

Ab initio treatment of noncollinear spin systems within the atomic-sphere approximation and beyond

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The properties of noncollinear magnets are often calculated within the framework of density-functional theory in local-spin-density approximation with the additional use of the atomic-sphere approximation for the spin directions. Thereby the intra-atomic noncollinearity is neglected for the calculation of the exchange-correlation energy by taking into account only those components of the spin density which are parallel to spin quantization axes (SQAs) defined for the whole atomic spheres. When the magnetic moment directions are calculated in a self-consistent manner, e.g., for systems with intrinsic noncollinearity or when calculating the response of the system to a weak external field with components perpendicular to the moment directions, the SQAs are conventionally chosen to be parallel to the magnetic moments. We present both theoretical arguments and test calculations showing that this choice of SQAs is not the best and may in certain situations lead to wrong results. As a consequence of our arguments we can suggest a better choice of SQAs. Furthermore, a version of the linear-muffin-tin-orbital method is presented where the atomic-sphere approximation for the spin directions and the introduction of local SQAs are not required so that the intraatomic noncollinearity appears already in the basis functions.

I. ATOMIC-SPHERE APPROXIMATION FOR THE SPIN DIRECTIONS

The investigation of noncollinear spin systems by the electron theory has attracted considerable interest in the past years, for instance, the determination of the ground states of noncollinear spin systems, the calculations of the exchange interactions and of magnon spectra, finite-temperature magnetism, and *ab initio* spin dynamics (for a review see Ref. 1). The calculational techniques encompass semiempirical tight-binding models² with a Hubbard term in the Hamiltonian to generate the spin polarization and *ab initio* methods based on the density-functional theory in local-spin-density approximation³ (LSDA) like the Korringa-Kohn-Rostocker method,⁴ the augmented-spherical-wave method,^{1,5} the full-potential linearized-augmented-plane-wave method,⁶ and the linear-muffin-tin-orbital method⁷⁻¹⁰ (LMTO).

In noncollinear spin systems the direction of the spin density $\mathbf{m}(\mathbf{r})$ varies from site to site. There are systems (Fe, e.g.) where $\mathbf{m}(\mathbf{r})$ is strongly localized deep in the interior of the atomic spheres and where $\mathbf{m}(\mathbf{r})$ is essentially parallel to the average spin density in the sphere except for regions close to the sphere boundary where $\mathbf{m}(\mathbf{r})$ is already small. Nevertheless, the directions of the average spin density may be drastically different for different spheres (interatomic noncollinearity). We call such systems magnets with weak intra-atomic noncollinearity. On the other hand, there are systems with a more delocalized spin density where the intraatomic noncollinearity may be very important (e.g., U compounds) and systems in between (presumably Ni, e.g.).

Calculations for noncollinear spin systems are performed on various levels of sophistication. The noncollinearity is related to a nondiagonal exchange-correlation potential matrix $\mathbf{V}_{xc} = \delta E_{xc} / \delta \boldsymbol{\rho}$, where $\boldsymbol{\rho}(\mathbf{r}) = \frac{1}{2}(n(\mathbf{r})\mathbb{1} + \mathbf{m}(\mathbf{r})\boldsymbol{\sigma})$ is the density matrix with the charge density $n(\mathbf{r})$, the vector of

Pauli matrices $\boldsymbol{\sigma}$, and $E_{xc}[\boldsymbol{\rho}]$ is the exchange-correlation functional which in the LSDA may be written as

$$E_{xc} = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r}), |\mathbf{m}(\mathbf{r})|) d^3r, \quad (1)$$

with the modulus $|\mathbf{m}(\mathbf{r})|$ of the spin density. Since the eigenvalues of the density matrix are $[n(\mathbf{r}) \pm |\mathbf{m}(\mathbf{r})|]/2$, Eq. (1) is equivalent to the more customary form using these eigenvalues as variables, e.g., Eq. (3.5) in Ref. 3. In all of the above quoted *ab initio* methods (except for Ref. 6) the atomic-sphere approximation (ASA) is applied where $n(\mathbf{r})$, $\mathbf{m}(\mathbf{r})$, and hence $\boldsymbol{\rho}(\mathbf{r})$ are spherically averaged in each atomic sphere α before E_{xc} is approximated by

$$E_{xc} = \sum_{\alpha} \int_{\Omega_{\alpha}} n(r) \epsilon_{xc}(n(r), |\mathbf{m}(r)|) d^3r, \quad (2)$$

where Ω_{α} is the volume of the atomic sphere α . (We denote this as *ASA for the structure*.) Note that in this approximation \mathbf{V}_{xc} is still nondiagonal and hence there is both inter- and intra-atomic noncollinearity. The various methods quoted above are distinguished by the way the intra-atomic noncollinearity is accounted for in E_{xc} . In most methods it is neglected by approximating E_{xc} of Eq. (2) further by the *ASA for the spin direction*. To do this, local spin quantization axes (SQAs) described by unit vectors \mathbf{e}_{α} are defined for each atomic sphere, and ϵ_{xc} is approximated by taking into account only the projections $\mathbf{e}_{\alpha} \cdot \mathbf{m}(\mathbf{r})$ of the spin density onto these axes, i.e.,

$$E_{xc}^{ASA} = \sum_{\alpha} \int_{\Omega_{\alpha}} n(r) \epsilon_{xc}(n(r), \mathbf{e}_{\alpha} \cdot \mathbf{m}(r)) d^3r. \quad (3)$$

The projection formalism using $\mathbf{e}_\alpha \cdot \mathbf{m}(r)$ is equivalent to replacing the eigenvalues of $\boldsymbol{\rho}(r)$ by its diagonal elements if $\boldsymbol{\rho}(r)$ is represented in the local spin coordinate system defined by the SQAs.

As a result of the ASA, the exchange-correlation potential matrix $\mathbf{V}_{\text{xc}}(r) = \delta E_{\text{xc}} / \delta \boldsymbol{\rho}(r)$ is diagonal when represented in the local spin coordinate systems with z axes parallel to the \mathbf{e}_α , and the exchange-correlation field \mathbf{B}_{xc} defined via $\mathbf{V}_{\text{xc}}(r) = \bar{V}_{\text{xc}}(r) \mathbb{1} - \mu_{\text{B}} \mathbf{B}_{\text{xc}}(r) \cdot \boldsymbol{\sigma}$ is parallel to the SQAs in each atomic sphere.

In order to use Eq. 3, we need to specify how the SQAs should be chosen for a given input spin density \mathbf{m} . The conventional choice is given by

$$\mathbf{e}_\alpha = \mathbf{M}_\alpha / |\mathbf{M}_\alpha|, \quad (4)$$

with the magnetic moments

$$\mathbf{M}_\alpha = \int_{\Omega_\alpha} \mathbf{m}(r) d^3 r. \quad (5)$$

It is generally assumed that the ASA for the spin directions works well for systems with strongly localized $\mathbf{m}(r)$ and hence for systems with weak intra-atomic noncollinearity (e.g., Fe). The first objective of the present paper is to demonstrate that even in such systems the atomic-sphere approximation may be critical when calculating in a self-consistent manner the linear response of the spin system on a small external magnetic field \mathbf{B}_{ext} , i.e., when calculating the linear susceptibility $\chi(\mathbf{q})$ as a function of the wave vector \mathbf{q} , and that another choice of the SQAs is more appropriate. This is demonstrated in Sec. II both by theoretical arguments and by test calculations using our recently developed LMTO code for noncollinear spin systems which is based on the ASA for the spin directions (see, e.g., Refs. 7 and 10).

In order to shed more light on the problems arising from the atomic-sphere approximation for the spin direction, Eq. (3), one has to develop methods which calculate the exchange-correlation energy from Eq. (2). We will do this in two steps. In the first step we have written an LMTO code where total energy, effective potential, and the Hamiltonian matrix elements are all calculated from Eq. (2). Yet the minimal basis set for the representation of the crystal wave functions is still the conventional basis set of the LMTO method for noncollinear spin systems and thus by its construction still depends on the choice of SQAs. It will be shown in Sec. III that the results of such a method (a similar code has been written for the augmented-spherical-wave method¹¹) may in special situations again depend critically on the choice of the SQAs. In a second step we therefore outline in Sec. IV a version of the LMTO method which takes into account the intra-atomic noncollinearity in the construction of the basis set in such a manner that the introduction of local SQAs is not required at all.

II. OPTIMUM CHOICE FOR THE SPIN-QUANTIZATION AXES

A. Criterion for the optimum choice

In the following we distinguish between three different situations. In the first situation we refrain from the self-

consistent calculation of the SQAs according to Eq. (4) but prescribe fixed SQAs. The density matrix $\boldsymbol{\rho}$ is calculated as the self-consistent solution of the Kohn-Sham equations¹² and thus minimizes the functional of total energy for given SQAs. Since the SQAs are fixed, the solution will in general not be consistent with Eq. (4). Thus we call this calculation scheme *weakly self-consistent*.

When using the ASA approximation for the spin directions the exchange-correlation fields \mathbf{B}_{xc} are parallel to the \mathbf{e}_α , and therefore the magnetic moments \mathbf{M}_α obtained from $\boldsymbol{\rho}(r)$ are almost parallel to the \mathbf{e}_α provided we deal with strongly localized spin densities $\mathbf{m}(r)$. Thus, this scheme is often used as an approximate method of incorporating constraints for the magnetic moment directions.¹³ (To ensure that the magnetic moments are completely parallel to the \mathbf{e}_α , one had to minimize the density functional total energy subject to corresponding constraints.¹⁴) One possible example of the application of this scheme is the *ab initio* calculation of spin-wave frequencies via the total energy⁹ or via the torques^{10,15,16} of various frozen magnon configurations defined by prescribing the SQAs according to a spin spiral. Since the directions of the prescribed axes and the resulting moments are almost parallel, they are often not clearly distinguished.

A second calculation scheme is necessary when we consider systems with intrinsic noncollinearity (e.g., due to competing exchange interactions⁷) or systems for which the noncollinearity is generated by an inhomogeneous external field, e.g., which has the form of a spiral in order to calculate the linear response $\chi(\mathbf{q})$ and from $\chi(\mathbf{q})$ again the spin-wave frequencies.^{15,16} In this situation the directions of the magnetic moments and of the SQAs have to be determined self-consistently. This is typically done by using Eq. (4). Note that this equation gives the SQAs as a function of the spin density. Since the spin density through the Kohn-Sham equations depends on the SQAs, both the density matrix and the SQAs have to be calculated self-consistently. This is typically done simultaneously in the same iteration cycle. We will refer to a calculation of this type as *strongly self-consistent*.

When using this calculation scheme, we can, e.g., start with a ferromagnetic configuration, calculate by use of Eq. (3) the spin density $\mathbf{m}(r)$ which is noncollinear in the considered systems, construct the new SQAs according to Eq. (4), and repeat this procedure until in self-consistency the directions of \mathbf{M}_α and \mathbf{e}_α coincide. Thus, in a calculation of this type, the directions of the magnetic moments and of the respective SQAs will be slightly different in the course of the iteration cycle, but they will coincide in the converged result.

It must be noted, however, that there is no compelling reason why one should use Eq. (4) when using the ASA for the spin direction, Eq. (3). Clearly, Eq. (4) looks like a very plausible choice. It is also the conventional choice. Yet there is no proof that Eq. (4) is the optimum choice in some well-defined sense. We therefore want to find a criterion that allows a comparison of different choices for the SQAs and ultimately the construction of the optimum SQAs.

When using the ASA for the spin direction the total energy depends both explicitly and implicitly [via $\boldsymbol{\rho}(\{\mathbf{e}_\alpha\})$] on the chosen set $\{\mathbf{e}_\alpha\}$ of SQAs, $E^{\text{ASA}} = E^{\text{ASA}}(\{\mathbf{e}_\alpha\}, \boldsymbol{\rho}(\{\mathbf{e}_\alpha\}))$. As a criterion for comparing different sets of SQAs we suggest

that the total energy as calculated using the ASA for the spin directions [E_{xc} given by Eq. (3)] should deviate as little as possible from the true LSDA total energy E^{LSDA} that one would get with E_{xc} given by Eq. (2). Thereby, the optimum choice for the SQAs is given by requiring that

$$\frac{d(E^{\text{ASA}} - E^{\text{LSDA}})}{d\mathbf{e}_\alpha} = 0 \quad (6)$$

for all \mathbf{e}_α . Because E^{LSDA} does not contain the \mathbf{e}_α , Eq. (6) reduces to the demand that E^{ASA} be variational not only with respect to $\boldsymbol{\rho}$ but also with respect to the \mathbf{e}_α . Since minimization of the total energy is the guiding principle of density-functional theory, this result is also aesthetically very pleasing.

The quantity $dE^{\text{ASA}}/d\mathbf{e}_\alpha$ is related¹⁰ to the torque \mathbf{T}_α acting on the magnetic moments of sphere α via

$$\mathbf{T}_\alpha = \frac{dE}{d\mathbf{e}_\alpha} \times \mathbf{e}_\alpha, \quad (7)$$

and therefore Eq. (6) is fulfilled when choosing the SQAs in such a way that the torques are zero when self-consistency for the moment directions is obtained [see the Appendix for a discussion on the interpretation of the torque defined via Eq. (7)]. Assuming that the density matrix $\boldsymbol{\rho}$ exactly minimizes the functional $E^{\text{ASA}}(\{\mathbf{e}_\alpha\})$, we obtain

$$0 = \frac{dE}{d\mathbf{e}_\alpha} = \frac{\partial E}{\partial \mathbf{e}_\alpha} + \frac{\delta E}{\delta \boldsymbol{\rho}} \frac{\partial \boldsymbol{\rho}}{\partial \mathbf{e}_\alpha} = \frac{\partial E}{\partial \mathbf{e}_\alpha} \quad (8)$$

because of the variational property $\delta E/\delta \boldsymbol{\rho} = 0$. [Equation (8) is the well-known Hellmann-Feynman theorem.] It has been shown in Ref. 10 that then $\partial E/\partial \mathbf{e}_\alpha$ may be written in the form

$$\frac{\partial E}{\partial \mathbf{e}_\alpha} = \mathbf{N}_\alpha = \frac{1}{2} \int_{\Omega_\alpha} [V_{xc\uparrow}(r) - V_{xc\downarrow}(r)] \mathbf{m}(r) d^3r. \quad (9)$$

By the way, the derivation of Eq. (9) remains valid if in the presence of an external field $\mathbf{B}_{\text{ext}}(\mathbf{r})$ the Zeemann term

$$E_Z[\mathbf{m}] = -\mu_B \int \mathbf{m}(\mathbf{r}) \cdot \mathbf{B}_{\text{ext}}(\mathbf{r}) d^3r \quad (10)$$

is added to the total energy. This becomes obvious from noting that E_Z from Eq. (10) does not explicitly depend on the SQAs. Thus all contributions of an external field to the torque (7) are implicitly hidden in the spin density $\mathbf{m}(r)$ entering in Eq. (9).

Self-consistency according to Eq. (6) thus is obtained by calculating after each iteration step from the actual spin density $\mathbf{m}(r)$ the new set of SQAs for the next iteration step from the equation

$$\mathbf{e}_\alpha = \mathbf{N}_\alpha / |\mathbf{N}_\alpha|. \quad (11)$$

This choice, Eq. (11) with Eq. (9), implies that the SQAs again are calculated as weighted averages over the directions of the spin density, as was the case for the conventional choice (4), the only difference being that the weights are chosen differently. Thereby, when working with strongly localized spin densities $\mathbf{m}(r)$, and starting from the same input

density, one would obtain very similar SQAs and consequently very similar directions for the output magnetic moments with either choice. This is no longer true, however, if we consider the converged self-consistent results. These can be drastically different. This will be shown below by explicit calculations with our LMTO code with the ASA for the spin directions, but can also be understood qualitatively: Remember that angle differences between the directions of the input and output magnetic moments are small, anyhow, for strongly localized spin densities, regardless which choice for the SQAs is adopted and even if the input directions are far from the self-consistent directions. To obtain self-consistency, input and output spin densities must coincide; i.e., the angle differences must vanish. Since the angle differences are small anyway, small changes of the output angles as induced by going from one definition of the SQAs to another may significantly alter the self-consistent solution.

In the specific case of calculating the susceptibility $\chi(\mathbf{q})$ one can also think about the importance of the choice of SQAs in this way: Changing the SQAs by a small angle $\Delta\vartheta$ essentially rotates the exchange-correlation field by that angle. This changes the exchange-correlation field by approximately $\langle B_{xc} \rangle \Delta\vartheta$. Since we have to choose a small external field $B_{\text{ext}} \ll B_{xc}$, in order to calculate the *linear* response, small changes in the SQAs can cause effects which are of the same magnitude as the response to the external field.

It should be noted that in reality the situation is slightly more complicated as compared to Eq. (9) because due to the use of an incomplete basis set the calculated density matrix $\boldsymbol{\rho}$ does not exactly minimize the energy functional. In this case incomplete-basis-set corrections must be introduced,¹⁰ yielding $dE/d\mathbf{e}_\alpha = \mathbf{N}_\alpha + \mathbf{N}_{\alpha,\text{IBSC}}$. Hence, \mathbf{N}_α in Eq. (11) should be replaced by the sum $\mathbf{N}_\alpha + \mathbf{N}_{\alpha,\text{IBSC}}$. Because in most systems the $\mathbf{N}_{\alpha,\text{IBSC}}$ are very small, this is not a serious problem in practice.

We will refer to a calculation using Eq. (11) instead of the usual equation (4) as *strongly self-consistent with modified SQAs*.

B. Test calculations

In our test calculations we considered bcc Fe with the ferromagnetic ground state magnetization parallel to the z axis. We then applied a small transverse external field in the form of a spiral,

$$\mathbf{B}_{\text{ext}}^{\mathbf{T}} = B_{\text{ext}} \begin{pmatrix} \cos(\mathbf{q} \cdot \mathbf{T}) \\ \sin(\mathbf{q} \cdot \mathbf{T}) \\ 0 \end{pmatrix}, \quad (12)$$

where \mathbf{T} represents a translation vector and \mathbf{q} denotes the spiral wave vector. We inserted $\mu_B B_{\text{ext}} = 250 \mu\text{Ry}$ [whereas $\mu_B \langle B_{xc}(r) \rangle$ equals about 85 mRy for Fe].

We then chose the SQAs according to

$$\mathbf{e}_{\mathbf{T}} = \begin{pmatrix} \sin \vartheta \cos(\mathbf{q} \cdot \mathbf{T}) \\ \sin \vartheta \sin(\mathbf{q} \cdot \mathbf{T}) \\ \cos \vartheta \end{pmatrix} \quad (13)$$

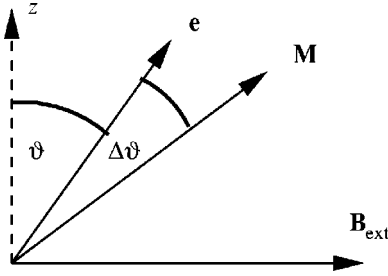


FIG. 1. Geometry of our test calculation (see text). For the sake of clarity the angles ϑ and $\Delta\vartheta$ are strongly enlarged.

and determined the magnetic moments \mathbf{M}_T and the total energy for fixed \mathbf{e}_T in a weakly self-consistent calculation. We then performed the calculation for various values of ϑ . For each calculation we obtained a direction of \mathbf{M}_T which deviates from \mathbf{e}_T by a small angle $\Delta\vartheta$ (see Fig. 1). Figure 2 represents for three different wave vectors \mathbf{q} the results for the total energy and the deviation $\Delta\vartheta$. It becomes obvious that $\Delta\vartheta$ is always very small; i.e., the \mathbf{M}_T are almost parallel to the \mathbf{e}_T . For the calculation of the total energy in the presence of the external field, the Zeeman term E_Z from Eq. (10) was added to the usual functional of the total energy.

The shape of the total energy curve can be understood by

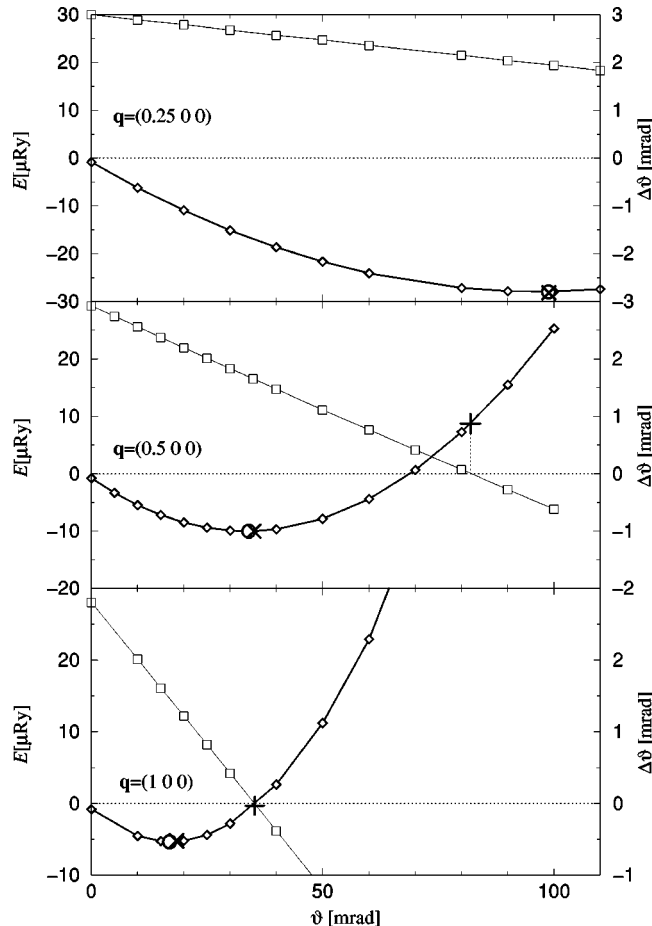


FIG. 2. The total energy E (diamonds) and the angle deviation $\Delta\vartheta$ (squares) as functions of ϑ (see text) for bcc Fe at various values of the spiral wave vector \mathbf{q} . For the meaning of the various other symbols on the total energy curve see text.

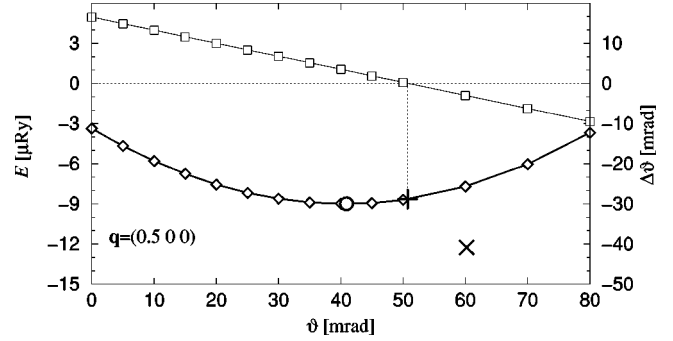


FIG. 3. As Fig. 2, but for fcc Ni.

some simple considerations: If B_{ext} were 0, the total energy would be an even function of ϑ , i.e.,

$$E(\vartheta, B_{\text{ext}}=0) = E_0 + \frac{1}{2}J(\mathbf{q})\vartheta^2 + O(\vartheta^4). \quad (14)$$

When we switch on the magnetic field, the Zeeman term is added to the functional of the total energy. Assuming that the magnetic moment is parallel to the prescribed SQAs and remains unchanged in modulus, the Zeeman term may be approximated as $E_Z \approx -B_{\text{ext}}|\mathbf{M}|\sin\vartheta$. Thus the Zeeman term adds a linear term in ϑ and shifts the minimum of total energy to some nonzero value of ϑ .

If we use the strongly self-consistent calculation scheme with the conventional choice of SQAs the calculation converges [as prescribed by Eq. (4)] to a state with $\mathbf{e}_\alpha \parallel \mathbf{M}_\alpha$. This corresponds to $\Delta\vartheta=0$. The respective solution $(\vartheta, E(\vartheta))$ is marked by a plus symbol in Fig. 2. As can be seen from Fig. 2, this solution does not minimize the total energy. The respective angle is indeed too large by a factor of 2–3 as compared to the angle that actually minimizes $E(\vartheta)$. The latter solution is reached by a strongly self-consistent calculation scheme if our choice, Eq. (11), is employed; this result is marked by the bold circle on the energy curve. Consequently, the respective susceptibilities $\chi(\mathbf{q})$ deduced from the two calculation schemes differ by the same factor of 2–3.

The crosses near the minima of the energy curve of Fig. 2 have the following meaning: By using weakly self-consistent calculations with $\vartheta \neq 0$ but $B_{\text{ext}}=0$ we can easily obtain $J(\mathbf{q})$. Using the simple approximation $E_Z = -MB_{\text{ext}}\vartheta$, we may write $E(\vartheta) = E_0 - MB_{\text{ext}}\vartheta + \frac{1}{2}J(\mathbf{q})\vartheta^2$, resulting in a minimum at $\vartheta = MB_{\text{ext}}/J(\mathbf{q})$ with $E_{\text{min}} = E_0 - (MB_{\text{ext}})^2/[2J(\mathbf{q})]$. Thus by using results from calculations with $B_{\text{ext}}=0$, we can predict the location of the minimum of total energy when B_{ext} is switched on. These predicted minima are marked by crosses in Fig. 2. The fact that they correspond well to the actual minima indicates that the code for the evaluation of the Zeeman energy is correct. It is perhaps interesting to note that the value $J(\mathbf{q})$ is closely related to the frequency of a magnon as calculated in a frozen magnon scheme.⁹

Figure 3 shows the same results for the case of Ni, for which the spin density $\mathbf{m}(r)$ is less localized than in Fe. Again, the angle ϑ for which $\Delta\vartheta$ is zero differs considerably from the angle for which the energy is minimum. In contrast to Fe, here the predicted minimum—again marked by the plus symbol—is quite different from the actual minimum of

$E(\vartheta)$. Since the magnetic moment and therefore the exchange-correlation field which is parallel to the SQA are much smaller for Ni than for Fe, the SQA has a much smaller influence on the resulting direction of the magnetic moment \mathbf{M}_α as is evidenced by the large values of $\Delta\vartheta$ in Fig. 3. Thus the SQA cannot be used as an approximate constraint for the direction of the magnetic moment in this case, and the model used to predict the minimum position breaks down.

C. Summary

We have thus demonstrated that the conventional choice of SQAs does not always lead to the minimum of the total energy. In contrast to this, our choice of SQAs by its very construction guarantees that the minimum of the total energy is reached. When one calculates the self-consistent response to a small external field, i.e., the susceptibility $\chi(\mathbf{q})$, the two calculation schemes lead to significantly different results, demonstrating that the proper choice of SQAs is essential at least for this problem.

The preceding discussion should in principle be applicable to any self-consistent calculation of noncollinear spin systems involving the ASA for the spin directions (3). Yet there may well be problems for which the results do not depend strongly on the choice of the SQAs. The differences between the results for the two different choices of the SQAs should be much less important when considering systems with strong intrinsic noncollinearity, e.g., due to competing exchange interactions.⁷ In these systems the errors associated with the use of the ASA for the spin directions depend on the ratio $\Delta B_{xc}/B_{xc}$ where ΔB_{xc} is the ASA error for B_{xc} , whereas for the calculation of $\chi(\mathbf{q})$ the errors depend on the much larger ratio $\Delta B_{xc}/B_{ext}$ as discussed above.

Finally, there are situations for which the choice of the SQAs is dictated by the symmetry of the problem. In this case the choices (4) and (11) coincide. A prominent example is spin spirals according to Eq. (13) with $\vartheta = \pi/2$ as studied, e.g., in Ref. 1 and references therein.

III. CALCULATIONS BEYOND THE ASA BUT WITH BASIS FUNCTIONS DEPENDING ON THE SQAs

In the preceding Sec. II we have discussed problems arising from the application of the ASA for the spin direction which are related to the choice of the SQAs. The natural consequence is to develop methods for which the choice of the SQAs is less relevant or for which the introduction of SQAs is not required at all.

In a first step we have written an LMTO code^{15,17} where we refrain from the ASA for the spin direction by calculating E_{xc} from Eq. (2). Wanting to construct basis functions that are as similar as possible to the conventional ones, we nevertheless introduce in this code local SQAs \mathbf{e}_α . The exchange-correlation matrix, which now also contains off-diagonal elements, is split into two parts, i.e., $\mathbf{V}_{xc}(r) = \mathbf{V}_{xc}^{\parallel}(r) + \mathbf{V}_{xc}^{\perp}(r)$, where $\mathbf{V}_{xc}^{\parallel}$ contains the diagonal and \mathbf{V}_{xc}^{\perp} contains the off-diagonal elements with respect to the coordinate systems with z axes parallel to the \mathbf{e}_α . The basis functions for the representation of the crystal wave functions then are constructed from the atomic functions ϕ and $\bar{\phi}$ of the

LMTO method^{18,19} which are calculated from the spherically averaged effective Hamiltonian in each atomic sphere where the components \mathbf{V}_{xc}^{\perp} are neglected. With the so-obtained basis functions the Hamiltonian matrix elements are calculated with the full $\mathbf{V}_{xc}(r)$. Thus the errors arising from the approximation, Eq. (3), for the calculation of the exchange-correlation potential are avoided. It is of course artificial to split the exchange-correlation matrix into two parts. This approach was dictated by our wish to obtain basis functions constructed in a way that is as close as possible to the conventional LMTO basis functions for noncollinear magnets. Since the split $\mathbf{V}_{xc} = \mathbf{V}_{xc}^{\parallel} + \mathbf{V}_{xc}^{\perp}$ depends on the choice of the SQAs, so will the basis set obtained in this way.

It will be shown in this section that numerical errors arise because this set of basis functions is not complete so that the results depend on the choice of the SQAs used for their construction. To demonstrate this we perform the following test calculation. We start with the ferromagnetic ground state for bcc Fe with magnetization parallel to the z direction. Then we assign fixed SQAs according to Eq. (13) to the atomic spheres with $\mathbf{q} = (2\pi/a)(0.25, 0, 0)$ and $\vartheta = 100$ mrad. In a first weakly self-consistent calculation we determine the resulting magnetic moments \mathbf{M}_T by our LMTO method based on the ASA for the spin directions^{7,10} by use of Eqs. (3) and (4). The resulting \mathbf{M}_T are almost parallel to the SQAs \mathbf{e}_T ; i.e., we find a frozen magnon configuration with an amplitude of 98.9 mrad. The second calculation is performed with our LMTO method based on the true LSDA according to Eq. (2) but with basis functions which depend on the SQAs, as explained above. If the set of basis functions was complete, then the ferromagnetic ground state should be preserved independent of the choice of the SQAs because in the second calculation the SQAs enter only into the construction of the basis functions. However, it turns out that the resulting magnetic moments are canted by 67 mrad with respect to the z axis, an effect which is totally due to the incompleteness of the basis set. A very similar result (86 mrad) was obtained²⁰ by a totally analogous test calculation with the augmented-spherical-wave method based on the true LSDA and again with basis functions which depend on the choice of the SQAs.

The dependence of the basis functions on the choice of the SQAs again may have a considerable influence on the determination of the linear response to an external field, whereas for systems with strong intrinsic noncollinearity it should not constitute a serious problem.

IV. MODIFIED VERSION OF THE LMTO METHOD FOR NONCOLLINEAR SPIN SYSTEMS

We describe a version of the LMTO method which does not use the ASA for the spin direction and which does not require local SQAs at all. In contrast to the code described in Sec. III, the basis functions now are constructed from atomic functions which correspond to the spherically averaged but otherwise complete nondiagonal effective Hamiltonian in each atomic sphere; i.e., these atomic functions take into account from the very beginning the intra-atomic noncollinearity and are therefore well adapted to the situation in the crystal.

The two remaining approximations are (a) the use of a

finite set of basis functions and (b) the ASA approximation for the structure, where for the calculation of E_{xc} and \mathbf{V}_{xc} the density matrix $\rho(\mathbf{r})$ is spherically averaged in each atomic sphere.

For the construction of the basis functions therefore only that part of the intra-atomic noncollinearity is taken into account which survives this spherical averaging. However, it should be noted that the output density matrix obtained after each iteration step is not spherically symmetric. What is neglected in this type of calculation is the asphericity of the input potential for the next iteration step originating from the aspherical part of the output spin density matrix, but this problem holds for all currently used computer codes for non-collinear spin systems (except for Ref. 6). The general idea of our method can of course also be used within the framework of other linear band structure methods.

To elucidate the difference between the former version and the present version of the LMTO method, we first describe the former version based on the ASA for the spin direction where the basis functions are constructed very much on the line introduced by Kübler *et al.*⁵ for the augmented-spherical-wave method, consisting basically of the following three steps.

(i) Local spin coordinate systems for all spheres α with z parallel to the direction \mathbf{e}_α of the local spin quantization axes are introduced. For these systems the respective potential matrix $\mathbf{V}_{xc}^{ASA} = \delta E_{xc}^{ASA} / \delta \rho$ is diagonal. Within each atomic sphere the atomic functions

$$|\phi_{\alpha l m \sigma}\rangle = |\zeta_{\alpha \sigma}\rangle Y_{lm}(\widehat{\mathbf{r} - \mathbf{R}_\alpha}) \phi_{\alpha l \sigma}(|\mathbf{r} - \mathbf{R}_\alpha|) \quad (15)$$

are defined, where the $|\zeta_{\alpha \sigma}\rangle$ with $\sigma = 1, 2$ are the spin eigenfunctions of the Pauli operator $\hat{\sigma}_z$ for the local z axis, and these eigenfunctions may be represented in a fixed external coordinate system. The Y_{lm} are spherical harmonics, and the $\phi_{\alpha l \sigma}$ are solutions of the radial Schrödinger equation in the local coordinate system, for which the effective ASA-Hamiltonian is diagonal so that we can write

$$\hat{H}_{\text{eff}, \sigma \sigma} \phi_{\alpha l \sigma} = \epsilon_{\alpha l \sigma} \phi_{\alpha l \sigma}, \quad (16)$$

where $\epsilon_{\alpha l \sigma}$ is a given energy parameter. From the radial functions $|\phi_{\alpha l m \sigma}\rangle$ the energy derivatives

$$|\dot{\phi}_{\alpha l m \sigma}\rangle = \frac{\partial}{\partial \epsilon_{\alpha l \sigma}} |\phi_{\alpha l m \sigma}\rangle \quad (17)$$

are obtained which are orthogonal to $|\phi_{\alpha l m \sigma}\rangle$,

$$\langle \phi_{\alpha l m \sigma} | \dot{\phi}_{\alpha l m \sigma} \rangle = 0, \quad (18)$$

if $|\phi_{\alpha l m \sigma}\rangle$ is normalized for each $\epsilon_{\alpha l \sigma}$.

(ii) The LMTO-ASA basis functions are Bloch functions composed of linear-muffin-tin orbitals which are constructed by a generalization of the procedure introduced by Andersen¹⁸ for collinear systems. First, a basis set of envelope spinors

$$|K_{\mathbf{R}+\mathbf{T}, l m \sigma}(\mathbf{r})\rangle = K_{\mathbf{R}+\mathbf{T}, l}^0(|\mathbf{r} - \mathbf{R} - \mathbf{T}|) Y_{lm}(\widehat{\mathbf{r} - \mathbf{R} - \mathbf{T}}) |\zeta_{\mathbf{R}+\mathbf{T}, \sigma}\rangle, \quad (19)$$

is introduced where the translation vector \mathbf{T} and the basis vector \mathbf{R} describe the position of the atomic sphere in the

crystal [i.e., $\alpha = (\mathbf{R}, \mathbf{T})$] to which the function $K_{\mathbf{R}+\mathbf{T}, l}^0(|\mathbf{r} - \mathbf{R} - \mathbf{T}|)$ is attached. For $K_{\mathbf{R}+\mathbf{T}, l}^0$ the spherical Hankel function is used or appropriately defined and better localized linear combinations of spherical Hankel functions when working with the tight-binding version of the LMTO method.¹⁹ The LMTOs then are defined via

$$\begin{aligned} |\chi_{\mathbf{R}+\mathbf{T}, l m \sigma}\rangle &= \tilde{\phi}_{\mathbf{R}+\mathbf{T}, l m \sigma}^H |\zeta_{\mathbf{R}+\mathbf{T}, \sigma}\rangle \\ &\quad - \sum_{\mathbf{R}', \mathbf{T}', l' m' \sigma'} \tilde{\phi}_{\mathbf{R}'+\mathbf{T}', l' m' \sigma'}^T |\zeta_{\mathbf{R}'+\mathbf{T}', \sigma'}\rangle \\ &\quad \times S_{\mathbf{R}'+\mathbf{T}', l' m' \sigma', \mathbf{R}+\mathbf{T}, l m \sigma}, \end{aligned} \quad (20)$$

with

$$\tilde{\phi}_{\mathbf{R}+\mathbf{T}, l m \sigma}^H = (A_{\mathbf{R} l \sigma} \phi_{\mathbf{R}+\mathbf{T}, l \sigma} + B_{\mathbf{R} l \sigma} \dot{\phi}_{\mathbf{R}+\mathbf{T}, l \sigma}) Y_{lm}, \quad (21)$$

$$\tilde{\phi}_{\mathbf{R}+\mathbf{T}, l m \sigma}^T = (D_{\mathbf{R} l \sigma} \phi_{\mathbf{R}+\mathbf{T}, l \sigma} + C_{\mathbf{R} l \sigma} \dot{\phi}_{\mathbf{R}+\mathbf{T}, l \sigma}) Y_{lm}, \quad (22)$$

$$S_{\mathbf{R}'+\mathbf{T}', l' m' \sigma', \mathbf{R}+\mathbf{T}, l m \sigma}$$

$$= \langle \zeta_{\mathbf{R}'+\mathbf{T}', \sigma'} | \zeta_{\mathbf{R}+\mathbf{T}, \sigma} \rangle S_{\mathbf{R}'+\mathbf{T}', l' m', \mathbf{R}+\mathbf{T}, l m}, \quad (23)$$

where $S_{\mathbf{R}'+\mathbf{T}', l' m', \mathbf{R}+\mathbf{T}, l m}$ is the matrix of structure constants.

The coefficients A, B, D, C are uniquely determined in such a way that $|\chi_{\mathbf{R}+\mathbf{T}, l m \sigma}\rangle$ matches continuously and with continuous derivative to the envelope spinors $|K_{\mathbf{R}+\mathbf{T}, l m \sigma}\rangle$ at each atomic site.

(iii) For the effective Hamiltonian of the whole crystal the same ASA for the spin directions is used as for the construction of the basis set. Then the Hamiltonian matrix elements are easily calculated, whereby only radial integrals of the type

$$\langle \dot{\phi}_{\mathbf{R}+\mathbf{T}, l \sigma} | \dot{\phi}_{\mathbf{R}+\mathbf{T}, l \sigma} \rangle = P_{\mathbf{R} l \sigma} \quad (24)$$

have to be evaluated numerically.

In the new version of the LMTO method we refrain from the ASA for the spin direction, and therefore there is no need for the introduction of local spin coordinate systems. Thus all functions may be represented in a fixed external coordinate system. Again a set of envelope functions is constructed,

$$|K_{\mathbf{R}+\mathbf{T}, l m \sigma}(\mathbf{r})\rangle = K_{\mathbf{R}+\mathbf{T}, l}^0(|\mathbf{r} - \mathbf{R} - \mathbf{T}|) Y_{lm}(\widehat{\mathbf{r} - \mathbf{R} - \mathbf{T}}) |\zeta_\sigma\rangle, \quad (25)$$

where the $|\zeta_\sigma\rangle$ are the eigenfunctions ($\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}$) and ($\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}$) of $\hat{\sigma}_z$ in the external system. The new type of LMTO is defined as

$$\begin{aligned} |\chi_{\mathbf{R}+\mathbf{T}, l m \sigma}\rangle &= |\tilde{\phi}_{\mathbf{R}+\mathbf{T}, l m \sigma}^H\rangle \\ &\quad - \sum_{\mathbf{R}' \mathbf{T}'} \sum_{l' m'} |\tilde{\phi}_{\mathbf{R}'+\mathbf{T}', l' m' \sigma'}^T\rangle S_{\mathbf{R}'+\mathbf{T}', l' m', \mathbf{R}+\mathbf{T}, l m \sigma}. \end{aligned} \quad (26)$$

Please note that only spinors with the same index σ occur in Eq. (26) [in contrast to Eq. (20)]. Furthermore, the functions $\tilde{\phi}^{H, T}$ from Eq. (20) are replaced by spinors $|\tilde{\phi}\rangle$ defined via

$$\begin{aligned} |\tilde{\phi}_{\mathbf{R}+\mathbf{T},lm\sigma}^{\text{H}}\rangle &= A_{\mathbf{R}l\sigma}^{\text{I}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I}}\rangle + B_{\mathbf{R}l\sigma}^{\text{I}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I}}\rangle \\ &+ A_{\mathbf{R}l\sigma}^{\text{II}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{II}}\rangle + B_{\mathbf{R}l\sigma}^{\text{II}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{II}}\rangle, \end{aligned} \quad (27)$$

$$\begin{aligned} |\tilde{\phi}_{\mathbf{R}+\mathbf{T},lm\sigma}^{\text{T}}\rangle &= D_{\mathbf{R}l\sigma}^{\text{I}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I}}\rangle + C_{\mathbf{R}l\sigma}^{\text{I}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I}}\rangle \\ &+ D_{\mathbf{R}l\sigma}^{\text{II}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{II}}\rangle + C_{\mathbf{R}l\sigma}^{\text{II}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{II}}\rangle. \end{aligned} \quad (28)$$

The spinors $|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I,II}}\rangle$ are solutions of the Schrödinger equation

$$\hat{\mathbf{H}}_{\text{eff}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I,II}}\rangle = \epsilon_{\mathbf{R}}|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I,II}}\rangle, \quad (29)$$

with the effective Hamiltonian $\hat{\mathbf{H}}_{\text{eff}}$ which is spherically averaged in each atomic sphere α but nondiagonal because it contains the nondiagonal part $\mathbf{V}_{\text{xc}} = \delta E_{\text{xc}}/\delta \boldsymbol{\rho}$ with E_{xc} given by Eq. (2).

As a result, the spinors exhibit neither pure spin-up nor pure spin-down character; i.e., both of their components $\phi_1^{\text{I,II}}$ and $\phi_2^{\text{I,II}}$ are nonzero. Equation (29) thus represents a system of two coupled ordinary differential equations for the two components which has to be solved numerically subject to, e.g., the following four boundary conditions:

- (1) $\phi_1(r \rightarrow 0) \sim r^{l+1}$.
- (2) $\phi_2(r \rightarrow 0) \sim r^{l+1}$.
- (3) Normalization of $|\phi\rangle$.
- (4) For the spinor $|\phi^{\text{I}}\rangle$: $\phi_2^{\text{I}}(r = S_{\mathbf{R}}) = 0$, where $S_{\mathbf{R}}$ denotes the radius of the respective atomic sphere. For the spinor $|\phi^{\text{II}}\rangle$: $\phi_1^{\text{II}}(r = S_{\mathbf{R}}) = 0$.

Other choices for the boundary condition (4) are possible and would lead to solutions $|\phi^{\text{I,II}}\rangle$ that are linear combinations of the ones used here. However, it will be shown below that this would not change the basis set.

Because of the boundary condition (4), the spinors $|\phi^{\text{I}}\rangle$ and $|\phi^{\text{II}}\rangle$ exhibit pure spin-up and spin-down character, respectively, at the boundary of each atomic sphere (whereas their radial derivatives are spinors with two nonvanishing components at the sphere boundaries). The spinors $|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I,II}}\rangle = (\partial/\partial \epsilon_{\mathbf{R}})|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I,II}}\rangle$ are again orthogonal to $|\phi_{\mathbf{R}+\mathbf{T},lm}^{\text{I,II}}\rangle$ because of the normalization of the latter spinors. Finally, the coefficients $A^{\text{I}}, A^{\text{II}}, B^{\text{I}}, B^{\text{II}}, D^{\text{I}}, D^{\text{II}}, C^{\text{I}}, C^{\text{II}}$ are uniquely obtained by demanding that the LMTOs $|\chi_{\mathbf{R}+\mathbf{T},lm\sigma}\rangle$ match the envelope functions $|K_{\mathbf{R}+\mathbf{T},lm\sigma}\rangle$ continuously and with continuous derivatives at each sphere boundary. Thereby, if we had chosen different boundary conditions for the construction of the functions ϕ_1 , ϕ_2 , ϕ_1 , and ϕ_2 , we would be led to correspondingly modified coefficients A , B , C , and D , yielding unchanged functions $|\tilde{\phi}^{\text{H,T}}\rangle$ in Eqs. (27) and (28) and consequently unchanged basis functions in Eq. (26). Thus we need not be much concerned with the question as to how to choose the boundary conditions best.

The numerical effort of our version should be not much larger than the effort of the former versions. On the one hand, additional work is required for the calculation of the atomic functions: Instead of solving the separate differential equations (16) for the spinor components in the former version, the system of coupled equations (29) has to be solved now. Furthermore, the calculation of the matrix elements for the crystal Hamiltonian will require the evaluation of several additional one-dimensional integrals, e.g., $\langle \phi_{\mathbf{R},lm}^{\text{I}}|\phi_{\mathbf{R},lm}^{\text{II}}\rangle$

etc., but this does not constitute a problem. On the other hand, the main part of the computation time is required for the diagonalization of the Hamiltonian matrix which has the same dimension in both versions, so that the relative increase of computer time should be small.

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APPENDIX: THE INTERPRETATION OF THE TORQUE

In Sec. II A we used the name torque to refer to the quantity \mathbf{T}_{α} defined via Eq. (7). This choice of name is not entirely correct and deserves some discussion.

From a physical point of view, the torque should rather be defined via the derivative of the total energy with respect to the direction of the magnetic moment, i.e.,

$$\mathbf{T}'_{\alpha} = \frac{dE}{d\mathbf{M}_{\alpha}} \times \mathbf{M}_{\alpha}. \quad (A1)$$

If we deal with strongly localized magnetizations, the directions of the SQAs \mathbf{e}_{α} used in the definition (7) and of the magnetic moments \mathbf{M}_{α} used in Eq. (A1) are essentially parallel so that both definitions yield basically the same result. This motivated our choice of the name torque. For less localized magnetizations the directions of the SQAs and of the magnetic moments must be clearly distinguished and the physical interpretation of the quantity \mathbf{T}_{α} is not clear.

There are, however, two reasons why we prefer the ‘‘unphysical’’ definition (7) over Eq. (A1) in the context of this paper: First, we were looking for a criterion on how to choose the SQAs. In this context, the derivatives of the total energy with respect to these SQAs arose naturally. Second, we can evaluate the torques as defined by Eq. (7) with reasonable numerical effort, as is seen by Eq. (9) and the discussion in Ref. 10.

In contrast to the latter point, one would have to solve several severe problems if one wanted to calculate torques from the definition Eq. (A1): First, the energy is a functional of the spin density so that Eq. (A1) becomes

$$\mathbf{T}'_{\alpha} = \int \frac{\delta E}{\delta \mathbf{m}(\mathbf{r})} \frac{\partial \mathbf{m}(\mathbf{r})}{\partial \mathbf{M}_{\alpha}} d^3r. \quad (A2)$$

Here we must note that the spin density $\mathbf{m}(\mathbf{r})$ cannot be easily calculated from \mathbf{M}_{α} . Thus it is not clear how $\partial \mathbf{m}(\mathbf{r})/\partial \mathbf{M}_{\alpha}$ should be evaluated. Second, when we try to evaluate the variational derivative $\delta E/\delta \mathbf{m}(\mathbf{r})$, we note that in density-functional theory the functional of the total energy is expressed as a sum over several terms. Of these, the exchange-correlation energy E_{xc} from, e.g., Eq. 3 and the Zeeman energy from Eq. (10) [provided an external field $\mathbf{B}_{\text{ext}}(\mathbf{r})$ is present] obviously depend on the spin density $\mathbf{m}(\mathbf{r})$ and pose no special problem. Somewhat less obviously, also the kinetic energy, defined as

$$T[n(\mathbf{r}), \mathbf{m}(\mathbf{r})] = \min_{\{\psi_i\} \rightarrow n, \mathbf{m}} \sum_i \left\langle \psi_i \left| -\frac{\hbar^2}{2m} \Delta \right| \psi_i \right\rangle, \quad (A3)$$

where the minimum is taken over all sets of one-particle functions $\{\psi_i\}$ giving rise to the densities n, \mathbf{m} , is a functional of the spin density. It is not clear how the derivative $\delta T / \delta \mathbf{m}(\mathbf{r})$ can be evaluated.

Note that as a consequence of the local approximation, the pure LSDA exchange correlation functional from Eq. (1) does not depend on the relative orientation of the spins at two different positions. If no external field is present, then the only energy term that actually depends on relative spin orientations is the kinetic energy. Thus in the nomenclature of density-functional theory the kinetic energy and not the exchange-correlation energy is responsible for the energy

differences associated with different relative orientations of the spin directions, i.e., what is usually denoted as the “exchange energy.”

In using definition (7) we take the derivative with respect to the SQA \mathbf{e}_α which has the role of a parameter in the energy functional. Thus the Hellmann-Feynman theorem is applicable and easily yields Eq. (9) (see also Ref. 10). In contrast, the magnetic moment \mathbf{M}_α used in definition (A1) is a variational quantity of the energy functional. Thus the Hellman-Feynman theorem cannot be applied to calculate \mathbf{T}'_α .

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