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Transition levels of defects in ZnO: Total energy and Janak's theorem methods

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Transition levels of defects are commonly calculated using either methods based on total energies of defects in relevant charge states or energy band single particle eigenvalues. The former method requires calculation of total energies of charged, perfect bulk supercells, as well as charged defect supercells, to obtain defect formation energies for various charge states. The latter method depends on Janak's theorem to obtain differences in defect formation energies for various charge states. Transition levels of V_{Zn} , V_O , and V_{ZnO} vacancy defects in ZnO are calculated using both methods. The mean absolute deviation in transition level calculated using either method is 0.3 eV. Relative computational costs and accuracies of the methods are discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739316>]

I. INTRODUCTION

Transition levels (TL) of a defect are Fermi level positions at which the energies of the defect in two distinct charge states are equal. Sweeping the Fermi level position through the TL results in a change of charge state. For example, the oxygen vacancy defect in ZnO, V_O , can exist in neutral, 1+, and 2+ states and the $\epsilon(+/2+)$ TL is the Fermi level position at which the total energies of V_O^+ and V_O^{2+} become equal. Defect TL is important in understanding the absorption and emission properties of off-stoichiometrically grown semiconductor materials. In this work, we compare two different methods for calculating TL: a total energy (TE) method requires total energies of defect and perfect bulk supercells in either charge state and a method based on Janak's theorem¹ requires single-particle eigenvalues (SPE) for the defect supercell in either charge state. The former method is relatively inexpensive in computer time, but contains approximations which are not made in the latter. We apply both methods to acceptor and donor vacancy defects in ZnO in order to compare their performance.

TL for defects in ZnO and other oxides have been estimated using both TE (Refs. 2–7) and SPE (Ref. 8) methods. Earlier work mainly used local density approximation (LDA) or LDA+U (Ref. 2) Hamiltonians. These methods underestimate the band gaps of wide gap oxides² and so corrections to the band gap are necessary when calculating TL. Here, we use the B3LYP hybrid density functional^{9,10} which predicts a single particle band gap for ZnO (3.17 eV, this work) in good agreement with experiment (3.47 eV (Ref. 11)). The B3LYP functional has previously been applied to calculations of TL in ZnO.^{8,12}

While it is widely recognized that relaxation of defect supercells is important for obtaining accurate TL, the drastic changes which can occur in predicted TL when supercells

are relaxed may not be fully appreciated. In particular, hybrid density functional theory (DFT) methods are particularly expensive in computer time. In this work, all supercells have been fully relaxed for all charge states considered. However, in some cases supercells are relaxed using less expensive, non-hybrid DFT methods before hybrid DFT methods are used to calculate TL. This may lead to significant error in predicted TL in some defects where there is a large lattice relaxation.

In Sec. II, we outline the TE and SPE methods. This is followed by results of calculations of TL of three intrinsic vacancy defects in ZnO: the oxygen vacancy, V_O , the zinc vacancy, V_{Zn} , and the ZnO divacancy, V_{ZnO} .

II. FORMATION ENERGIES AND TRANSITION LEVELS

The formation energy for defect X with charge q , $E_{X^q}^f$, is^{13,14}

$$E_{X^q}^f = E_{X^q} - E_{bulk^0} + n_i \mu_i + q(E_F - E_V), \quad (1)$$

where E_{bulk^0} and E_{X^q} are total energies from supercell calculations for the bulk crystal and the bulk crystal with a defect, X , in charge state, q , respectively. n_i is the change in number of species, i , removed from or added to the supercell to create the defect, μ_i is the chemical potential of species i , and $E_F - E_V$ is the position of the Fermi level relative to the valence band maximum level.

In a total energy calculation, the absolute positions of the valence band maximum or conduction band minimum are unknown and the energy required to transfer an electron from the valence band maximum (VBM) to an acceptor defect or from a donor defect to the conduction band minimum (CBM) must be calculated directly. As noted above, a defect TL is the Fermi level position at which the formation energies of a defect in its two different charge states become equal. The position of an acceptor level relative to the CBM is equal to the energy released when an electron moves from the CBM to the acceptor level. For a donor, it is the energy released when

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a hole moves from the VBM to the donor level. For ease of comparison of TL for both acceptor and donor defects, we refer acceptor levels to the VBM rather than the CBM using the band gap energy, E_g , obtained from the ionization potential and electron affinity of the bulk supercell.⁷ A TL is denoted $\epsilon(q'/q)$, where q and q' are two different charge states of the defect, and is obtained from the difference in formation energies of a defect in two distinct charge states using Eq. (1),

$$\epsilon(q'/q) = E_v + \frac{E_{X^q}^f - E_{X^{q'}}^f}{q' - q}. \quad (2)$$

In the TE method, differences in total energies of defects in different charge states are calculated from the energies of the bulk supercell and the bulk supercell with a defect and the TL is given by⁷

$$\epsilon(q'/q) = \frac{[E_{X^q} - E_{bulk^q}] - [E_{X^{q'}} - E_{bulk^{q'}}]}{q' - q}, \quad (3)$$

where, as before, E_{X^q} is the total energy of the supercell with defect X in charge state q and E_{bulk^q} is the bulk supercell with the same charge state. Equation (3) is used for a donor defect. An acceptor defect is charged by adding an electron to the supercell. Equation (3) yields the TL with respect to the conduction band in this case; the TL with respect to the valence band maximum is obtained by adding the band gap energy. The TL for an acceptor defect is therefore given by

$$\epsilon(q'/q) = \frac{[E_{X^q} - E_{bulk^q}] - [E_{X^{q'}} - E_{bulk^{q'}}]}{q' - q} + E_g, \quad (4)$$

where $E_g = \text{IP} - \text{EA}$ is the band gap calculated from the difference of the ionization potential ($\text{IP} = E_{bulk^+} - E_{bulk^0}$) and electron affinity ($\text{EA} = E_{bulk^0} - E_{bulk^-}$). The values of IP and EA for ZnO are 7.14 eV and 11.06 eV (Ref. 7) from differences in total energies of charged and neutral bulk $3 \times 3 \times 3$ supercells. The absolute IP and EA values have no meaning

since they are obtained using charged unit cells. Their difference, however, gives the band gap, which is 3.92 eV.

Gallino *et al.*⁸ have shown that TL in ZnO can be estimated from Janak's theorem.¹ This theorem states that the i th eigenvalue of a Kohn-Sham Hamiltonian, ϵ_i , is equal to the change in total energy with respect to occupancy of the level,

$$\frac{\partial E}{\partial n_i} = \epsilon_i. \quad (5)$$

The change in total energy as a defect energy level becomes occupied is obtained from the change in its eigenvalue with occupation,

$$E_{X^{q-1}} - E_{X^q} = \int_0^1 e_{h+1}(N+n) dn, \quad (6)$$

where $e_{h+1}(N)$ is the Γ point eigenvalue of the lowest unoccupied state for the N -electron defect supercell in charge state, q , and n is the fraction of an electron added. In practice, Eq. (6) is simplified to

$$E_{X^{q-1}} - E_{X^q} \approx \frac{e_{h+1}(N) + e_{h+1}(N+1)}{2}. \quad (7)$$

III. RESULTS

TL of three intrinsic vacancies, V_O , V_{Zn} , and V_{ZnO} , were calculated using both methods for fully relaxed supercells for each charge state. When the bulk supercell is charged, the electron in the conduction band or hole in the valence band results in a metallic state. A high k-point density is therefore necessary to achieve accurate calculations of the total energies of these states. The Crystal code was used for all calculations.¹⁵ Details of calculations, including basis sets and k-point sampling densities used in the calculations are given in the Appendix.

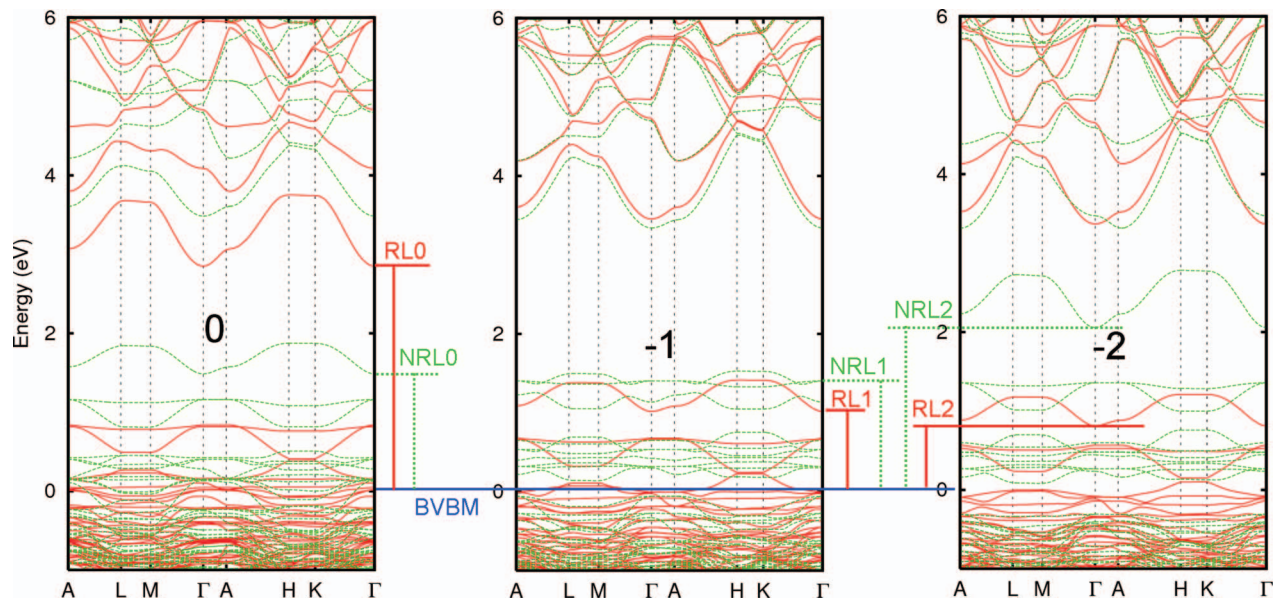


FIG. 1. Energy band diagrams for V_{ZnO} , majority spin V_{ZnO}^- and V_{ZnO}^{2-} (left to right). Green/dashed and red/solid lines denote energy bands before and after lattice relaxation, respectively. Bands which are relevant for the estimation of TL values are indicated (see text for details).

TABLE I. Comparison of transition levels (eV) predicted by TE and SPE methods obtained using $3 \times 3 \times 3$ supercells. Differences in predictions of the two methods are given under the Δ heading.

| Defect | q/q' | TE | SPE | Δ |
|-----------|--------|-----|-----|----------|
| V_O | +/0 | 1.7 | 1.5 | -0.2 |
| | 2+/+ | 2.5 | 2.1 | -0.4 |
| | 2+/0 | 2.1 | 1.8 | -0.3 |
| V_{Zn} | -/0 | 0.6 | 0.2 | -0.4 |
| | 2-/- | 0.6 | 0.4 | -0.2 |
| | 2-/0 | 0.6 | 0.4 | -0.2 |
| V_{ZnO} | 2+/0 | 1.5 | 2.0 | 0.5 |
| | 2+/+ | 0.9 | 1.0 | 0.1 |
| | +/0 | 0.6 | 0.8 | 0.2 |
| | -/0 | 2.4 | 1.9 | -0.5 |
| | 2-/- | 1.9 | 2.2 | 0.3 |
| | 2-/0 | 2.2 | 2.1 | -0.1 |

Figure 1 shows how the electronic structure of the V_{ZnO} divacancy depends on charge state and structure relaxation. The left panel shows the band structure of the neutral state of V_{ZnO} with and without relaxation. In what follows, unrelaxed supercell energy levels are denoted NR and relaxed supercell energy levels are denoted R. The lowest unoccupied state of the unrelaxed, neutral supercell is localized mainly on Zn 4s states on Zn ions neighboring the vacant O site and is marked NRL0. It shifts upward by over 1 eV when the cell is relaxed (RL0) and the degree of dispersion increases considerably. The states immediately below the NRL0 level are O 2p states associated with the vacant Zn site in V_{ZnO} (Ref. 7) and these shift downward by 0.5 eV on relaxation. The position of the defect free bulk VBM (BVBM) is also shown.

The majority spin band structure for V_{ZnO}^- is shown in the center panel of Fig. 1 and the shifted (N)RL0 levels containing the added electron are marked (N)RL1. When an electron is added to form V_{ZnO}^- it enters the (N)RL0 level which then shifts downward by over 1 eV. The energy difference, $E_{V_{ZnO}^-} - E_{V_{ZnO}^0}$, is obtained from the mean value of the RL0 and RL1 levels measured with respect to BVBM (Eq. (7)). The energy difference and corresponding $\epsilon(0/-)$ TL (Eq. (2)) is 1.9 eV, which compares to 2.4 eV using the TE method (Table I).

The band structure for the doubly charged defect is shown in the right panel in Fig. 1. The positions of the doubly occupied levels which accommodate the two added electrons in the unrelaxed or relaxed supercells are marked NRL2 and RL2. In this case, the relaxed level, RL2, shows considerably less dispersion than the unrelaxed level. The $\epsilon(-/2-)$ TL is the average of the V_{ZnO}^- minority spin, empty state partners of the RL1 (not shown) and RL2 levels. The energy difference, $E_{V_{ZnO}^{2-}} - E_{V_{ZnO}^-}$, is 2.2 eV, which compares to 1.9 eV obtained using the TE method (Table I).

Results for transition levels of all defects considered using both methods are given in Table I. TL obtained by either method are compared in graphical format in Fig. 2, which shows that there is good overall agreement between the two methods for the vacancies and charge states considered. The mean absolute difference between TE and SPE methods is 0.3 eV. The largest differences in TL predicted by TE and SPE

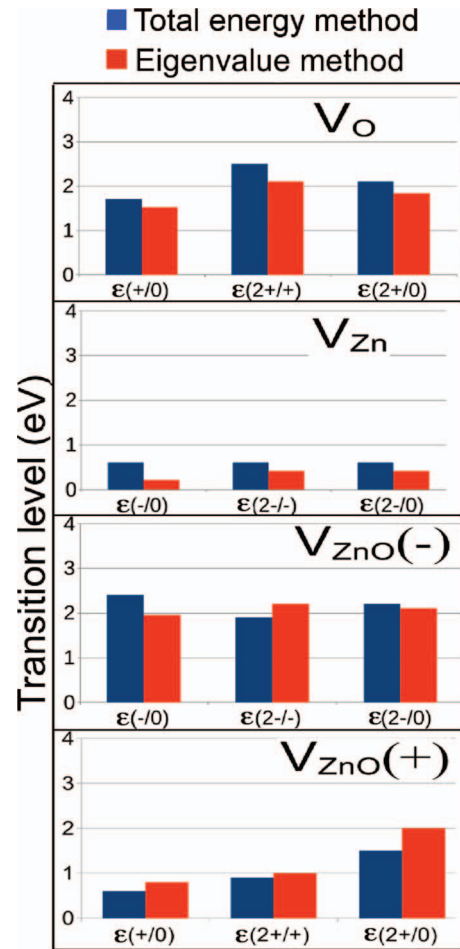


FIG. 2. Transition levels for V_{ZnO} , V_{Zn} , and V_O calculated using SPE and TE methods.

methods are ± 0.5 eV for the $\epsilon(2+/0)$ and $\epsilon(-/0)$ levels for V_{ZnO} .

Figure 1 shows the importance of full relaxation of atomic positions in defect TL calculations. It also shows that the dispersion of a defect level can increase or decrease significantly on change of occupancy or lattice relaxation. For example, the vacant RL0 level in V_{ZnO} has a bandwidth of around 1 eV which decreases to less than 0.5 eV when it becomes occupied in RL1 or RL2. An increase in the degree of dispersion of a level implies a more diffuse defect wave function. Hence, filling of this level results in a more compact defect wave function. The approximation that has been used to calculate SPE TL (Eq. (7)) implicitly assumes that the degree of dispersion does not change when the occupancy of a defect level changes, since the position of the level is calculated at the Γ point only. In an extreme case, such as the V_{ZnO} $\epsilon(-/0)$ transition, neglect of the decrease in bandwidth of the defect level when it accepts an electron will lead to an underestimate of the TL position by up to 0.5 eV. This could be corrected by sampling the band position over the Brillouin zone. The part of the Crystal09 code used in this work¹⁵ to calculate band structures is not parallelized (although the self-consistent field part is), hence a full sampling of the Brillouin zone in the SPE method would greatly increase the time taken and the efficiency of the method vis-a-vis the TE method would be lost.

TABLE II. Transition levels in eV relative to E_V compared to literature values.

| Defect | q'/q | LDA ^a | LDA + U ^a | B3LYP ^b | B3LYP ^c | HSE ^d |
|-----------|--------|------------------|----------------------|--------------------|--------------------|------------------|
| V_O | +/0 | 0.1 | 0.5 | 1.7 | 1.8 | |
| | 2+ / + | 1.0 | 1.4 | 2.5 | 2.7 | |
| | 2+ / 0 | | | 2.1 | 2.2 | 2.2 |
| V_{Zn} | -/0 | 0.1 | 0.1 | 0.6 | | 0.9 |
| | 2- / - | 0.3 | 0.4 | 0.6 | | 2.5 |
| | 2- / 0 | | | 0.6 | | |
| V_{ZnO} | 2+ / 0 | | | 1.5 | | |
| | 2+ / + | | | 0.9 | | |
| | + / 0 | | | 0.6 | | |
| | - / 0 | | | 2.4 | | |
| | 2- / - | | | 1.9 | | |
| | 2- / 0 | | | 2.2 | | |

^aReference 3.^bThis work.^cReference 8.^dReference 4.

IV. SUMMARY

In this paper, we have compared two methods for calculating the transition levels of point defects. In the TE method, TL values are calculated from the total energies of bulk supercells and supercells containing defects. In the SPE method, TL values are calculated using single-particle eigenvalues. Comparison of results from the two methods shows that they agree to within 0.5 eV, with a mean average deviation of 0.3 eV. This deviation arises from the systematic and numerical error sources contained in the two methods considered here for predicting defect transition levels. The B3LYP functional used offers improved estimates of the band gaps of semiconducting and insulating oxides^{16–19} compared to the LDA, but predicted and measured optical band gaps still differ. There is little experimental information available on defect transition levels, which makes it impossible to be certain that defect transition levels are predicted correctly, even when the optical band gap is in agreement with experiment. Numerical errors in these calculations arise from limited k-point sampling, use of an incomplete local orbital basis and approximations inherent in solving Eq. (6) numerically via the approximation in Eq. (7). Predictions for transition levels also depend on defect-defect separation. Various schemes have been devised to eliminate contributions of defect-defect interactions to defect transition levels by extrapolating the calculations to large defect separation using several defect supercell sizes.^{20,21} This has not been done here as we are simply comparing predictions of the two methods. Table II shows a comparison of TL values in literature with the values obtained in this work using the TE method. The k-point $6 \times 6 \times 6$ Monkhorst-Pack sampling density²² used here was found to be sufficient to yield IP and EA values which extrapolate correctly to the single particle band gap. Effects of varying the basis set on predicted transition levels have not been investigated.

The mean absolute difference of 0.3 eV between TL calculated by TE and SPE methods is acceptable when TL are of the order of 1–2 eV in a wide gap oxide, however shallow levels such as the donor H interstitial in ZnO (Ref. 8) lie within 0.1 eV of the band edge, where such a difference

is unacceptable. In this case, the SPE method is likely to be more accurate as it requires only shifts in band positions with occupation, whereas the TE method requires pairs of differences in large total energies of the order of 10^5 eV. In any case, calculation of TL positions by both methods will provide an important check on the reliability of a calculation and the SPE calculation can be performed at little extra expense in comparison to the TE calculation.

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APPENDIX: DETAILS OF CALCULATION

All calculations were performed using the Crystal program.¹⁵ The Gaussian orbital basis for Zn (Ref. 23) is the basis previously used by Jaffe and co-workers. The Gaussian orbital basis for O (Ref. 24) is the basis previously used by Towler and co-workers.²³ A $6 \times 6 \times 6$ Monkhorst-Pack net was used for self-consistent field calculations; a denser $12 \times 12 \times 12$ net was used for total energy evaluations. It was necessary to use this high k-point density to obtain converged total energies for metallic states which are encountered when an electron is added to (or removed from) the perfect bulk cell in transition level calculations. Tolerances for lattice sum convergence within the Crystal program were chosen to be 8, 8, 8, 8, and 16.

¹J. F. Janak, *Phys. Rev. B* **18**, 7165 (1978).²S. Lany and A. Zunger, *Phys. Rev. B* **72**, 035215 (2005).³A. Janotti and C. G. V. de Walle, *Phys. Rev. B* **76**, 165202 (2007).⁴F. Oba, A. Togo, I. Tanaka, J. Paier, and G. Kresse, *Phys. Rev. B* **77**, 245202 (2008).⁵S. J. Clark, J. Robertson, S. Lany, and A. Zunger, *Phys. Rev. B* **81**, 115311 (2010).⁶R. Vidy, P. Ravindran, H. Fjellvg, B. G. Svensson, E. Monakhov, M. Ganchenkova, and R. M. Nieminen, *Phys. Rev. B* **83**, 045206 (2011).⁷A. Chakrabarty and C. H. Patterson, *Phys. Rev. B* **84**, 054441 (2011).⁸F. Gallino, G. Pacchioni, and C. DiValentin, *J. Chem. Phys.* **133**, 144512 (2010).⁹A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).¹⁰P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).¹¹*Numerical Data and Functional Relationships in Science and Technology Landolt-Börnstein New Series Group III Vol. 17a and 22a*, edited by K. H. Hellwege and O. Madelung (Springer, New York, 1982).¹²C. H. Patterson, *Phys. Rev. B* **74**, 144432 (2006).¹³A. F. Kohan, G. Ceder, D. Morgan, and C. G. V. de Walle, *Phys. Rev. B* **61**, 15019 (2000).¹⁴C. V. de Walle and J. Neugebauer, *J. Appl. Phys.* **95**, 3851 (2004).¹⁵R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalieri, K. Doll, N. M. Harrison, I. Bush, P. D'Arco, and M. Llunell, *Crystal09 User's Manual*, University of Torino, Torino, 2009.¹⁶J. Muscat, A. Wander, and N. M. Harrison, *Chem. Phys. Lett.* **342**, 397 (2001).¹⁷I. D. P. R. Moreira, F. Illas, and R. M. Martin, *Phys. Rev. B* **65**, 155102 (2002).¹⁸S. Piskunov, E. Heifets, R. I. Eglitis, and G. Borstel, *Comput. Mater. Sci.* **29**, 165 (2004).

¹⁹F. Cora, *Mol. Phys.* **103**, 2483 (2005).

²⁰G. Makov and M. C. Payne, *Phys. Rev. B* **51**, 4014 (1995).

²¹C. Freysoldt, J. Neugebauer, and C. V. de Walle, *Phys. Rev. Lett.* **102**, 016402 (2009).

²²H. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

²³J. E. Jaffe and A. C. Hess, *Phys. Rev. B* **48**, 7903 (1993).

²⁴M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt, and E. Aprà, *Phys. Rev. B* **50**, 5041 (1994).