle_0}.
\tag{7.243}
$$

7.I Wolfram Mathematica Code Used for the Calculation of the Observables

```
(*////////////////////////////////////////////////*)

(*
From the methods described in Appendix (7.D) of the
  thesis using the theory of angular momentum and the Clebsch-
 Gordan series as well as the expansion of the potential E_i
  in terms of spherical harmonics (Eq. (7.5) of thesis),
these are the various coefficients d^{l1,l2,m}_{l1+i,l2+j,m+k} for dipole-
  dipole interaction (they are listed in appendix 7.B of the thesis).
    Note that the variable I corresponds to the imaginary number √(-1) = i.
*)

(* d^{l1,l2,m}_{l1,l2,m} = p_{l1,l2,m} *)
p[l1_, l2_, m_, σ_] :=
  -((1/2) * l1 * (l1 + 1) - σ * ((l1 * (l1 + 1) - 3 * m^2) / ((2 * l1 - 1) * (2 * l1 + 3)))) -
   ((1/2) * l2 * (l2 + 1) - σ * ((l2 * (l2 + 1) - 3 * m^2) / ((2 * l2 - 1) * (2 * l2 + 3))));

(* d^{l1,l2,m}_{l1+2,l2,m}= ū_{l1,l2,m} *)
uhat[l1_, l2_, m_, σ_] := -σ * ((l1) / (2 * l1 + 3)) *
   Sqrt[((((l1 + 1)^2 - m^2) * ((l1 + 2)^2 - m^2)) / ((2 * l1 + 1) * (2 * l1 + 5)))];

(* d^{l1,l2,m}_{l1,l2-2,m}= v̄_{l1,l2,m} *)
vhat[l1_, l2_, m_, σ_] := σ * ((l2 + 1) / (2 * l2 - 1)) *
   Sqrt[((((l2)^2 - m^2) * ((l2 - 1)^2 - m^2)) / ((2 * l2 + 1) * (2 * l2 - 3)))];

(* d^{l1,l2,m}_{l1,l2+1,m}= s_{l2,l1,m} *)
s[l2_, l1_, m_, σ_, ξ_, ς_, α_] := -(((ξ) / (2)) * l2 + ((I * (σ - ς)) / (α)) * m) *
   Sqrt[(((l2 + 1)^2 - m^2) / (4 * (l2 + 1)^2 - 1))];

(* d^{l1,l2,m}_{l1-1,l2,m}= r_{l2,l1,m} *)
r1[l2_, l1_, m_, σ_, ξ_, ς_, α_] := (((ξ) / (2)) * (l1 + 1) + ((I * (σ - ς)) / (α)) * m) *
   Sqrt[(((l1)^2 - m^2) / (4 * (l1)^2 - 1))];

(* d^{l1,l2,m}_{l1+1,l2+1,m}= u_{l1,l2,m} *)
u[l1_, l2_, m_, σ_, ς_] := -ς * (l1 + l2) * Sqrt[((((l1 + 1)^2 - m^2) * ((l2 + 1)^2 - m^2)) /
      ((2 * l1 + 1) * (2 * l1 + 3) * (2 * l2 + 1) * (2 * l2 + 3)))];

(* d^{l1,l2,m}_{l1-1,l2-1,m}= v_{l1,l2,m} *)
v[l1_, l2_, m_, σ_, ς_] := ς * (l1 + l2 + 2) * Sqrt[((((l1)^2 - m^2) * ((l2)^2 - m^2)) /
      ((2 * l1 - 1) * (2 * l1 + 1) * (2 * l2 - 1) * (2 * l2 + 1)))];

(* d^{l1,l2,m}_{l1+1,l2-1,m}= p̄_{l1,l2,m} *)
phat[l1_, l2_, m_, σ_, ς_] :=
  ς * (l2 - l1 + 1) * Sqrt[((((l1 + 1)^2 - m^2) * ((l2)^2 - m^2)) /
      ((2 * l1 + 1) * (2 * l1 + 3) * (2 * l2 - 1) * (2 * l2 + 1)))];

(* Note that the variable pm only has values of ±1 where for example if pm =
 1 we get d^{l1,l2,m}_{l1+1,l2+1,m+1}= u^+_{l1,l2,m} and when  pm = -1 we get d^{l1,l2,m}_{l1+1,l2+1,m-1}= u^-_{l1,l2,m} *)
(* d^{l1,l2,m}_{l1+1,l2+1,m±1}= u^±_{l1,l2,m} *)
upm[l1_, l2_, m_, σ_, ς_, pm_] := -(1/4) * ς * (l1 + l2) *
   Sqrt[(((l1 + (pm) * m + 1) * (l1 + (pm) * m + 2) * (l2 + (pm) * m + 1) * (l2 + (pm) * m + 2)) /
```

```
    ((2 * l1 + 1) * (2 * l1 + 3) * (2 * l2 + 1) * (2 * l2 + 3)))];

(* d^{l1,l2,m}_{l1+1,l2-1,m±1}= p̄^{±}_{l1,l2,m} *)
phatpm[l1_, l2_, m_, σ_, ς_, pm_] := - (1/4) * ς * (l2 - l1 + 1) *
  Sqrt[(((l1 + (pm) * m + 1) * (l1 + (pm) * m + 2) * (l2 + (-pm) * m - 1) * (l2 + (-pm) * m)) /
    ((2 * l1 + 1) * (2 * l1 + 3) * (2 * l2 - 1) * (2 * l2 + 1)))];

(* d^{l1,l2,m}_{l1-1,l2-1,m±1}= v^{±}_{l1,l2,m} *)
vpm[l1_, l2_, m_, σ_, ς_, pm_] := (1/4) * ς * (l1 + l2 + 2) *
  Sqrt[(((l1 + (-pm) * m - 1) * (l1 + (-pm) * m) * (l2 + (-pm) * m - 1) * (l2 + (-pm) * m)) /
    ((2 * l1 - 1) * (2 * l1 + 1) * (2 * l2 - 1) * (2 * l2 + 1)))];

(* d^{l1,l2,m}_{l1,l2+1,m±1}= s^{±}_{l2,l1,m} *)
spm[l2_, l1_, m_, σ_, ς_, α_, pm_] := -pm * ((I * ς) / (4 * α)) *
  Sqrt[(((l2 + (pm) * m + 1) * (l2 + (pm) * m + 2) * (l1 + (pm) * m + 1) * (l1 + (-pm) * m)) /
    ((2 * l2 + 1) * (2 * l2 + 3)))];

(* d^{l1,l2,m}_{l1-1,l2,m±1}= r^{±}_{l2,l1,m} *)
rpm[l2_, l1_, m_, σ_, ς_, α_, pm_] := -pm * ((I * ς) / (4 * α)) *
  Sqrt[(((l2 + (pm) * m + 1) * (l2 + (-pm) * m) * (l1 + (-pm) * m - 1) * (l1 + (-pm) * m)) /
    ((2 * l1 - 1) * (2 * l1 + 1)))];

(*///////////////////////////////////////////////*)

(*The following functions make use of the coefficients d^{l1,l2,m}_{l1+i,l2+j,m+k} for dipole-
 dipole interaction defined earlier to generate the submatrices p_{n,m}, p̄_{n,m}, s_{n,m},
r_{n,m}, u_{n,m}, ū_{n,m}, v_{n,m}, v̄_{n,m} as defined in Eqs. (7.73) and (7.74) of the thesis.
  These will later in the code be used to generate the submatrices P_m,
R_m, S_m, V_m, U_m which make up the tridiagonal matrices Q^-_n,
Q_n and Q^+_n in the matrix three term recurrence relation *)

(* p_{n,m} *)
pmatrix[n_, m_, σ_] :=
  (Block[{A, r, rp, a, b, middlerow, middlecolumn},
    (* This variable controls the number of rows the submatrix will have. The
     Min[x_1,x_2,...] function yields the numerically smallest value of the x_i. *)
    r = Min[n, m];

    (*This variable controls the number of columns the
     submatrix will have. As described in appendix 7.C of the thesis,
    all the submatrices will have the same number of rows, namely,
    2*r+1. The number of columns is given as 2*r_x+1,
    however each submatrix defined has its own number r_x=Min[n+i,m+j],
    where the integers i and j will have different values
     for each submatrix as defined in appendix 7.C *)
    rp = Min[n, m];

    (* a and b are varables which will store the
     number of rows and columns respectively as calculated earlier.*)
    a = 2 * r + 1;
    b = 2 * rp + 1;

    (* A is defined here as a zero matrix to initialise the submatrix before
```

```
   assigning the coefficients to their appropriate positions in the matrix *)
  A = ConstantArray[0, {a, b}];

  middlerow = ((a - 1) / (2)) + 1;
  middlecolumn = ((b - 1) / (2)) + 1;


  (*Here we make use of the Switch[expr,form1,value1,form2,value2,...] function
   (which evaluates expr, then compares it with each of the formi in turn,
    evaluating and returning the valuei corresponding to the first match found)
     to assign the p_{l1,l2,m} coefficients to their appropriate positions in the
   p_{n,m} submatrix.*)
  (*In the case of the Switch function here,
  it is placed in a Table[expr,{i,imin,imax},{j,jmin,jmax}] function which
   will generate a nested list of the values of expr (where i is outermost)
    when i runs from imin to imax and for each i,j runs from jmin
   -jmax.*)

  (*The  output of this is a matrix
   containing all the evaluated terms based on the expr defined.*)
  (*The Switch function used here evaluates the difference between the values i
     and j for all their values through the execution of the Table function. If i-
    j = 0, then the Switch function will output the p[n,m,i,σ]
   function with the appropriate value of i that meets this condition,
  otherwise (the insertion of the form, _ , means that if i-j≠0,
     then we output 0).*)

  A = Table[Switch[i - j, 0, p[n, m, i, σ], _, 0], {i, -r, r}, {j, -rp, rp}];

  (*The function will return the matrix A.*)
  A

 ]);

(*---------------------------------------------*)

(* p̄_{n,m} *)
phatmatrix[n_, m_, σ_, ς_, α_] :=
  (Block[{A, r, rphat, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    rphat = Min[n + 1, m - 1];

    a = 2 * r + 1;
    b = 2 * rphat + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    (*As was done previously,
    the Switch function used here evaluates the difference between the values i
     and j for all their values through the execution of the Table function.*)
    (*If i-j = 0, then the Switch function will output the p[n,m,i,σ]
```

```
 function with the appropriate value of i that meets this condition.*)
(*This time however we have two other conditions to consider.*)
(*If i-j = -1,
then the function will output phatpm[n,m,i,σ,ς,1] (which is $\overline{p}^{+}_{n,m,i}$) and if i-j =
 1, the function will output phatpm[n,m,i,σ,ς,-1] (which is $\overline{p}^{-}_{n,m,i}$).*)
(*For the resulting matrix these two conditions will have the consequence
 of placing placing phatpm[n,m,i,σ,ς,-1] one row above phat[n,m,i,σ,ς] if
 the condition for it is met (i-j = -1) and placing phatpm[n,m,i,σ,ς,1]
 one row below phat[n,m,i,σ,ς] if the condition for it is met (i-j = 1)*)
A = Table[Switch[i - j, 0, phat[n, m, i, σ, ς], -1, phatpm[n, m, i, σ, ς, 1],
   1, phatpm[n, m, i, σ, ς, -1], _, 0], {i, -r, r}, {j, -rphat, rphat}];

A

]);

(* The basic procedure for constructing the submatrices $p_{n,m}$,
$\overline{p}_{n,m}$ described earlier apply to the rest of the submatrices $s_{n,m}$,
$r_{n,m}$, $u_{n,m}$, $\overline{u}_{n,m}$, $v_{n,m}$, $\overline{v}_{n,m}$*)

(*-----------------------------------------------*)

(* $\overline{u}_{n,m}$ *)
uhatmatrix[n_, m_, σ_] :=
 (Block[{A, r, ruhat, a, b, middlerow, middlecolumn},

   r = Min[n, m];
   ruhat = Min[n + 2, m];

   a = 2 * r + 1;
   b = 2 * ruhat + 1;
   A = ConstantArray[0, {a, b}];

   middlerow = ((a - 1) / (2)) + 1;
   middlecolumn = ((b - 1) / (2)) + 1;

   A = Table[Switch[i - j, 0, uhat[n, m, i, σ], _, 0], {i, -r, r}, {j, -ruhat, ruhat}];

   A

 ]);

(*-----------------------------------------------*)

(* $\overline{v}_{n,m}$ *)
vhatmatrix[n_, m_, σ_] :=
 (Block[{A, r, rvhat, a, b, middlerow, middlecolumn},

   r = Min[n, m];
   rvhat = Min[n, m - 2];

   a = 2 * r + 1;
   b = 2 * rvhat + 1;
   A = ConstantArray[0, {a, b}];
```

```
    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0, vhat[n, m, i, σ], _, 0], {i, -r, r}, {j, -rvhat, rvhat}];

    A

   ]);

(*---------------------------------------------*)

(* s_{n,m} *)
smatrix[n_, m_, σ_, ξ_, ς_, α_] :=
  (Block[{A, r, rs, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    rs = Min[n + 1, m];

    a = 2 * r + 1;
    b = 2 * rs + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0, s[n, m, i, σ, ξ, ς, α], -1, spm[n, m, i, σ, ς, α, 1],
       1, spm[n, m, i, σ, ς, α, -1], _, 0], {i, -r, r}, {j, -rs, rs}];

    A

   ]);

(*---------------------------------------------*)

 (* s*_{n,m} *)
sasterixmatrix[n_, m_, σ_, ξ_, ς_, α_] :=
  (Block[{A, r, rs, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    rs = Min[n + 1, m];

    a = 2 * r + 1;
    b = 2 * rs + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0,
       Conjugate[s[n, m, i, σ, ξ, ς, α]], -1, Conjugate[spm[n, m, i, σ, ς, α, 1]],
       1, Conjugate[spm[n, m, i, σ, ς, α, -1]], _, 0], {i, -r, r}, {j, -rs, rs}];

    A
```

```
  ]) ;

(*----------------------------------------------*)

(* r_{n,m} *)
rmatrix[n_, m_, σ_, ξ_, ς_, α_] :=
  (Block[{A, r, rr, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    rr = Min[n, m - 1];

    a = 2 * r + 1;
    b = 2 * rr + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0, r1[n, m, i, σ, ξ, ς, α], -1, rpm[n, m, i, σ, ς, α, 1],
       1, rpm[n, m, i, σ, ς, α, -1], _, 0], {i, -r, r}, {j, -rr, rr}];

    A

  ]) ;

(*----------------------------------------------*)

(* r*_{n,m} *)
rasterixmatrix[n_, m_, σ_, ξ_, ς_, α_] :=
  (Block[{A, r, rr, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    rr = Min[n, m - 1];

    a = 2 * r + 1;
    b = 2 * rr + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0,
       Conjugate[r1[n, m, i, σ, ξ, ς, α]], -1, Conjugate[rpm[n, m, i, σ, ς, α, 1]],
       1, Conjugate[rpm[n, m, i, σ, ς, α, -1]], _, 0], {i, -r, r}, {j, -rr, rr}];

    A

  ]) ;

(*----------------------------------------------*)

(* u_{n,m} *)
umatrix[n_, m_, σ_, ς_] :=
```

```
  (Block[{A, r, ru, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    ru = Min[n + 1, m + 1];

    a = 2 * r + 1;
    b = 2 * ru + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0, u[n, m, i, σ, ς], -1, upm[n, m, i, σ, ς, 1],
       1, upm[n, m, i, σ, ς, -1], _, 0], {i, -r, r}, {j, -ru, ru}];

    A

   ]);

(*----------------------------------------------*)

(* v_{n,m} *)
vmatrix[n_, m_, σ_, ς_] :=
  (Block[{A, r, rv, a, b, middlerow, middlecolumn},

    r = Min[n, m];
    rv = Min[n - 1, m - 1];

    a = 2 * r + 1;
    b = 2 * rv + 1;
    A = ConstantArray[0, {a, b}];

    middlerow = ((a - 1) / (2)) + 1;
    middlecolumn = ((b - 1) / (2)) + 1;

    A = Table[Switch[i - j, 0, v[n, m, i, σ, ς], -1, vpm[n, m, i, σ, ς, 1],
       1, vpm[n, m, i, σ, ς, -1], _, 0], {i, -r, r}, {j, -rv, rv}];

    A

   ]);

(*/////////////////////////////////////////////////*)

(*Here we define the submatrices P_m, R_m, S_m,
V_m, U_m which make up the Matrices Q_n^- , Q_n^+, Q_n*)
(*As was done previously in the case of the generation of submatrices p_{n,m},
p̄_{n,m}, s_{n,m}, r_{n,m}, u_{n,m}, ū_{n,m}, v_{n,m}, v̄_{n,m},
the Switch function used here evaluates the difference between the values
 i and j for all their values through the execution of the Table function,
leading to the creation of a matrix. This time however,
the output for each condition in the switch function will be a submatrix,
leading to the creation of a matrix of matrices. The result is then converted to a
 single flattened matrix through the use of the ArrayFlatten[...] function.*)
```

```
(* See Appendix 7.C for information on the structures of the matrices Pm,
Rm, Sm, Vm, Um *)

(* Pm *)
P[m_, σ_, ς_, α_] :=
 (Block[{A, i, j},

   A = ArrayFlatten[
     Table[Switch[i - j, 0, pmatrix[m - i, i, σ], -1, phatmatrix[i, m - i, σ, ς, α],
       1, phatmatrix[m - i, i, σ, ς, α], _, 0], {i, 0, m}, {j, 0, m}]];

   A
  ])

(*----------------------------------------------*)

(* Rm *)
R[m_, σ_, ξ_, ς_, α_] :=
 (Block[{A, i, j},

   A = ArrayFlatten[Table[Switch[j - i, 0, rmatrix[i, m - i, σ, ξ, ς, α], -1,
       rasterixmatrix[m - i, i, σ, ξ, ς, α], _, 0], {i, 0, m}, {j, 0, m - 1}]];

   A
  ])

(*----------------------------------------------*)

(* Sm *)
S[m_, σ_, ξ_, ς_, α_] :=
 (Block[{A, i, j},

   A = ArrayFlatten[Table[Switch[j - i, 0, sasterixmatrix[m - i, i, σ, ξ, ς, α],
       1, smatrix[i, m - i, σ, ξ, ς, α], _, 0], {i, 0, m}, {j, 0, m + 1}]];

   A
  ])

(*----------------------------------------------*)

(* Vm *)
V[m_, σ_, ς_] :=
 (Block[{A, i, j},

   A = ArrayFlatten[
     Table[Switch[j - i, 0, vhatmatrix[i, m - i, σ], -1, vmatrix[m - i, i, σ, ς],
       -2, vhatmatrix[m - i, i, σ], _, 0], {i, 0, m}, {j, 0, m - 2}]];

   A
  ])

(*----------------------------------------------*)

(* Um *)
```

```
U[m_, σ_, ς_] :=
 (Block[{A, i, j},

   A = ArrayFlatten[
     Table[Switch[i - j, 0, uhatmatrix[m - i, i, σ], -1, umatrix[m - i, i, σ, ς],
       -2, uhatmatrix[i, m - i, σ], _, 0], {i, 0, m}, {j, 0, m + 2}]];

   A
  ])

(*///////////////////////////////////////////////*)

(*Here we use the ArrayFlatten function again to construct the Q⁻n ,
Q⁺n, Qn matrices from the submatrices Pm, Rm,
Sm, Vm, Um in the manner seen in appendix 7.C*)

Qminus[n_, σ_, ξ_, ς_, α_] :=
  ArrayFlatten[{{V[2 * n - 1, σ, ς], R[2 * n - 1, σ, ξ, ς, α]}, {0, V[2 * n, σ, ς]}}];

(*---------------------------------------------*)

Q[n_, σ_, ξ_, ς_, α_] := ArrayFlatten[{{P[2 * n - 1, σ, ς, α], S[2 * n - 1, σ, ξ, ς, α]},
    {R[2 * n, σ, ξ, ς, α], P[2 * n, σ, ς, α]}}];

(*---------------------------------------------*)

Qplus[n_, σ_, ξ_, ς_, α_] :=
  ArrayFlatten[{{U[2 * n - 1, σ, ς], 0}, {S[2 * n, σ, ξ, ς, α], U[2 * n, σ, ς]}}];

(*///////////////////////////////////////////////*)

(*Here we define the two matrix continued fractions which
  are used in solving the differential-recurrence relation using
  the techniques described in section 4.6 of the the thesis. *)

(*The matrix continued fraction Sn represents Eq. (4.42) in the thesis where s = 0,
meaning that we solve for Sp(0).*)
(*The purpose of this matrix continued fraction
 which is Eq. (2.7.5) in the 4th edition of the book
 "The Langevin Equation: With Applications to Stochastic Problems in
   Physics, Chemistry and Electrical Engineering"  is to solve for
 the initial conditions vector Cn(0) through the use of Eqs. (2.7.15)
 (which is equivalent to Eq. (7.77) in the thesis) in the
 Langevin equation book and Eq. (7.78) in the thesis.*)

(* Sn *)
S[n_, t_, σ_, ξ_, ς_, α_] :=
  (Block[{B1, j},
    (*We start by defining a zero square matrix which will have
     the dimensions (4(t+1)^2 + 2(t+1) + 1) × (4(t+1)^2 + 2(t+1) + 1)*)
    (*t is an integer which defines for any matrix continued fraction Sn the
     number of iterations of the continued fraction that we see to evaluate,
    i.e. the continued fraction will iterate t-i times. For example,
    if we seek to evaluate S1 and we set t=10, then the continued fraction will
```

```
  be iterated on 10 times, whereas if we seek to evaluate S2 with t=10,
 the continued fraction will be iterated on 9 times *)

 B1 = Table[0, {(4 * (t + 1)^2 + 2 * (t + 1) + 1)}, {(4 * (t)^2 + 2 * (t) + 1)}];

 (*This for loop evaluates the matrix
   continued fraction by starting with the max iteration value j=t,
 and then iterating for decreasing values j=j-1, until we iterate the
  necessary number of times to obtain the answer we seek (Sn)*)
 (*For every iteration of the For loop, the variable B1 stores the
  previously evaluated answer so that it can be further iterated on.*)

 For[j = t, j ≥ n, j--,
  B1 = Inverse[-Q[j, σ, ξ, ς, α] - Qplus[j, σ, ξ, ς, α].B1].Qminus[j, σ, ξ, ς, α];
 ];

 B1
]);

(*-----------------------------------------------*)

(*The matrix continued fraction Δn represents Eq. (7.19) in the thesis *)
(* Δn is later used in Eq. (7.18) of the thesis to solve for C̃1(iω)*)

(* Δn *)
Δ[n_, t_, ω_, σ_, ξ_, ς_, α_] :=
 (Block[{B1, j},

  B1 = Table[0, {(4 * (t + 1)^2 + 2 * (t + 1) + 1)}, {(4 * (t + 1)^2 + 2 * (t + 1) + 1)}];

  For[j = t, j ≥ n, j--,
   B1 = Inverse[I * ω * IdentityMatrix[4 * j^2 + 2 * j + 1] -
      Q[j, σ, ξ, ς, α] - Qplus[j, σ, ξ, ς, α].B1.Qminus[j + 1, σ, ξ, ς, α]]
  ];

  B1
 ]);

(*///////////////////////////////////////////////*)

(* This function allows us to evaluate the initial value column vector Cn(0) *)
(*It is based on Eq. (7.78) in the thesis, *)
(*where we utilise Eq. (2.7.15) in the 4th edition of the
 book "The Langevin Equation: With Applications to Stochastic
   Problems in Physics, Chemistry and Electrical Engineering"
 to solve for F^I_n and F^II_n to ultimately obtain Cn(0)*)

(*This function will output a vector which will contain calculations of Cn(0) from n=
 1 to n=nm and them store them all in a single column vector of column vectors*)
C1[nm_, t_, σ_, ξI_, ξII_, ς_, α_] := (
  Block[{C1, C2, CV1, CV2, CR, res, k, l},
   (* This will store out evaluations of Cn(0) from n=1 to n=nm*)
   CR = {};
```

```
(* These correspond to F_n^i=1/(4π) *)
CV1 = {{1/(4*π)}}; CV2 = {{1/(4*π)}};

(*This do function evaluates F_n^I and F_n^II and then using the Join function,
the difference between them is stored in the vector CR. this is done from i=
 1 to i=nm, and the final result is that CR will
 contain all the evalations of C_n(θ) up to C_nm(θ)*)
Do[
 CV1 = S[i, t, σ, ξI, ς, α].CV1;
 CV2 = S[i, t, σ, ξII, ς, α].CV2;
 CR = Join[CR, CV1 - CV2], {i, 1, nm}];

(*For[k=1,k≤ nm,k++,

  CV1 = S[k,t,σ,ξI,ς,α].CV1;
  CV2 = S[k,t,σ,ξII,ς,α].CV1;

  CR=Join[CR,CV1-CV2];
 ];*)

CR
])

(*----------------------------------------------*)

(*This function make use of Eqs. (7.18),
(7.19) and (7.25) in the thesis to calculate
 the complex susceptibility χ(ω)=χ'(ω)-iχ''(ω)*)

χ[nm_, t_, σ_, ξI_, ξII_, ς_, α_, ω_] := (
 Block[{C1laplace, c1, Cn, res},

  (*This vector will store the output of C1 which is a
    vector that contains calculations of C_n(θ) from n=1 to n=nm*)
  c1 = C1[nm, t, σ, ξI, ξII, ς, α];

  C1laplace = Table[{0}, {4*(nm+1)^2 + 2*(nm+1) + 1}];

  Do[

   (*The vector which the function C1 is a vector contain the vectors C_1(θ) to C_nm
    (θ), *)(*but for every iteration we need one of them at a time, *)
   (*so we use the Take function to extract the individual vectors C_1(θ)
    to C_nm(θ) so that they can *)(*be used at the appropriate times in the
    calculation. In order to do this however, *)(*we need to know the range
    of values in the storage vector Cn that correspond to the each C_n(θ) *)
   (*vector. The length of the vector C_n(θ) is 4n^2+2n+1, so if nm = 2, *)
   (*C_2(θ) will have 21 entries and C_1(θ) will have 7 entries, *)
   (*meaning that the vector that stores these entires will have
    28 entries. So for the first iteration *)(*of the Do function,
   we take entries 28 to 8 in the Cn vector to extract , *)
   (*then for the second and final iteration, we take entries 7 to 1.*)
```

```
    (*To generalise this process for any nm value,
    for the first iteration onwards, *)(*we take entries j*
      (2-3*j+4*j^2)/3 to j*(8+9*j+4*j^2)/3 where j=nm,nm-1,nm-2,...,1 *)

    Cn = Take[c1, {j * (2 - 3 * j + 4 * j^2) / 3, j * (8 + 9 * j + 4 * j^2) / 3}];
    Print[TimeObject[]];
    (* Here we perform the calculation for C̃1(iω) through the use of Eq. (7.18). *)
    C1laplace = Δ[j, t, ω, σ, ξII, ς, α].(Cn + Qplus[j, σ, ξII, ς, α].C1laplace),
    {j, nm, 1, -1}];
   (* Here we use Eq. (7.25) to obtain the desired observable χ(ω)=χ'(ω)-iχ''(ω) *)
   res = 1 - i * ω * C1laplace[[1, 1]] / c1[[1, 1]];
   res
  ])

(*----------------------------------------------*)

(*This function make use of Eqs. (7.18),
(7.19) and (7.22) in the thesis to calculate the integral
 relaxation time τint. The procedure for this this is similar to
 the procedure for calculating χ(ω) in the previous function,
with the key differences being that now we are solving for C̃1(0) (ω=0) and
 the calculation at the end makes use of Eq. (7.22) instead of Eq. (7.25)  *)

τint[nm_, t_, σ_, ξI_, ξII_, ς_, α_] := (
  Block[{C1laplace, c1, Cn, res},

   c1 = C1[nm, t, σ, ξI, ξII, ς, α];

   C1laplace = Table[{0}, {4 * (nm + 1)^2 + 2 * (nm + 1) + 1}];

   Do[
    Cn = Take[c1, {j * (2 - 3 * j + 4 * j^2) / 3, j * (8 + 9 * j + 4 * j^2) / 3}];
    Print[TimeObject[]];

    C1laplace = Δ[j, t, 0., σ, ξII, ς, α].(Cn + Qplus[j, σ, ξII, ς, α].C1laplace),
    {j, nm, 1, -1}];
   (* Here we use Eq. (7.22) to obtain the desired observable τint *)
   res = C1laplace[[1, 1]] / c1[[1, 1]];
   res
  ])
```

8. Comparison of the Response for Dipole-Dipole Interaction to the Response for Exchange Interaction

We now compare the results of the response for dipole-dipole interaction with those for exchange interaction for the same value of the interaction parameter ς. Figure 8.1a shows the effect of ς on τ_{int} in linear response, i.e., the correlation time. Clearly the effect of increasing ς is generally to increase the relaxation time. However, for the particular circularly symmetric configuration studied the effect of dipole-dipole coupling is much more pronounced than that of exchange coupling for the same ς. Indeed, increase of ς exceeding ~ 1 causes a marked increase in τ_{int} for dipole-dipole coupling as compared to exchange coupling. A similar increase also occurs with exchange interaction. However, a much larger value of ς would now be needed relative to that for dipole-dipole coupling. Figure 8.1b shows the relaxation time as a function of ς, with the anisotropy or inverse temperature as a parameter. Again, for both types of interaction the tendency is to markedly increase the integral relaxation time with the enhancement effect being much greater for dipole-dipole rather than exchange interaction.

Figure 8.2 shows both τ_{int} and $\tau = 1/\lambda_1$ vs. the anisotropy (or inverse temperature) parameter σ. Without the external field, i.e., $h_{\text{II}} = 0$, the temperature dependence of τ_{int} (like $\tau = 1/\lambda_1$) has the customary Arrhenius behaviour, i.e., *exponentially increasing* with *decreasing temperature* (see Figure 8.2a), while the slopes of both $\tau_{\text{int}}(T^{-1})$ and $\tau(T^{-1})$ markedly depend on ς.

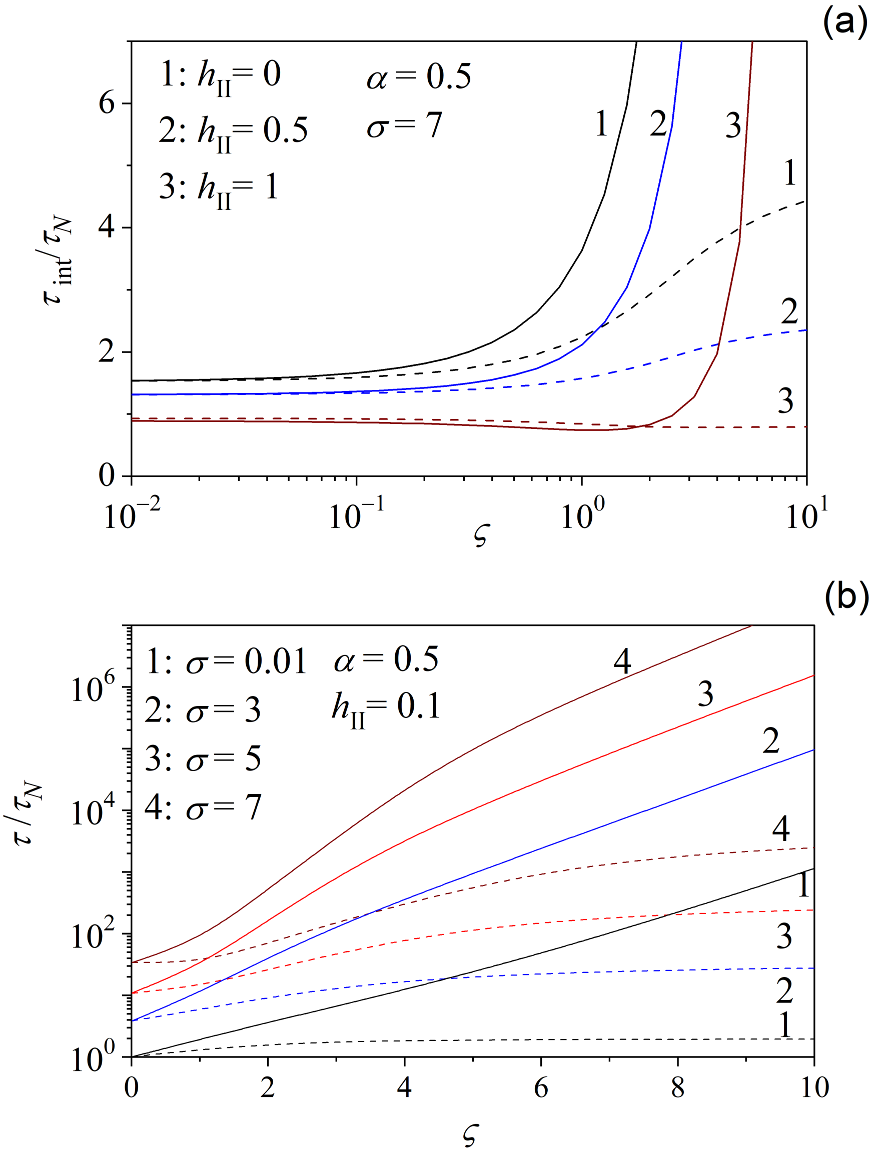

Figure 8.1: Integral relaxation time $\tau_{\rm int}/\tau_N$ as a function of the interaction parameter ς (a) for various external field parameters $h_{\rm II}$ subject to the linear response condition $h_{\rm I} - h_{\rm II} = 0.001$ and (b) for various σ and $h_{\rm I} = 0.101$, $h_{\rm II} = 0.1$; $\alpha = 0.5$. Solid and dashed lines: the matrix continued fraction solution for dipole-dipole and exchange interaction, respectively. Note the pronounced effect of dipole-dipole interaction (for the particular geometry considered), which for large ς greatly increases the relaxation time as compared to exchange interaction.

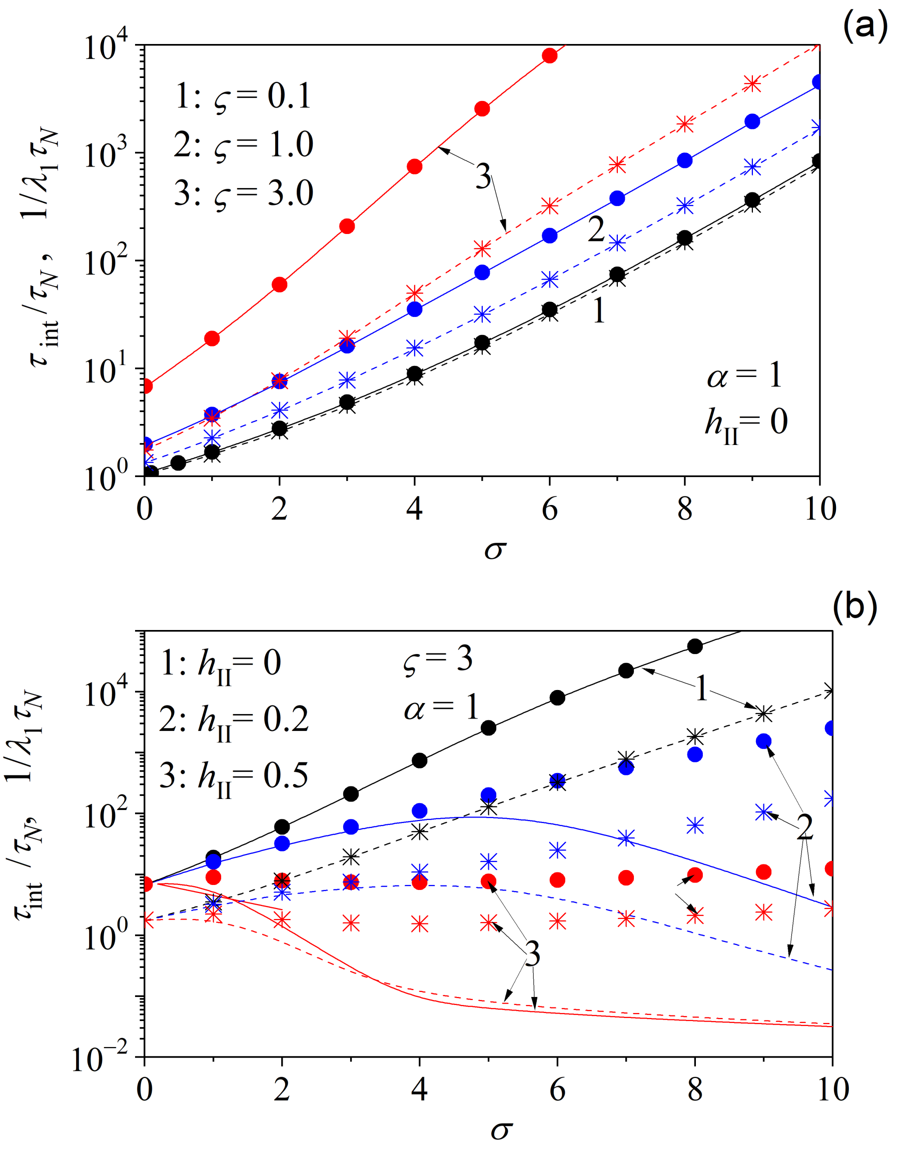

Figure 8.2: Integral relaxation time $\tau_{\rm int}/\tau_N$ (solid and dashed lines) and inverse smallest non-vanishing eigenvalue $(\lambda_1\tau_N)^{-1}$(circles and asterisks) vs. the anisotropy (inverse temperature) parameter σ (a) for various interaction parameters ς and $h_{\rm II} = 0$ and (b) for various external field parameters $h_{\rm II} = 0, 0.2, 0.5$ and $\varsigma = 3$ subject to the linear response condition $h_{\rm I} - h_{\rm II} = 0.001$. Solid and dashed lines: $\tau_{\rm int}/\tau_N$ calculated via the matrix continued fraction solution for dipole-dipole and exchange interactions, respectively; circles and asterisks: $(\lambda_1\tau_N)^{-1}$ calculated via the analytic matrix continued fraction solution for dipole-dipole and exchange interactions, respectively.

Notice that $\tau_{\rm int}$ and $\tau = 1/\lambda_1$ increase as the interaction parameter is raised, with the effect of dipole-dipole interaction again dominating. Furthermore with $h_{\rm II} = 0$, $\tau_{\rm int}$ provides an accurate approximation to the magnetization reversal time $\tau = 1/\lambda_1$. However, as the dc field increases, so that, taking zero exchange coupling described by a bistable potential as a particular example, the wells of the interaction potential now become markedly nonequivalent then $\tau_{\rm int}$ can *decrease* with *increasing* σ (see Figure 8.2b). Thus the (global) $\tau_{\rm int}$ may *differ exponentially* from the reversal time. This effect was first reported in [122, 123] and was qualitatively explained in [124] for an assembly of noninteracting uniaxial nanomagnets, i.e., for $\varsigma = 0$. In the low temperature limit, the effect is due to the depletion of the population of the shallower potential well consequent on the escape of many particles from that well and their subsequent descent to the deeper well from which it is very difficult for them to escape due to the high energy barrier. Thus $\tau_{\rm int}$ can now deviate considerably from the reversal time $\tau = 1/\lambda_1$ and so is no longer a good approximation to the latter (see Figure 8.2b).

The role played by interactions in the behaviour of the real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of the dynamic susceptibility $\chi(\omega)$ is shown in Figure 8.3a. The spectra $\chi'(\omega)$ and $\chi''(\omega)$ for dipole-dipole interaction resemble those for exchange interaction. Like noninteracting magnetic dipoles [2, 122], two distinct peaks appear in the spectra of the magnetic loss $\chi''(\omega)$. Their characteristic frequencies, i.e., where $\chi''(\omega)$ attains local maxima, are τ^{-1} and $\omega_{\rm pr}$ where $\omega_{\rm pr}$ is the precession frequency of the magnetic moment in the effective magnetic field near the bottom of the deepest well. The high-frequency peak is due to the (fast) near-degenerate intrawell modes which are virtually indistinguishable in the spectrum appearing as a single high frequency band. For small dc fields, the amplitude of the high-frequency peak is far weaker than that of the low-frequency one (see Figure 8.3b). However, in a strong dc field, the high-frequency intrawell modes can ultimately dominate the spectrum because as $h_{\rm II}$ increases, the magnitude of the low frequency band decreases and may even disappear altogether (curves 3).

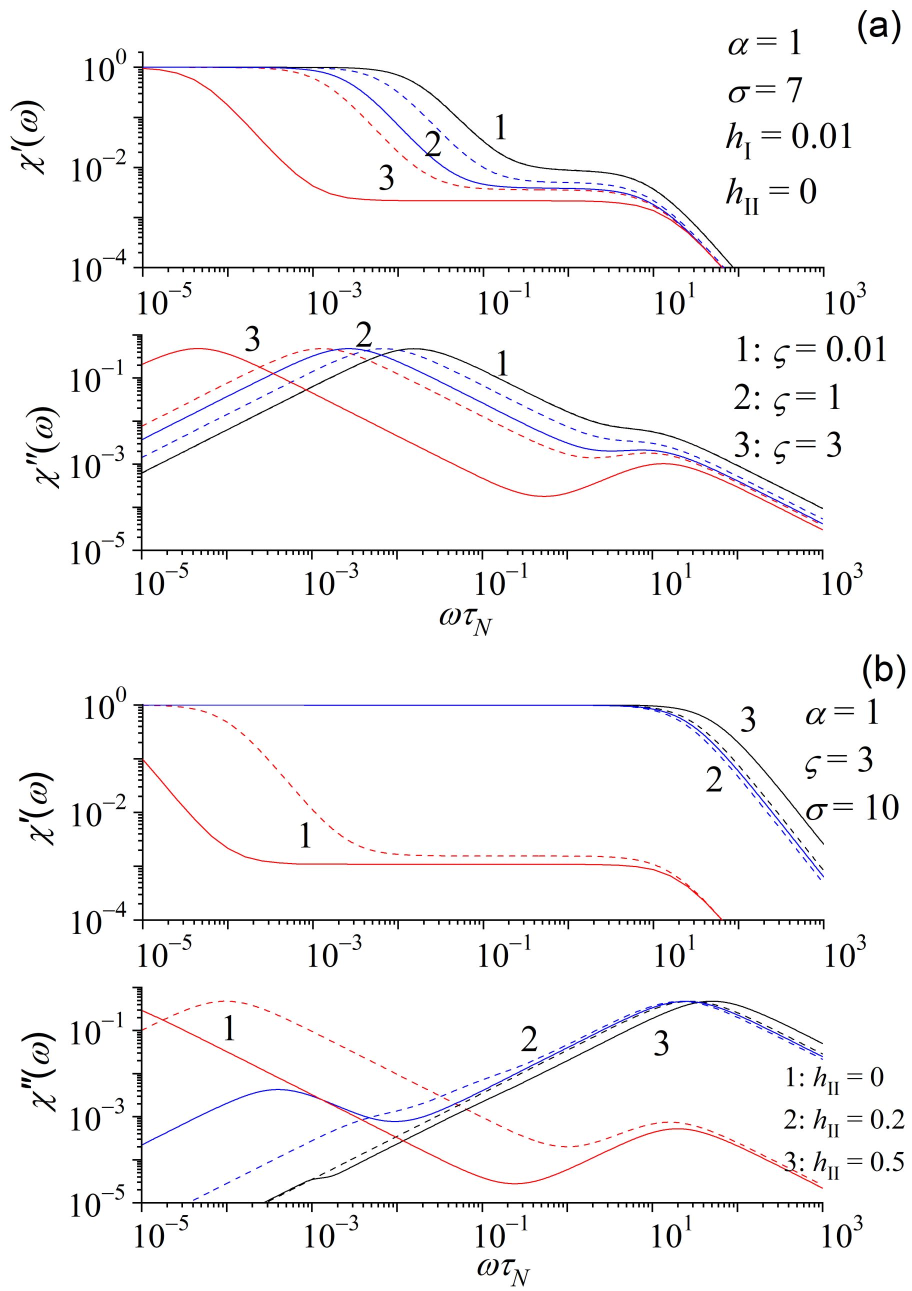

Figure 8.3: The real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of the complex susceptibility vs. $\omega\tau_N$ (a) for $\alpha = 1, \sigma = 7, h_{II} = 0$, and various interaction parameters $\varsigma = 0.01, 1.0$, and 3 and (b) for various external field parameters $h_{II} = 0, 0.2, 0.5$ and $\alpha = 1, \sigma = 10, \varsigma = 3$. Solid and dashed lines: the analytic matrix continued fraction solution for dipole-dipole and exchange interactions, respectively (the solid and dashed lines for $\varsigma = 0.01$ lie on top of each other).

This is again due to the depletion effect, which may be succinctly described as follows: in strong fields, at some critical value of h_{II}, the relaxation switches from being dominated by the slowest barrier-crossing or reversal mode to being dominated by the fast intrawell modes. As the low-frequency behaviour of $\chi''(\omega)$ is due to the exponentially slow barrier-crossing relaxation mode, the reversal time τ can be evaluated from the characteristic frequency ω_{max}, where $\chi''(\omega)$ attains a maximum, and/or the bandwidth $\Delta\omega$ of the spectrum of $\chi''(\omega)$ as

$$\tau \approx \omega_{\mathrm{max}} \approx \Delta\omega. \tag{8.1}$$

Comparison of τ as extracted from the spectra $\chi''(\omega)$ via Eq. (8.1) with $\tau = 1/\lambda_1$ as determined by an entirely independent method, viz. numerical calculation of the smallest non-vanishing eigenvalue λ_1 of the system, by solving the secular Eq. (7.28), demonstrates that both results are identical. In accordance with the previous figures, this maximum $\chi''(\omega)$ exhibits a more pronounced shift to lower frequencies for dipole-dipole interactions than for exchange ones.

9. Conclusions

It has been demonstrated how Budó's generalisation of the microscopic Debye theory of relaxation to a dielectric composed of complex molecules containing interacting rotating polar groups can be applied to anomalous diffusion in the presence of a weak microwave field in the non-inertial limit [19]. This is a good example of the role played by 2 body interactions in relaxation processes.

A second example is the relaxation of single-domain ferromagnetic particles. Here the relative effects of dipole-dipole and exchange interaction on the relaxation process have been considered, albeit in the most simple case where both easy axes of magnetisation are parallel to each other and also to the direction of the applied dc field [21]. Moreover the latter is taken as parallel to the reference Z-axis while the anisotropy is represented by the simplest possible uniaxial potential. This circumvents some of the considerable mathematical difficulties which are otherwise encountered. In both cases we commence with the appropriate Langevin equations and then for polar molecules, write a fractional Smoluchowski equation for the orientation distribution based on the continuous-time random walk *Ansatz*. This is accomplished via the non-inertial Langevin equations for the dynamics of a molecule consisting of two similar polar groups. These cannot rotate freely relative to one another owing to their mutual potential energy (causing hindered rotation). The fractional Smoluchowski equation is then converted to a scalar differential-recurrence relation for the statistical moments.

Furthermore for single-domain ferromagnetic particles, an exact system of equations for the statistical moments is derived. This is achieved by directly averaging (in the manner of Einstein) the Landau-Lifshitz-Gilbert equations with appropriate changes of variable as suggested by the form of the potential for the motion of the magnetisation augmented by a random field due to the heat bath over its realisations. Hence the calculation of the response is again reduced to solving a system of linear differential-recurrence relations for the statistical moments (averaged products of spherical harmonics). Once the respective differential-recurrence relations are obtained, one can then solve them by calculating successive convergents of continued fractions in the frequency domain for the appropriate relaxation responses. Furthermore, I have via the Appendices in Chapters 5 and 7 elaborated (in step by step fashion) on the derivation of all the relevant differential-recurrence relations from the respective Langevin equations. Moreover, I have shown in detail how they are solved via matrix continued fractions.

In particular for dielectrics, restriction to the linear response (following Budó) is enough to describe many dielectric phenomena in a liquid. The main advance consists in writing the *appropriate non-inertial Langevin equations*, thereby allowing consideration of two interacting dipole moments including anomalous diffusion. I have also given in detail the exact complex susceptibility for both normal and anomalous diffusion, now written as an easily calculated scalar continued fraction rather than as a sum of Debye or Cole-Cole mechanisms. Furthermore, as observed in Figures 6.1 and 6.3, the single mode Cole-Cole approximation provides a good representation of the exact susceptibility. Moreover the corrected Figure 6.2 alias of Figure 3 of the paper [19] shows this approximation is accurate for all σ_V of interest. The continued fraction solution also avoids the Sturm-Liouville problem encountered by Budó. As far as comparison with experiment, ample evidence exists of Cole-Cole like behaviour (as in Figure 6.2) in the low frequency dispersion and absorption of viscous liquids. See Chapter 5 of [49]. Notice that the version of the fractional Smoluchowski equation obtained is one where the jump lengths have a distribution with a *finite* variance. Also the waiting times are scale-free, with power-law exponent α. The latter determines the order of the fractional derivative. For such fractional models the relaxation of modes changes from exponential ($\alpha = 1$) to a Mittag-Leffler function decay, with power-law long-time tail in accordance with experimental observations in [49]. In the frequency domain this corresponds to the Cole-Cole equation [2]. For a discussion of alternative models see [125].

For single-domain ferromagnetic particles, it can be seen that the solution is subject to considerable symmetry-based restrictions. Therefore, it can be reasonably argued that such a model cannot provide a reliable description of the many spin relaxation problem. Nevertheless, even that *drastically simplified* configuration exemplifies the relative roles of dipole-dipole and exchange interactions. The main conclusion is that including them causes a marked increase in the reversal time. As we noted the particular case of parallel easy axes (also parallel to the direction of the applied dc field) is analysed merely to simplify the calculations. Then the dipole-dipole interaction between the particles increases the effective energy barrier for the magnetisation reversal leading to the results described above. However due to the anisotropic nature of that interaction one may expect completely different behaviour if the external magnetic field makes an arbitrary angle with respect to the line connecting the particle centres. This conclusion may be justified along the following lines. In linear response the reversal time is effectively the *correlation time*, i.e., a *global* feature of the response indicating that additional high frequency modes (due to exchange and dipole interactions over and above those appearing without such interactions) now contribute to the magnetisation decay. This conclusion is analytically supported by that of Zwanzig [17] (based on a lattice model) that dipole-dipole interactions give rise to a discrete set of relaxation times. For example, in his model [17] permanent point *electric* dipoles of moment $\boldsymbol{\mu}$ are located at the sites of a rigid cubic lattice. Consequently, one finds from his Eq. (6) for the complex susceptibility at high temperatures that (in his notation) the integral relaxation time is given by

$$\frac{\tau_{\text{int}}}{\tau} \approx 1 + \frac{4}{3}\pi\rho\alpha + \left[\frac{16\pi^2}{9} + \left(\frac{5}{6} - \frac{3}{128\pi^2}\right) R\right] (\rho\alpha)^2 + \left[\frac{64\pi^3}{27} + \left(\frac{68\pi}{27} - \frac{1}{24\pi}\right) R\right] (\rho\alpha)^3 + O(\rho\alpha)^4. \tag{9.1}$$

Here ρ is the number of dipoles per unit volume of the lattice, R is a certain lattice sum which is about 16.8 for a simple cubic lattice $\alpha = \mu^2/(3kT)$ and τ is the *relaxation time associated with the rotational Brownian motion of a non-interacting dipole (Debye* 1^{st} *model).* Although the Néel (overbarrier) mechanism is blocked, the value of this expression in the magnetic relaxation context is that it may be directly applied to dipole-dipole coupling effects by simply replacing electric quantities by the corresponding magnetic ones. This obviously cannot be done if the Néel mechanism is active because then the dipole-dipole coupling will affect the overbarrier process. Similar conclusions were drawn by Déjardin [126] via Berne's theory of interacting electric dipoles [127] adapted to spins. A reference made by Zwanzig [17] to unpublished calculations of J.I. Lauritzen, where the elementary process is the flip of a single dipole and all other dipole interactions are ignored, save electrostatic ones, is highly relevant to this case.

The theory presented may serve as a basis for future development. For the Budó model utilised for polar dielectrics, future researchers may seek to extend it to include inertial effects for both normal and anomalous diffusion via the Fokker-Planck equation in the phase space of configurations and momenta. In other words the rotational Klein-Kramers equation obtained from the inertial Langevin equations rather than the non-inertial ones which suffice for the low frequencies considered here. Such a procedure allows one to consider high-frequency effects such as the resonant (or Poley) absorption [2] in the far infrared due to the inertia of the molecules. This absorption could then be ascribed to hindered rotation combined with inertia giving rise to small oscillations of the groups relative to each other.

For single-domain ferromagnetic particles, it should be reiterated that throughout the calculations the two-spin problem is treated where the two easy axes are both parallel to each other and to the applied field. The general situation of an arbitrary angle between the easy axes (when the symmetry is broken) can be treated in like manner, however with much more difficulty because of the extra index in the governing recurrence relations. Nevertheless, even the simplified solution will provide a useful benchmark with which the more general solution must agree in the appropriate limit. Thus the calculations outlined can serve as a precursor to analysis of the high temperature dipole lattice including the anisotropy-Zeeman energy.

Notice that only a bare outline of the many involved calculations in both the dielectric and magnetic cases has been given in the two published papers:

(a) Generalization to anomalous diffusion of Budó's treatment of polar molecules containing interacting rotating groups by Serguey V. Titov, William T. Coffey, Marios Zarifakis, Yuri P. Kalmykov, Mohammad H. Al Bayyari, and William J. Dowling, published by "The Journal Of Chemical Physics" (Volume 153, Issue 4, Page 044128) in 2020.

(b) Dipole-dipole and exchange interaction effects on the magnetization relaxation of two macrospins: Compared by Yuri P. Kalmykov, Serguey V. Titov, Declan J. Byrne, William T. Coffey, Marios Zarifakis, and Mohammad H. Al Bayyari, published by the "Journal of Magnetism and Magnetic Materials" (Volume 507, Page 166814) in 2020.

Thus our main objective of providing an archived record of the calculations has been achieved.

10. Future Perspectives: Outstanding two Body Problems: Combined Rotational Diffusion of a Superparamagnetic Particle and Its Magnetic Moment: Solution of the Kinetic Equation - Brief Summary of the work of I.S. Poperechny

As previously discussed Brown has made crucial contributions to the formulation of a statistical approach which explicitly accounts for the thermal fluctuations of the magnetic moment in the analysis of the magnetic response of superparamagnets. We saw that he introduced using the general ideas of Brownian motion theory, the concept of a random magnetic field, simulating thermal fluctuations, and wrote down stochastic Langevin equations for the magneto-dynamics of an isolated *mechanically fixed* nanosized particle. Upon doing so, Brown then (under the assumption that the stochastic field has the statistical properties of white noise) obtained a kinetic equation in the form of the Fokker-Planck equation for the distribution functions of orientations of the particle's magnetic moment. Thus he obtained an asymptotic expression for the greatest relaxation time for the particular simple case where the applied field is coincident with the easy axis of magnetisation of the single domain ferromagnetic nanoparticles. However in a ferrofluid which is a colloidal suspension of single domain particles (i.e., they are in a liquid matrix) the particles undergo a rotational Brownian motion under the influence of random torques imposed by the molecules of the surrounding media. Thus even if we don't take into consideration the dipole-dipole interaction of the particles, the kinetics of the magnetic moments of all the dispersed particles do not obey the Brown Fokker-Planck equation for immobilised particles and therefore need to be generalised.

The answer to this question was partly provided by Stepanov and Shliomis [128, 129], who obtained an equation for the joint distribution function of the orientations of the anisotropy axis and magnetic moment of the particle and have found solutions to said equation in certain limited cases. Stepanov and Shliomis called their theory the "egg model", where the internal magnetisation dynamics coupled to the Brownian rotation of a magnetic nanoparticle is analogous to an egg, with the magnetic moment represented by the yolk and the mechanical rotational motion of the particle body represented by the shell. However, integration of the equation for arbitrary values of parameters is difficult due to the high dimensionality (4 polar angles are involved) of the configuration space. This equation was later derived by others [130, 131], who followed the general procedure of deriving the Fokker-Planck equation from the Langevin ones.

Essentially the Langevin simulation (Langevin dynamics) method sidesteps the complexity of the kinetic equation in the description of magneto-dynamics subjected to thermal noise. In this method, a direct numerical integration of the equations of the rotational dynamics of the particles body and its magnetic moment in the presence of random torques and fields [132–135] is performed. The main advantage of this is that it uses a well-developed computational procedure (e.g. [136]). However, severe limitations to this procedure exist:

1. There is a requirement for multiple repetitions of simulations in order to obtain a time sweep of the average (observed) magnetisation, which involves considerable computational costs, especially in the analysis of low frequency

and/or high temperature processes.

2. The Langevin dynamics method precludes the closed form calculation and analysis of the dependence of the relaxation spectrum of a system on the applied magnetic field.

We now summarise Poperechny's theory of rotation diffusion of a uniaxial superparamagnetic particle, suspended in a fluid [137]. A kinetic equation for the joint distribution function of orientations of anisotropy axis and magnetic moment of the particle is analysed and a consistent method of its solution is described. The approach introduces a kinetic operator that generates the time evolution of the distribution function, and using quantum-mechanical formalism. In particular, aspects of representation theory and the addition of angular momenta. The matrix of the kinetic operator is specified to have a sparse, close to diagonal form. The evolution equation takes the form of a linear differential-recurrence relation for statistical moments of the distribution function. Numerical integration can then be performed via the standard methods, giving the average (observed) magnetisation of the system for any instant of time. It is assumed in the proposed methodology that the frequency of an applied magnetic field is well below the ferromagnetic resonance range, which does not impose any other restrictions on the field amplitude, material parameters of the particle, viscosity of the fluid or temperature. This paper can serve as the theoretical basis for a consistent description of the relaxation spectrum, dynamic magnetic susceptibility and non-linear magnetic response of a dilute magnetic fluid while considering the interplay between mechanical and magnetic degrees of freedom of suspended nanoparticles. It can also provide for cross-checking of approximate models.

The kinetic equation obtained has the general form (which at first glance seems irreconcilable with the earlier treatment of a frozen or immobilised particle grain by Brown, we shall show however that this is not the case)

$$\begin{aligned}\frac{\partial W}{\partial t} + \left(\hat{\mathbf{J}}_{\mathbf{n}} + \hat{\mathbf{J}}_{\mathbf{e}}\right) \cdot (\boldsymbol{\Omega} W) =& \frac{T}{6\eta V} \left(\hat{\mathbf{J}}_{\mathbf{n}} + \hat{\mathbf{J}}_{\mathbf{e}}\right) \cdot W \left(\hat{\mathbf{J}}_{\mathbf{n}} + \hat{\mathbf{J}}_{\mathbf{e}}\right) \left(\frac{U}{T} + \ln W\right) \\ &+ \frac{\alpha\gamma T}{(1+\alpha^2)\,\mu} \hat{\mathbf{J}}_{\mathbf{e}} \cdot W \hat{\mathbf{Q}}_{\mathbf{e}} \left(\frac{U}{T} + \ln W\right). \end{aligned} \tag{10.1}$$

Here W is the joint distribution function $W(\mathbf{e}, \mathbf{n}, t)$ of the orientation of the magnetic moment of the particle and its anisotropy axis, $\mathbf{e} = \boldsymbol{\mu}/\mu$ is the magnetic moment unit vector ($\boldsymbol{\mu}$ is the magnetic moment) directed along the direction of the easy axis $\mathbf{n}$ fixed inside the particle, $\hat{\mathbf{J}}_\mathbf{n} = \mathbf{n} \times \frac{\partial}{\partial \mathbf{n}}$ and $\hat{\mathbf{J}}_\mathbf{e} = \mathbf{e} \times \frac{\partial}{\partial \mathbf{e}}$ are infinitesimal rotation operators, α is the *phenomenological* precession damping parameter, γ is the gyromagnetic ratio for electrons, η is the fluid viscosity, T is the temperature, $\boldsymbol{\Omega}$ is the local angular velocity of rotation of the liquid, $\hat{\mathbf{Q}}_\mathbf{e} = \hat{\mathbf{J}}_\mathbf{e} + \frac{1}{\alpha}\frac{\partial}{\partial \mathbf{e}}$, U is the orientation-dependent part of the magnetic energy of the particle in an external magnetic field $\mathbf{H}$ viz.,

$$U = -KV(\mathbf{e} \cdot \mathbf{n})^2 - \mu H (\mathbf{e} \cdot \mathbf{h}). \tag{10.2}$$

This consists of the anisotropy energy (first term) and the Zeeman energy (second term). Here K is the particle (uniaxial) anisotropy constant, V is the particle volume and $\mathbf{h}$ is the unit vector along the direction of the applied field. This kinetic equation of the particle is identical to that written by Stepanov and Shliomis [134, 135]. Furthermore Poperechny assumed that there is no external flow (i.e., the fluid in which the particle is suspended is at rest), meaning that in Eq. (10.1), $\boldsymbol{\Omega} = 0$. The resulting evolution equation is then

$$\frac{\partial W}{\partial t} = \hat{K} W, \tag{10.3}$$

where $\hat{K}$ is the *kinetic operator* given by

$$\hat{K} W = \frac{1}{2\tau_B}\left(\hat{\mathbf{J}}_\mathbf{n} + \hat{\mathbf{J}}_\mathbf{e}\right) \cdot W \left(\hat{\mathbf{J}}_\mathbf{n} + \hat{\mathbf{J}}_\mathbf{e}\right)\left(\frac{U}{T} + \ln W\right) + \frac{1}{2\tau_D}\hat{\mathbf{J}}_\mathbf{e} \cdot W \hat{\mathbf{J}}_\mathbf{e}\left(\frac{U}{T} + \ln W\right), \tag{10.4}$$

where

$$\tau_B = \frac{3\eta V}{T} \text{ and } \tau_D = \frac{(1+\alpha^2)\,\mu}{2\alpha\gamma T}. \tag{10.5}$$

Note that if the frequency of the applied field is far below the Ferromagnetic resonance region (1GHz), then we can neglect the role of gyration in the magnetic response of the system and consider only the relaxation processes. This is done formally through excluding the precessional term in the operator $\hat{\mathbf{Q}}_\mathbf{e}$ via making the damping constant $\alpha \to \infty$ in the operator $\hat{\mathbf{Q}}_{\mathbf{e}}$, leading to $\hat{\mathbf{Q}}_{\mathbf{e}}$ transforming to the operator $\hat{\mathbf{J}}_{\mathbf{e}}$.

10.1 Comparison with our notation accompanying notes on I.S. Poperechny Journal of Molecular Liquids, 2019

We first consider Eq. (1.17.12) of [2], which pertains to a frozen Brownian mechanism

$$\frac{\partial W}{\partial t} = k'\Delta W + \frac{h'}{\alpha}\mathbf{u}\cdot\left(\frac{\partial}{\partial \mathbf{u}}V \times \frac{\partial}{\partial \mathbf{u}}W\right) + h'\frac{\partial}{\partial \mathbf{u}}\cdot\left(W\frac{\partial}{\partial \mathbf{u}}V\right), \tag{10.6}$$

where Δ is the angular part of the Laplacian

$$\Delta = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}, \tag{10.7}$$

the operator $\partial/\partial\mathbf{u}$ means the gradient operator on the surface of the unit sphere $(1, \vartheta, \varphi)$

$$\frac{\partial}{\partial \mathbf{u}} = \frac{\partial}{\partial\vartheta}\mathbf{e}_\vartheta + \frac{1}{\sin\vartheta}\frac{\partial}{\partial\varphi}\mathbf{e}_\varphi, \tag{10.8}$$

$W(\vartheta, \varphi, t)d\Omega$ is the probability that $\mathbf{M}$ has orientation (ϑ, φ) within solid angle $d\Omega = \sin\vartheta d\vartheta d\varphi$, $\vartheta \in [0, \pi]$, $\varphi \in [0, 2\pi]$ and

$$k' = \frac{kTh'}{v} = \frac{1}{2\tau_{\mathrm{N}}}, \quad \tau_{\mathrm{N}} = \frac{vM_{\mathrm{S}}(1+\alpha^2)}{2kT\gamma\alpha}. \tag{10.9}$$

We are considering a statistical ensemble of superparamagnetic particles. In terms of τ_{N} Eq. (10.6) reads as

$$\frac{\partial W}{\partial t} = \frac{1}{2\tau_{\mathrm{N}}}\Delta W + \frac{1}{2\alpha\tau_{\mathrm{N}}}\mathbf{u}\cdot\left(\frac{\partial}{\partial \mathbf{u}}\frac{vV}{kT} \times \frac{\partial}{\partial \mathbf{u}}W\right) + \frac{1}{2\tau_{\mathrm{N}}}\frac{\partial}{\partial \mathbf{u}}\cdot\left(W\frac{\partial}{\partial \mathbf{u}}\frac{vV}{kT}\right), \tag{10.10}$$

In analysing Eq. (10.10) and comparing it with equation Eq. (33) of [137] for an immobilized particle (pure Néel relaxation)

$$\begin{aligned}\frac{\partial W}{\partial t} =& \frac{1}{2\tau_{\mathrm{N}}}\hat{\mathbf{J}}_e \cdot W\hat{\mathbf{J}}_e\left(\frac{V}{kT} + \ln W\right) \\ =& \frac{1}{2\tau_{\mathrm{N}}}\left(\hat{\mathbf{J}}_e^2 W + \hat{\mathbf{J}}_e \cdot W\hat{\mathbf{J}}_e\frac{V}{kT}\right) \\ =& \frac{1}{2\tau_{\mathrm{N}}}\left(\hat{\mathbf{J}}_e^2 W + W\hat{\mathbf{J}}_e^2\frac{V}{kT} + \hat{\mathbf{J}}_e W \cdot \hat{\mathbf{J}}_e\frac{V}{kT}\right),\end{aligned} \tag{10.11}$$

where

$$V = -KV\left(\mathbf{e}\cdot\mathbf{n})^2\right) - \mu H\left(\mathbf{e}\cdot\mathbf{h}\right), \tag{10.12}$$

and

$$\mathbf{e} = \boldsymbol{\mu}/\mu. \tag{10.13}$$

We need to show that Eqs. (10.6) and (10.11) are identical.

It is important that we establish the exact definition of the various operators. Here

$$\hat{\mathbf{J}}_e = \mathbf{e}\times\frac{\partial}{\partial\mathbf{e}}, \tag{10.14}$$

$$\hat{\mathbf{J}}_n = \mathbf{n}\times\frac{\partial}{\partial\mathbf{n}}, \tag{10.15}$$

are infinitesimal rotation operators for $\mathbf{e}$ and $\mathbf{n}$. Note that in Eq. (10.8) we also have used the infinitesimal rotation operator. Recall that rotational operators are very useful because such operators are merely the angular momentum operators of quantum mechanics ([34], page 137). The classical angular momentum of a particle is

$$\mathbf{L} = \mathbf{r}\times\mathbf{p}. \tag{10.16}$$

In quantum mechanics the orbital angular momentum may be defined in the coordinate representation as the dimensionless operator

$$\mathbf{L} = -i\left(\mathbf{r}\times\nabla\right), \tag{10.17}$$

where ∇ is the vector differential operator with the cartesian components in the laboratory coordinate system

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}. \tag{10.18}$$

Clearly, the rotation operators used in [137] are just particular form of the angular momentum operator of quantum mechanics (specifically $\mathbf{J} = -i\mathbf{L}$). This fact considerably eases subsequent calculations because we can make use of the relations

$$\mathbf{L}^2 Y_{lm} = l(l+1)Y_{lm}, \tag{10.19}$$

$$\mathbf{L}_z Y_{lm} = mY_{lm}, \tag{10.20}$$

and so on. Ultimately we are going to expand W in spherical harmonics Y_{lm} so we have to rearrange the Eq. (10.11) into a form so that only simple products of Y_{lm}, which may be expanded in Clebsch-Gordan series, are involved. We have (via the *Lemma* proved)

$$\hat{\mathbf{J}}_e W \cdot \hat{\mathbf{J}}_e \frac{V}{kT} = \frac{1}{2}\left\{\hat{\mathbf{J}}_e^2\left(W\frac{V}{kT}\right) - \frac{V}{kT}\hat{\mathbf{J}}_e^2 W - W\hat{\mathbf{J}}_e^2\frac{V}{kT}\right\}. \tag{10.21}$$

Hence we have from Eq. (10.11)

$$\begin{aligned}\frac{\partial W}{\partial t} &= \frac{1}{2\tau_{\mathrm{N}}}\left(\hat{\mathbf{J}}_e^2 W + W\hat{\mathbf{J}}_e^2\frac{V}{kT} + \frac{1}{2}\left\{\hat{\mathbf{J}}_e^2\left(W\frac{V}{kT}\right) - \frac{V}{kT}\hat{\mathbf{J}}_e^2 W - W\hat{\mathbf{J}}_e^2\frac{V}{kT}\right\}\right)\\ &= \frac{1}{2\tau_{\mathrm{N}}}\left(\hat{\mathbf{J}}_e^2 W + \frac{1}{2}W\hat{\mathbf{J}}_e^2\frac{V}{kT} + \frac{1}{2}\hat{\mathbf{J}}_e^2\left(W\frac{V}{kT}\right) - \frac{1}{2}\frac{V}{kT}\hat{\mathbf{J}}_e^2 W\right).\end{aligned} \tag{10.22}$$

This is Eq. (35) of [137], cf. Eq. (10.11) above which only involves the squared operator $\hat{\mathbf{J}}_e^2$.

Lemma

$$2\nabla v \cdot \nabla f = \Delta(vf) - v\Delta f - f\Delta v, \tag{10.23}$$

where

$$\Delta = \nabla^2 = -\mathbf{L}^2 = \mathbf{J}_e^2. \tag{10.24}$$

Proof

$$\begin{aligned}\Delta\left(vf\right) =& \nabla\cdot\left(v\nabla f + f\nabla v\right)\\ =& \nabla v\cdot\nabla f + v\Delta f + \nabla v\cdot\nabla f + f\Delta v\\ =& v\Delta f + 2\nabla v\cdot\nabla f + f\Delta v.\end{aligned} \tag{10.25}$$

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