Comparison of charged-defect finite-size supercell correction methods in a general framework

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Starting from the total energy expressions within density functional theory, we are able to perform a comparison of several currently used charged-defect finite-size supercell correction schemes in a unified manner. This approach also provides a framework for a further development of corrections not only for DFT supercell calculations, but also for more advanced methods and for complex geometries. The comparison is performed for three separate defect cases: a gallium vacancy in GaAs, a beryllium interstitial in GaAs and a vacancy in diamond. We found two methods working sufficiently well for all three cases: a method which is very similar to one presented by Freysoldt, † and a slightly altered potential alignment method.

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I. INTRODUCTION

The usual low concentration of defects in connection with the long-range Coulomb interaction is a difficult case for the supercell calculations within the density functional theory (DFT) framework. Especially if the defect is charged, the calculated formation energies strongly depend on the supercell size. Several correction schemes have been proposed to allow a calculation of defect properties in an effectively low concentration by using only a small supercell. [1, 2, 3, 4] However, a consensus on the validity and applicability of each method seems to be missing, although numerical comparisons have been done. [5]

In this paper, we start by deriving a generalized approach for the charged defect supercell calculations, which is based on the construction and comparison of the DFT total energy equations for the supercell and for a much larger cell. This is useful in several ways: a) This allows us to properly compare several contributions of the corrections and several previous correction methods. We show how several schemes come out as limits or approximations of the general equations. We particularly concentrate on the method recently introduced by Freysoldt et al.,[1] and also the Makov-Payne [2] and the potential alignment schemes [3] are reviewed. b) It shows the required approximations in a clear manner. Even if the final results look intuitively simple, the way to get there has a few corners. c) Paves the way for the development of even better schemes. We present two more schemes in this paper. d) It should prove useful in developing correction schemes for more advanced methods such as hybrid-functionals or GW, and for more complex geometries such as interfaces or clusters. The first three items are considered in detail in this article. The last one is briefly considered in the discussion part, but mostly left for later study.

Finally, we compare these methods for three defects: gallium vacancy in GaAs, carbon vacancy in diamond and beryllium interstitial in GaAs. In order to find the results to compare at, we use a set of calculations with increasing supercell sizes to extrapolate the results to the low concentration limit.

II. CORRECTION SCHEME

The defect calculation is usually approached through the concept of the formation energy, defined as [3]

\[
E_f[X^q] = E_{tot}[X^q] - E_{tot}[\text{bulk}] - \sum_i n_i \mu_i + q[E_F + E_v + \Delta V],
\]

(1)

where \(E_{tot}[X^q]\) is the total energy of the supercell with the defect \(X^q\) (in the charge state \(q\)) and \(E_{tot}[\text{bulk}]\) is the total energy of the supercell of bare GaAs or GaAsN bulk, depending on the case. The chemical potentials \(\mu_i\) of \(n_i\) added or removed atoms allow us to describe various growth conditions. Here, \(E_v\) is the valence band maximum (VBM) at \(\Gamma\)-point in the bulk material, \(E_F\) is the Fermi energy with respect to \(E_v\), and \(\Delta V\) is the shift term used to align the potentials in between the two supercells.

Before moving on to the finite-size supercell considerations, we divide the comparison of charge defect and bulk cases in to two parts: comparison of a neutral defect to the bulk, and the comparison of a charged defect to a neutral defect

\[
E_f[X^0] = E[X^0] - E[\text{bulk}] - \sum_i n_i \mu_i
\]

(2)

\[
E_f[X^q] = E_f[X^0] + \Delta E_f[X^q]
\]

(3)

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\[ \Delta E^f[X^q] = E_{\text{ext}}[X^q] - [E_{\text{ext}}[X^0] + q(E_{\text{xc}}[X^0] + E_{\text{p}})] \] (4)

We see, that in this approach the addition/removal of electrons, the VBM energy is in the energy reference of the neutral defect. The implications of this will be discussed later. Moreover, Comparison of charge densities and potentials between charged defect and bulk can be difficult, especially in the case of relaxed geometry. On the other hand, comparison of charged defect and neutral defect properties is often much easier.

Naturally, defect calculations within DFT-LDA also suffer from the band-gap problem. This problem is important to acknowledge in the analysis of the results, but does not affect the analysis of the supercell-size correction methods.

A. Charged-defect finite-size supercell corrections

We will start by writing and comparing the total energies for neutral defect, charged defect in a small supercell, and a charged defect in a much larger supercell. For the neutral defect charge distribution \( \rho_0 \) the total energy within the DFT framework is

\[ E[\rho_0] = T[\rho_0] + E_{\text{ext}}[\rho_0] + E_{\text{xc}}[\rho_0] \] (5)

Adding a localized charge distribution \( \delta q \) results in a redistribution of the surrounding electrons. We circumvent this problem, by just writing the total density as \( \rho_0 + q_d \). Moreover, we denote the periodically repeating charge distribution of small supercell as \( \tilde{q}_d \). The total energies for the supercell of volume \( \Omega \) and a large cell of volume \( \tilde{\Omega} \) are then

\[
\begin{align*}
E_{\text{tot}}^\Omega[\rho_0 + q_d] &= T^\Omega[\rho_0 + q_d] + E_{\text{ext}}^\Omega[\rho_0 + q_d] + E_{\text{xc}}^\Omega[\rho_0 + q_d] \\
E_{\text{tot}}^\tilde{\Omega}[\rho_0 + q_d] &= T^\tilde{\Omega}[\rho_0 + q_d] + E_{\text{ext}}^\tilde{\Omega}[\rho_0 + q_d] + E_{\text{xc}}^\tilde{\Omega}[\rho_0 + q_d]
\end{align*}
\]

Usually, one would like to calculate the formation energy of a single defect in an infinite crystal, or at least of much lower concentration of defects than is possible to obtain in the supercell calculations i.e., we would like to have \( E_{\text{tot}}^\Omega[\rho_0 + q_d] \). Instead, what we get from the supercell calculations is \( E_{\text{tot}}^\Omega[\rho_0 + q_d] \). Thus, what we are looking for in here, is a correction \( \Delta E \), such that \( E_{\text{tot}}^\Omega[\rho_0 + q_d] - E_{\text{tot}}^\Omega[\rho_0] \) required for Eq. 1 can be obtained from \( E_{\text{tot}}^\Omega[X^q] - E_{\text{tot}}^\Omega[X^0] + \Delta E \). Also notice, in the following, we have taken the ionic configuration to be the same in all three cases.

Due to the locality of the kinetic energy \( T \) and the exchange-correlation energy \( E_{\text{xc}} \), and the localization of \( q_d \) in the supercell, we will now assume that

\[
T^\Omega[\rho_0 + q_d] = T^\tilde{\Omega}[\rho_0 + q_d] + T^\Omega[\rho_0] - T^\tilde{\Omega}[\rho_0] \] (6)

and similarly for \( E_{\text{xc}} \), so it follows that \( T^\Omega[\rho_0 + q_d] - T^\Omega[\rho_0] = T^\tilde{\Omega}[\rho_0 + q_d] - T^\tilde{\Omega}[\rho_0] \). Unfortunately, this can not be done for the electrostatic energy, but we can now write the total energy differences in the large and small supercell, and find, that their difference, which is the correction that we are looking for, depends only on the electrostatic energy difference

\[
\Delta E = E_{\text{tot}}^\Omega[\rho_0 + q_d] - E_{\text{tot}}^\tilde{\Omega}[\rho_0] - \left( E_{\text{tot}}^\Omega[\rho_0] - E_{\text{tot}}^\tilde{\Omega}[\rho_0] \right)
\]

\[
= E_{\text{tot}}^\Omega[\rho_0 + q_d] - E_{\text{tot}}^\Omega[\rho_0] - E_{\text{tot}}^\tilde{\Omega}[\rho_0] + E_{\text{tot}}^\tilde{\Omega}[\rho_0]
\]

The electrostatic potential corresponding to \( \rho_0 \) is denoted as \( V_0 \) (consisting of the external potential and the Hartree potential). The electrostatic energy is (omitting \( dr^3 \) for brevity)

\[
E_{\text{es}}[\rho_0] = \int \rho_0 V_{\text{ext}} + \frac{1}{2} \int \rho_0 V_H = \int \rho_0 (V_{\text{ext}} + \frac{1}{2} V_H + \frac{1}{2} V_{q/0})
\]

where the \( \frac{1}{2} \) takes care of the double counting of electron-electron interactions. Moving on to the charged case, there is a change in the Hartree potential \( V_H \rightarrow V_H + V_{q/0} \) and subsequently in the electrostatic potential \( V_0 \rightarrow V_0 + V_{q/0} \). The electrostatic energy is then

\[
E_{\text{es}}[\rho_0 + q_d] = \int (\rho_0 + q_d + n)(V_{\text{ext}} + \frac{1}{2} V_H + \frac{1}{2} V_{q/0})
\]

where \( n = -q/\Omega \) is the neutralizing background. \( V_{q/0} \) is the change of electrostatic potential in small supercell, which is also, due to the linearity of Poisson equation, the solution for \( q_d \). In the periodic case, we have similarly added charge \( \tilde{q}_d \approx q_d \), but per unit cell of volume \( \tilde{\Omega} \), so the compensating background charge is \( \tilde{n} = -q/\tilde{\Omega} \), giving

\[
E_{\text{es}}[\rho_0 + \tilde{q}_d] = \int (\rho_0 + \tilde{q}_d + \tilde{n})(V_{\text{ext}} + \frac{1}{2} V_H + \frac{1}{2} V_{q/0})
\]

Notice, that often \( \tilde{n} \) (and \( n \) term is not included in DFT codes in the calculation of the electrostatic energy. However, for the moment, we still leave this term in.

It can be easily shown that

\[
\int (q_d + n)(V_{\text{ext}} + \frac{1}{2} V_H) = \int (\tilde{q}_d + \tilde{n})(V_{\text{ext}} + \frac{1}{2} V_H)
\]

and

\[
\int q_d V_0 = \int \rho_0 V_{q/0}
\]

so that we are left with

\[
\Delta E = \frac{1}{2} \int (q_d + n)V_{q/0} - \frac{1}{2} \int (\tilde{q}_d + \tilde{n})V_{q/0}
\]

We have arrived at a rather intuitive form, which is often taken as a starting point for developing the defect correction formulae. Deriving this formula, \( q_d \) was defined as the charge difference between the charged and
neutral defect calculations. In order to find more simple correction formula, an analytic form is assumed for \( q_d \). In this case, however, one should also keep in mind that the corresponding potential needs to be correctly screened, which depends on the whole system. One can use the static dielectric constant and arrive at the Makov-Payne correction \([2]\). Alternatively, as was done in Ref. \[1\], \( V_{q/0} \) can be divided in to the long- and short-range parts, where the screening only in the long-range potential is handled with the static dielectric constant.

1. Separation of long and short-range potentials

In Ref. \[1\] the long and short-range parts of the electrostatic potentials were separated as

\[
V_{q/0} = V_{q}^{lr} + V_{q/0}^{sr}
\]

where \( V_{q}^{lr} \) is the potential solved from \( q_d \) using the static dielectric constant. Similar separation is done for the \( V_{q/0} \), which is known from the calculation, and can then be used to determine the short-range potentials. Since \( q_d \) is localized to the unit cell, \( \int_\Omega q_d V_{q/0} \) can be changed to \( \int_\Omega q_d V_{q/0} \) and a little rearrangement results in

\[
-\Delta E = \frac{1}{2} \int_\Omega (q_d + \hat{n})(V_{q/0} - V_{q/0}) + \frac{1}{2} \int_\Omega V_{q/0} - \frac{1}{2} \int_\Omega V_{q/0}
\]

(14)

Which equals to Eqs. (6) and (7) in Ref. \[1\] when \( n \rightarrow 0 \), except the second last term has an extra \( \frac{1}{2} \). The minus sign comes from the difference in the definition of the potential. Note also, that when given in this form, it is possible to calculate the correction corresponding to any concentration of defects (i.e., per volume \( \Omega \)).

In calculations, the averages of potentials \( V_0, \hat{V}_q, \) and \( \hat{V}_{q/0} \) are all set to zero. Next, we can choose \( V_{q/0} \) such that it approaches zero as \( r \rightarrow \infty \). Moreover, let’s write

\[
V_{q/0}^{sr} = \sum_r V_{q/0}^{sr} + C \quad \text{as in Ref. \[1\].}
\]

With these considerations

\[
-\Delta E = \frac{1}{2} \int_\Omega (q_d + \hat{n})(V_{q/0}^{sr} - V_{q/0}) + \frac{1}{2} \int_\Omega V_{q/0}^{sr} - \frac{1}{2} \int_\Omega (V_{q}^{lr} + V_{q}^{sr})
\]

(15)

since

\[
\int V_{q}^{sr} = \int \hat{V}_{q}^{sr} - C = \int \hat{V}_{q/0}^{sr} - V_{q/0}^{sr} - C = \int C
\]

(16)

and \( \hat{n} \int_\Omega C = n \int_\Omega C \), we get

\[
-\Delta E = \frac{1}{2} \int_\Omega (q_d + \hat{n})(\hat{V}_{q}^{lr} - V_{q}^{lr}) + \frac{1}{2} \int_\Omega (V_{q}^{lr} + C) - \frac{1}{2} \int_\Omega (V_{q}^{lr} + C)
\]

(17)

\[
= \frac{1}{2} \int_\Omega (q_d + \hat{n})(\hat{V}_{q}^{lr} - V_{q}^{lr}) + \frac{1}{2} \int_\Omega V_{q}^{lr} - \frac{1}{2} \int_\Omega (V_{q}^{lr})
\]

(18)

Finally, because \( \int_\Omega \hat{n}\hat{V}_{q}^{lr} = 0 \) and \( \frac{1}{2} \int_\Omega V_{q}^{lr} \rightarrow 0 \) as \( \Omega \rightarrow \infty \), a very simple result is obtained:

\[
-\Delta E = \frac{1}{2} \int_\Omega (q_d + \hat{n})(\hat{V}_{q}^{lr} - V_{q}^{lr})
\]

(19)

We see that there is no dependence on the potential shift \( C \), nor shifts \( A \) or \( B \), but this is not really in disagreement with Ref. \[1\]. In our approach, similar potential alignment term comes from taking the VBM with respect to the neutral defect energy reference (see Eqs. \[2\]-\[4\]).

2. Makov-Payne

Makov-Payne correction \([2]\) is

\[
\Delta E = q^2 \alpha /2\varepsilon_r L + \frac{2\pi q Q_r}{3\varepsilon_r L^3}
\]

(20)

where

\[
Q_r = \int q_d r^2
\]

(21)

is the second radial moment of the density difference. For SC lattice \( \alpha = 2.8373 \). \[4\]. When \( q_d \) approaches delta-function, the Eq. \[19\] approaches Makov-Payne equation. This is demonstrated in Figure \[1\] for different supercell sizes and widths of \( q_d \). Similar calculations were also presented in Ref. \[7\].

When \( q_d \) is estimated as a gaussian distribution, the correction becomes somewhat smaller and the dependence on the supercell size decreases. Also note, that for a Gaussian \( q_d \), some of these terms can be calculated analytically (see e.g. Ref. \[8\]).
B. Potential alignment method

In the potential alignment scheme, the difference of the electrostatic potential far from defect with respect to the bulk, $\Delta V$, is read, essentially resulting in energy correction $\Delta E = q\Delta V$. We calculated $\Delta V$ for a simple model charge density of a (nearly) point charge and a neutralizing background in a simple-cubic supercell geometry, expecting to obtain a simple dependence of $\Delta V$ on dielectric constant and supercell size. Indeed, we find the following form for the potential at the farthest point

$$\Delta V \approx 0.78 \frac{q}{\varepsilon_r L}$$  \hspace{1cm} (22)

where $L$ is given in the units of bohr and the potential in the units of Hartree. The energy correction has again the same $q^2 / \varepsilon_r L$ scaling although the constant is smaller than in the Makov-Payne correction for the cubic cell (2.8373/2 $\approx$ 1.419). Later in this article, this energy correction is called analytic potential alignment.

The similarity of the calculated and analytic potential alignments can be seen in Figures 2, 3, and 6.

C. Energy comparison

Here we consider how to best evaluate the VBM energy $E_v[X^0]$ in Eq. 4. In case there are no defect states near the VBM, there is no problem in the first place. However, even if there are defect states mixing with VBM, in the case of neutral defect, the electrostatic potential should converge to the bulk value fast (faster than the extrapolated value from the uncorrected $\Delta E = q\Delta V$.)

We find that taking the electrostatic potential difference from the ion cores or the plane-averaged over the supercell far from defect gives very similar result. Especially so in the unrelaxed geometries, but in the relaxed geometries the former probably proves easier to use. The usage of $E_v[X^0]$ from the neutral defect calculation instead of bulk $E_v$ is later denoted as VBM alignment. Notice the difference to the potential alignment method, where the potential difference is taken for each charged supercell of interest.

D. Complete method and discussion

Here we outline two correction schemes that seemed to work well for the studied cases.

To sum up, the final correction scheme is then the following:

1. Obtain VBM alignment ($E_v[X^0]$) from the comparison of neutral defect and bulk.

2. Find gaussian $q_d$ which gives close match to the resulting change in the electrostatic potential between charged and neutral defects. (When far from the defect.)

3. Apply Eq. 19 to get the final formation energy, along with the Eqs. 22

This is the scheme I.

We also found, that the following scheme (scheme II) seems to work surprisingly well:

1. Obtain the VBM alignment ($E_v[X^0]$) as before

2. Correct the formation energies by using the analytical form for the potential alignment Eq. 22

III. APPLICATIONS

In all of the calculations, we use planewave density-functional theory code VASP within the PAW-LDA formalism. \cite{9, 10, 11} In GaAs calculations, we have chosen gallium to have 3d frozen in the core and 400 eV cutoff. In diamond calculations, the cutoff is 500 eV. We use 64-atom supercells with $4 \times 4 \times 4$ $k$-points, 216-atom supercells with $2 \times 2 \times 2$ $k$-points, and 512-atom supercells with $2 \times 2 \times 2$ $k$-points.

We will now consider three test cases: a gallium vacancy in GaAs, a vacancy in diamond, and a beryllium interstitial in GaAs. All of these are calculated in both the unrelaxed and the relaxed geometries. In all of the following formation energy figures, lines of the form $aL^{-1} + bL^{-3} + c$ are fitted to the calculated values to obtain extrapolated values in the limit $L^{-1} \to 0$ ($L \to \infty$).

A. Gallium vacancy in GaAs

The application of several correction schemes for the gallium vacancy are shown in Figure 2. Makov-Payne scheme seems to work well, potential alignment underestimates the formation energies. Scheme I tends to overestimate the formation energies about 100 meV in large supercells and somewhat more in the 64-atom supercell. With VBM alignment, formation energies converge to a lower value. Consequently, scheme II energies are slightly lower than the extrapolated value from the uncorrected energies. However, the energies have very little variation over the supercell sizes in this scheme.

B. Carbon vacancy in diamond

Similar to Ref. 1, we calculate the carbon vacancy in diamond for neutral, $+2$ and $-4$ charge states. In this case, due to the large band gap of diamond, there is no energy overlap of the defect states and the band edge states. This, along with large variations in stable charge
states, makes the case particularly suitable for studying finite-size supercell interactions without having to worry about the band-gap errors.

The formation energies are shown in figure 3. Especially for the +2 case, Makov-Payne notably overcorrects. Potential alignment seem to work fairly well. Scheme II surprises again, with very little variation and energies close to the extrapolated value. Note, however, that for the $V_{Ga}^{+2}$ defect the analytic and calculated potential alignments differ considerably.

Scheme I overcorrects again, but more than in the case of gallium vacancies. A reason can be traced to the charge distribution difference among the charged and neutral cases. The charge distribution difference of the relaxed $V_{Ga}^{+2}$ and $V_{Ga}^{-4}$ with respect to the bulk case are shown in Figure 5. The charge difference seems good in the neutral case, but in the charged cases, the added/removed charge is almost completely delocalized, except that e.g. $V_{Ga}^{-4}$ does not converge to $-4$, but $-3.5$. As the Poisson equation solution is also governed by the charge distribution away from the defect (large volume at large distance $r$), it seems worth trying to use these charges in the correction schemes. This fixes nicely the formation energies produced by scheme I, and also improves Makov-Payne results, except for the unrelaxed 64-atom supercell result.

In any case, these charge distribution graphs seem to contradict with the basic premise of the correction methods that there is a localized charge. Still, the corrections work fairly well. The occupied/emptied state was localized around the defect (not a host band), meaning that there must be a compensating change in the valence band electron density. This behavior in the charge differences was found in all three defect cases.

The potentials $\tilde{V}_q^r$ and $V_q^r$ and the calculated potential are shown in Figure 4. We see that the potentials match very well when compared to the neutral case. This justifies the division of formation energy calculation into two parts.

C. Beryllium interstitial in GaAs

In order to test the method with something other than a vacancy, we calculated beryllium interstitial in GaAs. It was chosen, because we know from our previous studies that the defect states are well localized with very little geometric distortion. The formation energies are shown in Figure 6. General features for the neutral and charged cases are similar to the gallium vacancy case.

Makov-Payne corrections work even better than in the case of gallium vacancy. Potential alignments without VBM correction tend to somewhat underestimate formation energies as before. Here, scheme I works really well, and scheme II also relatively well even if it extrapolates again to a lower value.

It seems, that using only the calculated potential alignment already corrects the formation energies about halfway, giving a fair confidence on the results reported in our previous study of beryllium defects.

Comparison of the relaxed and unrelaxed cases for all defect types (and as can be seen in Figures 2 and 3) show no systematic difference in the applicability of the correction methods. During the derivation, these effects were approximated to be small, and this would indeed seem to be the case, although these defect cases were chosen especially chosen to show no major relaxation effects.
Another problem with the extrapolation method is the amplification of errors in the set of calculations. If one of the calculations has an error of 100 meV for any reason, it can result in 1 eV difference in the extrapolated formation energy. Thus, it is advantageous to get rid of the extrapolation scheme. Taking this idea even further, a working correction scheme might allow to use lower precision in the calculation. One possibility would be to use coarser k-point meshes, although naturally other properties might also degrade. For example, it has been reported that coarse k-point mesh can lead to incorrect geometries. [12, 13, 14]

Extending these correction schemes to more complex geometries such as interfaces requires again a proper model for the screening. This is straightforward enough. Alternatively, one could try to divide the space even further and write the total energy as the sum of the contributions in these regions. So far, very limited number of studies has been performed on defects at interfaces and warrants further investigations.

When developing a correction for e.g the GW method, to the first approximation, the same trick could be done for the self-energy as was done here for the XC-energy, eventually yielding the same corrections. Of course, GW
provides a proper dielectric function for the screening which could be taken advantage of. Unfortunately, as GW calculations usually do not provide total energies, a somewhat different approach is probably needed.

V. CONCLUSIONS

A comparison of several previously introduced defect correction methods and a few new ones are compared in both analytical and numerical levels. First, we divide the problem of comparing charged defects in to bulk into comparison of neutral defect to bulk and further comparison of charged defect to neutral case. Then, by explicitly writing the total energies for a neutral defect, a charged defect in a small supercell, and a charged defect in a large supercell, it is possible to inspect the approximations hidden in each method. This framework should also prove helpful in future development of methods for more advanced methods and for more complex geometries.

We found that the method introduced by Freysoldt\[1\] works generally well. Moreover, during the inspection of the potential alignment method, we found a method which also worked surprisingly well, even if formally looks as just a scaled Madelung-energy.

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