

Comparative study of defect transition energy calculation methods: The case of oxygen vacancy in In_2O_3 and ZnO

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Theoretical calculation of defect properties, especially transition energy levels, is typically done by first-principles density-functional theory calculation using **supercells with finite size**. So far, three approaches—**band-filling corrections (BFC)**, **band-edge corrections (BEC)**, and **no corrections (NC)**—have been applied to deal with the potential inaccuracy caused by the finite size. In this paper, we compare these three approaches by calculating the **(0/2+) ionization energies of the oxygen vacancy (V_O) in In_2O_3 and ZnO** . We find that **a correction must be included whether or not the defect level is deep or shallow**, especially when the defect band has a large dispersion. **The BFC approach gives the best correction**. The BEC approach works well in GGA calculations only for certain systems in which the band gap underestimation is partially corrected by choosing effective band edges.

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The functionality of semiconductors and wide-band-gap oxides depends critically on the properties of point defects. First-principles methods based on density-functional theory (DFT) have been widely used to predict the behaviors of defects and to help experimental design of materials with desirable properties. In most modern first-principles density functional theory (DFT) defect calculations, the supercell approach with periodic boundary conditions is used.^{1,2} The supercell calculation can describe precisely the impurity states if the cell size is infinitely large. However, due to the current limit on the computational capacity and cost, the supercell size used in a defect calculation is unavoidably finite. The finite cell size inevitably introduces uncertainties^{3,4} that should be corrected. Currently, three approaches have been proposed to deal with the uncertainties: **band-filling correction (BFC)**, **band-edge correction (BEC)**, and **no correction (NC)**. The following three methods are essentially the same: mixed k -points scheme described by Wei,⁵ which corrects the uncertainties using the energy difference between the total energies calculated at special k points and single-electron level at Γ point; the shallow-level correction method described by Van de Walle and Neugebauer,⁶ and the so-called BFC method described by Lany and Zunger.⁷ The BEC approach was proposed by Zhang,⁸ in which the correction is obtained by averaging the band-edge energy over special k points. In many cases, results with no correction are also reported.⁹ Both the BFC and BEC corrections have mostly been applied for shallow defects. So far, there are still issues under debate about these correction methods: Are these corrections necessary for qualitative description of the defects? Are they also needed for deep levels? What are the differences between the different correction methods?

In this paper, we compare these three approaches by calculating the (0/2+) ionization energies of the oxygen vacancy (V_O) in In_2O_3 and ZnO . We also compare the results obtained by generalized gradient approximation (GGA) and hybrid functional theory (HSE06). We find that in both GGA and HSE06 calculations, without correction, the V_O could be a shallow donor state in In_2O_3 . However, the V_O level becomes

deep when the correction is added. In ZnO , V_O is found to be deep both in GGA and HSE06 calculations with and without correction. However, the transition energies have different values. Therefore the corrections are necessary whether or not the defect level is deep or shallow, especially, when the defect band has a large dispersion. The BFC approach gives the best correction. The BEC approach works well in the GGA calculation only for certain systems in which the band gap underestimation is partially corrected. We explain how the corrections work based on the fundamental electronic structure.

The calculations were performed using DFT as implemented in the **VASP** code¹⁰ using the standard frozen-core projector augmented-wave (PAW) method.¹¹ The cutoff energy for basis functions is 400 eV. Both **GGA**¹² and **HSE06**¹³ are used for comparative studies. **The $(2 \times 2 \times 2)$ special k point¹⁴ and Γ point are used in the total-energy calculations for comparison**. For HSE06, the portion of the exact exchange potential has been chosen as 0.27 for In_2O_3 and 0.36 for ZnO to correct their band gaps to match experimental values.

The formation energy for a V_O in the charge state q could be written as

$$\Delta H_f(V_{O,q}) = E(V_{O,q}) - E(\text{bulk}) + \mu_O + q(E_{\text{VBM}} + E_F), \quad (1)$$

where $E(V_{O,q})$ and $E(\text{bulk})$ are total energies of supercells with a q -charged V_O and without V_O . μ_O , E_{VBM} , and E_F are chemical potential of oxygen, **valence-band maximum (VBM) of the host**, and the Fermi energy referred to VBM, respectively. For V_O , which is usually a negative U system due to large q -dependent structural relaxation,¹⁵ the most interesting thermodynamic transition energy level $\varepsilon_t(0/2+)$ is determined by the Fermi energy at which

$$\Delta H_f(V_O, 0) = \Delta H_f(V_O, 2+). \quad (2)$$

Using Eqs. (1) and (2), the transition energy level could be calculated by

$$\varepsilon_t(0/2+) = [E(V_O, 0) - E(V_O, 2+)]/2 - E_{\text{VBM}}. \quad (3)$$

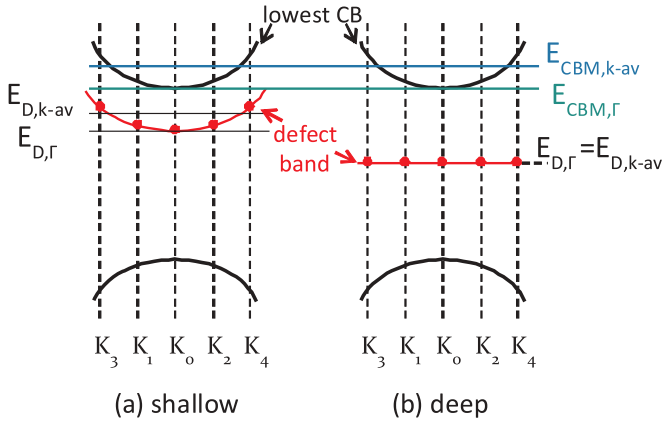


FIG. 1. (Color online) The schematic band structure of the deep and shallow V_O^0 states. The dashed lines represent the special k points used in the supercell calculations. The energy position of $E_{CBM,k-av}$, $E_{CBM,\Gamma}$, $E_{D,k-av}$, and $E_{D,\Gamma}$ are also indicated.

For a donor state, the behavior is usually described by the ionization energy ε_i [with $\varepsilon_i(0/2+)$ and $\varepsilon_t(0/2+)$ written in abbreviated form as ε_i and ε_t in the following], which is calculated by

$$\varepsilon_i = E_g - \varepsilon_t = E_{CBM} - [E(V_O, 0) - E(V_O, 2+)]/2. \quad (4)$$

To solve Eqs. (3) or (4), one often does the supercell calculation with special k points to get good k -point convergence on $E(V_O, 0)$ and $E(V_O, 2+)$ and choose the values of VBM and conduction-band minimum (CBM), which is usually at Γ point,² and the transition energy and ionization energy are then derived by

$$\varepsilon_{t,NC} = [E(V_O, 0) - E(V_O, 2+)]/2 - E_{VBM,\Gamma}, \quad (5a)$$

$$\varepsilon_{i,NC} = E_{CBM,\Gamma} - [E(V_O, 0) - E(V_O, 2+)]/2, \quad (5b)$$

where index NC in $\varepsilon_{t,NC}$ and $\varepsilon_{i,NC}$ indicates no corrections. However, the special k point used may overestimate total energy of neutral V_O within the finite cell. The schematic band structure diagrams of the shallow and deep donor states are shown in Fig. 1. A defect band should be flat and converge to a single point in the limit of an infinitely large supercell, whereas it is more dispersive in a finite supercell. For the neutral V_O , the extra two electrons will occupy the defect band. In the approximations adopted in Refs. 5 and 6, the shallow level is supposed to be the perturbation to the host band and with the same dispersion as in Fig. 1(a), and the deep level is supposed to be flat within the band gap as in Fig. 1(b). In the limit of shallow level [see Fig. 1(a)], the extra two electrons will occupy the dispersive band with an average energy ($E_{D,k-av} = \sum_i \omega_i \varepsilon_{D,i}$, with $\sum_i \omega_{D,i} = 2$). Here, ω_i is the weight of the defect state at the i th k point, and $\varepsilon_{D,i}$ is the eigenvalue of the defect band at the i th k point. In the infinite cell approximation, these two electrons will only occupy state at the Γ point. However, in a calculation using a finite cell size, the electrons will occupy the defect levels at many k points, resulting in errors. The so-called BFC term of $2(E_{D,k-av} - E_{D,\Gamma})$, which is described as E_{corr} ⁶ or ΔE_{bf} ,⁷ should be subtracted from the $E(V_O, 0)$, and its impact on transition energy is explicitly given as Eq. (3) in Ref. 5.

Here, we rewrite the formula for calculating the transition and ionization energy with BFC as

$$\varepsilon_{t,BFC} = [E(V_O, 0) - E(V_O, 2+)]/2 - E_{VBM,\Gamma} - (E_{D,k-av} - E_{D,\Gamma}), \quad (6a)$$

$$\varepsilon_{i,BFC} = E_{CBM,\Gamma} - [E(V_O, 0) - E(V_O, 2+)]/2 + (E_{D,k-av} - E_{D,\Gamma}). \quad (6b)$$

For the BEC method, the band edge (VBM/CBM) is also determined by the special k -point eigenvalues ($E_{CBM,k-av} = \sum_i \omega_i \varepsilon_{CBM,i}$ and $E_{VBM,k-av} = \sum_i \omega_i \varepsilon_{VBM,i}$ with $\sum_i \omega_i = 2$), rather than the band-edge states at the Γ point ($E_{VBM,\Gamma}$, $E_{CBM,\Gamma}$). In this way, all the energy terms are kept, and the band edge in Eqs. (3) and (4) is chosen as $E_{VBM,k-av}$ and $E_{CBM,k-av}$, respectively, and the transition and ionization energies in the BEC approach are calculated by

$$\varepsilon_{t,BEC} = [E(V_O, 0) - E(V_O, 2+)]/2 - E_{VBM,k-av}, \quad (7a)$$

$$\varepsilon_{i,BEC} = E_{CBM,k-av} - [E(V_O, 0) - E(V_O, 2+)]/2. \quad (7b)$$

Using GGA, we have calculated the V_O (0/2+) transition energy level and ionization energies of In_2O_3 defined by different correction methods above using various supercell sizes. The HSE06 is also used to check the results in the small supercell (≤ 80 atoms/supercell), and the physics discussed below does not change because the defect band structures of V_O in the 80-atom supercell calculated by GGA and HSE06 are similar.

The comparison of ionizations energies. With an 80-atom supercell, our calculated ionization energy of V_O in In_2O_3 using BFC ($\varepsilon_{i,BFC}$) is 0.18 eV (see Fig. 2), which is quite consistent with previous reported results using the same correction.¹⁶ Without correction, the transition level of V_O ($\varepsilon_{t,NC}$) is above $E_{CBM,\Gamma}$ (see Fig. 3) and the ionization energy ($\varepsilon_{i,NC}$) is -0.64 eV, consistent with the result in Ref. 9. With BEC, the transition energy level is referred to $E_{CBM,k-av}$ and the calculated ionization energy $\varepsilon_{i,BEC}$ is 0.56 eV. The V_O of In_2O_3 is predicted to be the resonant donor state without correction,⁹ which is obviously inconsistent with the band structure in Fig. 3(a) and localization character of V_O state at Γ point (not shown). From above, we see that the correction is indispensable to determine the behaviors of V_O in In_2O_3 . It is interesting to see that the calculated $\varepsilon_{i,\Gamma}$ (ionization energy with total energy calculated at only Γ point) by HSE06 is 0.57 eV, comparable to 0.56 eV of $\varepsilon_{i,BEC}$ calculated by GGA. We will discuss this occurrence later.

The origin of the correction term. The transition levels $\varepsilon_{i,NC}$ calculated using $(2 \times 2 \times 2)$ special k points and Γ point have large discrepancies, and their trends are opposite when cell size becomes large. For example, their difference is 0.82 eV for the 80-atom supercell and 0.39 eV for the 640-atom supercell. This difference is actually due to the correction term of $E_{D,k-av} - E_{D,\Gamma}$, which is about half of the V_O defect band width and could be understood easily from Fig. 1(a). As for the V_O in In_2O_3 , the defect band is dispersive, and the band width could remain a fraction of an electron volt, even when the supercell contains hundreds of atoms [see Fig. 4(a)]. In this case, the correction term is essential. It was stated that such a correction was only used in shallow defect.^{6,7} We observed here that even for some relatively deep defect, such

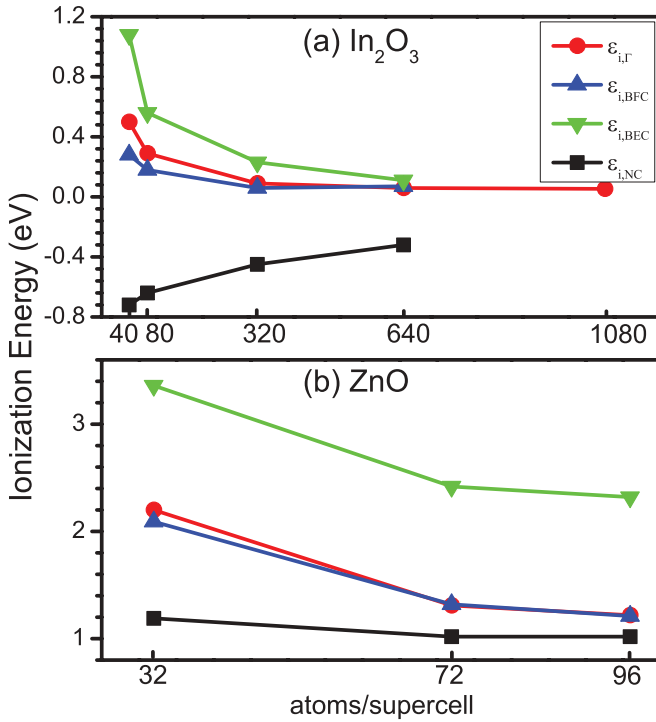


FIG. 2. (Color online) The ionization energy in (a) In_2O_3 and (b) ZnO as functions of the supercell size in different methods, namely, Γ -point-only calculation (red circles) and $(2 \times 2 \times 2)$ k -points calculation with NC by Eq. (5b) (black squares), with BFC by Eq. (6b) (blue triangles), with BEC by Eq. (7b) (green inverted triangles). The results of In_2O_3 are calculated by GGA and those of ZnO are by HSE06.

as V_O in In_2O_3 , the correction is necessary because the defect band is still dispersive. The width of the defect band should be a criterion for the correction, not the simple estimate of the deepness or shallowness of the defect level.

The difference between BFC and BEC. With an 80-stom supercell, the calculated ionization energies with BFC and BEC are 0.18 and 0.56 eV, respectively. Comparing Eqs. (6b) and (7b), the discrepancy is due to the difference between $(E_{\text{CBM},k-\text{av}} - E_{\text{CBM},\Gamma})$ and $(E_{\text{D},k-\text{av}} - E_{\text{D},\Gamma})$, which is roughly the difference between the band width of the lowest conduction band (CB) of bulk In_2O_3 and that of the V_O defect band. As shown in Fig. 3(a), even though the V_O band is dispersive and has similar curvature near Γ point as the bulk lowest CB, they are not exactly parallel, especially at k points far away from the Γ point. As a result, the band width of the lowest CB is wider than that of the V_O band. However, in the limit of shallow defect approximation, which considers the defect band as the perturbation of the host band, or the infinitely large supercell size in which both of the bandwidths are close to zero, the BFC and BEC will result in the same ionization energy.

The convergence on the supercell size. When total energy is calculated using the Γ point only (in this case, $E_{\text{CBM},k-\text{av}} = E_{\text{CBM},\Gamma}$, $E_{\text{VBM},k-\text{av}} = E_{\text{VBM},\Gamma}$, and $E_{\text{D},k-\text{av}} = E_{\text{D},\Gamma}$), the results by BFC, BEC, and NC are all the same. It is expected that the results by BFC and BEC using $(2 \times 2 \times 2)$ special k points should converge to the result obtained in the infinitely large supercell faster than the one with no correction. As

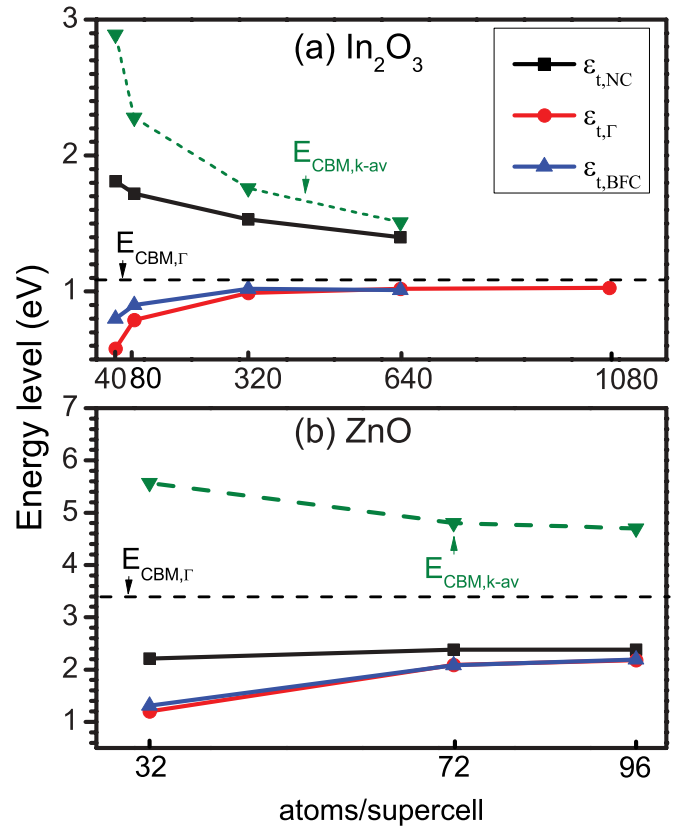


FIG. 3. (Color online) The V_O transition energy levels of (a) In_2O_3 and (b) ZnO as functions of the supercell size in different methods. The black squares and red circles are calculated transition levels directly from Eq. (5a) with NC. The black squares are calculated on $(2 \times 2 \times 2)$ k points and the red circles are on Γ -point only. The blue triangles are calculated on $(2 \times 2 \times 2)$ k points by Eq. (6a) with BFC. The averaged CBM ($E_{\text{CBM},k-\text{av}}$) and CBM at Γ point ($E_{\text{CBM},\Gamma}$) are also indicated. The results of In_2O_3 are calculated by GGA and those of ZnO are by HSE06. All the energies are referred to $E_{\text{VBM},\Gamma}$ ($E_{\text{VBM},\Gamma} = 0$).

shown in Fig. 2, ionization energy for the converged result is 0.08 eV. The result by BFC at $(2 \times 2 \times 2)$ special k points converges at the 320-atom supercell, whereas the result by only Γ converges at the 640-atom supercell. However, the result by BEC $(2 \times 2 \times 2)$ special k points does not converge well, even at the 640-atom supercell ($\epsilon_{i,\text{BEC}} = 0.11$ eV).

The behaviors of V_O in ZnO are a little different from that in In_2O_3 . Because the V_O band of ZnO is resonant inside the valence band in the GGA calculation, the HSE06 functional is used in this case. Comparing to In_2O_3 , we observed: fast convergence on the supercell size. The convergence of $\epsilon_{i,\text{BFC}}$, $\epsilon_{i,\text{NC}}$, and $\epsilon_{i,\Gamma}$ on the supercell size are quite good using a 72-atom cell. The difference between $\epsilon_{i,\text{BFC}}$ and $\epsilon_{i,\Gamma}$ is negligible and that between $\epsilon_{i,\text{BFC}}$ and $\epsilon_{i,\text{NC}}$ is small compared to that in In_2O_3 . The above difference between ZnO and In_2O_3 is due to different dispersion or band width of V_O band in ZnO and In_2O_3 . As shown in Fig. 4, the V_O band in ZnO is much flatter and narrower than that in In_2O_3 .

Qualitatively correct value without correction. In In_2O_3 , $\epsilon_{t,\text{NC}}$ is above $E_{\text{CBM},\Gamma}$, whereas in ZnO , $\epsilon_{t,\text{NC}}$ is below $E_{\text{CBM},\Gamma}$, because the whole V_O band in ZnO is much below the $E_{\text{CBM},\Gamma}$.

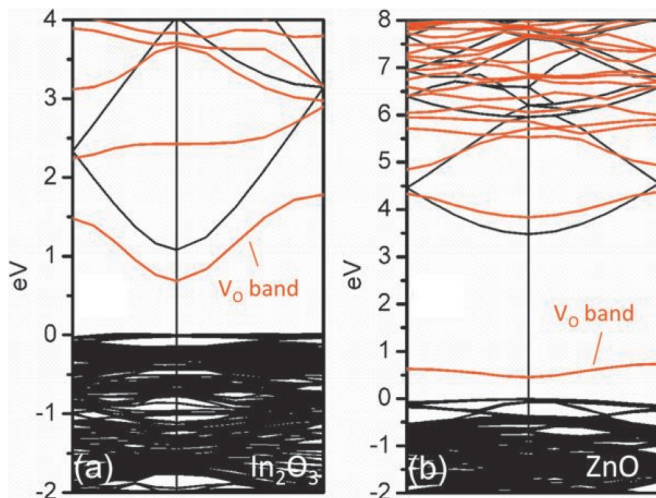


FIG. 4. (Color online) The band structures of (a) 80-atom In_2O_3 and (b) 96-atom ZnO supercells. Partial band structures with one V_O inside the supercell are highlighted as red (gray) lines. Their eigenvalues are aligned by comparing the O $1s$ core level away from V_O site with the bulk value. To clearly show the V_O defect bands derived from conduction band, all the valence bands are labeled as black. The results of In_2O_3 are calculated by GGA. The results of ZnO are calculated by HSE06 because the V_O band of ZnO is resonant inside the valence band in GGA calculation.

The calculated $\varepsilon_{i,\text{BFC}}$, $\varepsilon_{i,\text{BEC}}$, $\varepsilon_{i,\text{NC}}$, and $\varepsilon_{i,\Gamma}$ using a 72-atom cell are 1.32, 2.42, 1.02, and 1.31 eV, respectively. Because the $\varepsilon_{i,\text{NC}}$ is close to $\varepsilon_{i,\text{BFC}}$ and $\varepsilon_{i,\Gamma}$, the correction term is not important for qualitatively predicting V_O in ZnO , which is also due to the flat V_O band. Our calculated $\varepsilon_{i,\text{NC}}$ is consistent with the reported results in Ref. 9.

Overestimation by BEC. The $\varepsilon_{i,\text{BEC}}$ is much larger since the band width of the lowest CB is much wider than that of V_O band, and thus the BEC is inapplicable when the defect band is flat. Actually, the BEC is often used in the GGA/LDA calculation and sometimes gives reasonable results, such as the consistency of 0.56 eV of $\varepsilon_{i,\text{BEC}}$ by GGA and 0.57 eV by HSE06. One of the reasons for the sometimes reasonable results is that in GGA/LDA calculation, the effective band gap ($E_{\text{CBM},k-\text{av}} - E_{\text{VBM},k-\text{av}}$) is larger than the fundamental gap ($E_{\text{CBM},\Gamma} - E_{\text{VBM},\Gamma}$) and the band gap problem of GGA/LDA is partially corrected in the BEC approach with small supercell.⁸ However, in hybrid calculation, since the band gap ($E_{\text{CBM},\Gamma} - E_{\text{VBM},\Gamma}$) has already been recovered, the BEC results always overestimate the transition level and ionization energy in this case.

The corrections for the finite supercell may include many aspects^{1,3,17–19} and for each aspect, various schemes have been applied.^{4–8} The widely scattered data in literature for a particular defect were often attributed to the different corrections without giving further details, which could lead to contradict results in defect calculation. So far, there is no systematic study or comparison on different schemes of each aspect. In this paper, we focused on the particular issue of spurious band dispersion and compared the results obtained using various correction schemes. For a meaningful comparison, we kept all the correction methods for other aspects the same, i.e., the core level was chosen as the potential alignment and no Makov-Payne correction was applied for charged defects, because it could induce additional errors by overestimating the interaction.^{5,6} By considering the spurious defect band dispersion only, our results, which are consistent with many of previous published results, suggest that BFC was the most reliable one.

The correction for the spurious defect band dispersion should be larger when the defect band is more dispersive. For transparent conductive oxides (TCO), which are the interest in this paper, the donor state of V_O is considered since the lowest conduction band of TCO is mainly the dispersive cation s band so that the amount of correction could be non-negligible. For defects such as V_{In} and V_{Zn} , which are derived from the less dispersive valence band, the correction is relatively small. The calculated amount of corrections for V_{In} and V_{Zn} are within 0.02 and 0.14 eV, respectively.

In conclusion, we have compared different approaches for correcting the errors to calculated defect properties. We find that correction must be added when special k points are used in the calculation. Otherwise, some unphysical properties such as negative ionization energy (shallow level) may emerge as an artifact. If the cell size is too small, the results obtained by both BEC and BFC may not converge, but their results should be qualitatively correct. In GGA/LDA calculations, the BEC on a finite supercell could give reasonable results compared to the experiment, due to the band gap correction by effective band edges. However, it overcorrects by predicting much deeper levels when the band gap has already been corrected by advanced method such as HSE06.

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³The finite cell corrections needing to be considered may include (i) the k -point sampling corrections; (ii) the potential alignment corrections; (iii) total energy corrections for charged systems; and

(iv) LDA/GGA band gap corrections. To emphasize the effects by different approaches for (i), the corrections methods used in (ii)–(iv) are kept the same and are not discussed in the present paper.

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