ABSTRACT: Defect formation energy as well as the charge transition level (CTL) plays a vital role in understanding the underlying mechanism of the effect of defects on material properties. However, the accurate calculation of charged defects, especially for two-dimensional materials, is still a challenging topic. In this paper, we proposed a simplified scheme to rescale the CTLs from the semilocal to the hybrid functional level, which is time-saving during the charged defect calculations. Based on this method, we systematically calculated the formation energy of four kinds of intrinsic point defects in two-dimensional hexagonal boron nitride (2D h-BN) by uniformly scaling the supercells by which we found a time-saving method to obtain the “special vacuum size” (Komsa, H.-P.; Berseneva, N.; Krasheninnikov, A. V.; Nieminen, R. M. Phys. Rev. X, 2014, 4, 031044). Native defects including nitrogen vacancy (V_N), boron vacancy (V_B), nitrogen atom anti-sited on boron position (N_B), and boron atom anti-sited on nitrogen position (B_N) were calculated. The reliability of our scheme was verified by taking V_N as a probe to conduct the hybrid functional calculation, and the rescaled CTL is within the acceptable error range with the pure HSE results. Based on the results of CTLs, all the native point defects in the h-BN monolayer act as hole or electron trap centers under certain conditions and would suppress the p- or n-type electrical conduction of h-BN-based devices. Our rescale method is also suitable for other materials for defect charge transition level calculations.

KEYWORDS: defect formation energy, charge transition level, native point defects, two-dimensional materials, h-BN monolayer

1. INTRODUCTION

The intentional control for electronic conductivity can be achieved by engineering the native defects or impurities, and typical cases for the former include vacancies, substitutions, and interstitials.1 Full comprehension of semiconductor defects, especially charged defect physics, is desired owing to its decisive role in determining material properties such as optical, mechanical, electrical, and transport properties and thus the corresponding applications.2−6 It is rather difficult to directly investigate the charged defects in materials by experiments at the atomic level. Instead, first-principle calculations play vital roles in understanding defect properties and providing theoretical guidance in improving device performance, efficiency, and reliability.7−9

As widely reviewed, charged defects calculation for 3D (or bulk) materials is full of challenges, and one of the reasons is due to the spurious long-range Coulomb interactions between the periodic images and the neutralizing background charges, which are introduced to avoid the divergence during the self-consistent calculation. These, in turn, would influence the accuracy of the calculated defect formation energy and charge transition level (CTL).7,10 As for the 2D materials, i.e., slab models, more obstacles emerge. The in-homogeneous dielectric environments normal to the vacuum slab in 2D slab models would cause further troubles to precisely evaluate defect properties.3,10−14 Komsa and Pasquarello first developed a finite-size supercell correction scheme for removing spurious electrostatic interactions of charged defects for surfaces and interfaces,10 which could obtain the correct defect formation energy even for a relatively small supercell. They also stressed that the supercells need to be enlarged uniformly in three directions to guarantee the convergence of defect formation energy.10 The authors extended this scheme for 2D materials by choosing the dielectric constant profile to follow the charge density distribution of the system11 where they, for the first time, proposed the so-called “special vacuum size” (SVS).
method to precisely calculate the defect formation energy of 2D materials. In detail, they concluded that, for a given supercell, the defect formation energy varies with the different vacuum thickness. That is, the defect formation energy can be either lower or higher than the correct value under different vacuum sizes, indicating that there exists a vacuum size, i.e., SVS, to guarantee the exact formation energy without any correction or extrapolation. However, it is tedious to obtain the SVS because one needs to gain the correct defect formation energy in advance and then scales the vacuum sizes gradually for different supercell sizes. While in our study, we find that the SVS could be uniformly scaled as well, which counts because we can vary the vacuum size in a relatively small supercell to find a corresponding SVS and then scale the vacuum size with a fixed ratio to obtain an SVS for a much larger supercell to conduct new calculations. Recently, Freysoldt and Neugebauer reported a method to calculate the formation energy of charged defects at surfaces, interfaces, or two-dimensional materials\(^\text{14}\) where they applied periodic boundary conditions to the periodic slab case and open boundary conditions for the surface or 2D case in the same scheme, indicating that one does not need to resort to the finite-size extrapolation to obtain the isolated energy. Up to now, Freysoldt’s method is one of the time-saving and flexible schemes on the corrections of 2D charged defect calculations. Thus, we adopted this method to correct formation energy and compare the results with those obtained by the extrapolated method.

Another challenge is that the density functional theory using the local density approximation (LDA) or the generalized gradient approximation (GGA) often severely underestimates the band gap. As a result, the accuracy of defect formation energies and CTLs are significantly impacted.\(^\text{7,8}\) A hybrid functional such as Heyd–Scuseria–Ernzerhof (HSE\(^\text{15}\)) would overcome the band gap underestimation problem, but often the time consumption involved is prohibitive, especially for a large supercell, which is usually used to mimic the low defect concentration of realistic materials. It is noted that, despite the band gap narrowing by the semilocal GGA functional, the calculated formation energy is similar to that by the HSE functional.\(^\text{16,17}\) Thus, the derived charge transition level from the Perdew–Burke–Ernzerhof (PBE) functional can be rescaled to the HSE scale\(^\text{16,17}\) despite more or less shortcomings.\(^\text{18}\) Nieminen et al. compared the PBE CTLs with those calculated under the HSE functional by normalizing the band gaps,\(^\text{19}\) while in refs \(^\text{17}\) and \(^\text{19}\), the authors simply corrected the CTLs by adding half (all) of the bulk band gap difference between HSE and PBE functionals to the PBE derived CTLs. However, note that the HSE calculation does not necessarily open the band gap by repulsing conduction band minimum (CBM) and valence band maximum (VBM) identically.\(^\text{20}\) In this paper, we propose a new scaling scheme and consider the differences of the VBM position (i.e., the ionic potentials, IP) and band gap values under two different functionals (i.e., PBE and HSE functionals) so that the formation energy can be calculated more reasonably and reliably.

In this work, we apply our calculation scheme to the charged native defects in a hexagonal boron nitride (h-BN) monolayer, which has superior optical, electrical, and mechanical properties.\(^\text{21,22}\) Furthermore, single-photon emission has been observed in the h-BN monolayer at room temperature, which is promising for quantum information devices. Many defect configurations (i.e., color centers) are proposed for the possible single-photon emitters.\(^\text{23–29}\) Despite the fact that many works on defect calculations of h-BN have been reported during the past decades\(^\text{14,17,19,30–36}\), the authors either did not calculate charged defects in h-BN or did not correct the defect formation energy with a reasonable 2D correction method. Besides, the charged anti-sited defects with proper correction were not considered either. Van de Walle et al. reported the charged native defects and CTLs of h-BN, but they are in the 3D structure model, which will inevitably more or less vary from the monolayer 2D case.\(^\text{37,38}\) In this study, we systematically investigated the atomic structures, defect formation energies, and CTLs of native point defects in h-BN, including nitrogen vacancy (\(V_N\)), boron vacancy (\(V_B\)), nitrogen atom anti-sited on boron position (\(N_B\)), and boron atom anti-sited on nitrogen position (\(B_N\)) in multiple charge states with 2D defect correction as well as extrapolating methods. The extracted defect charge transition levels by rescaling correspond well with that by the practical HSE functional, indicating that our proposed rescaling methodology is reasonable. In principle, the proposed CTL rescale method can also be applicable for other 2D or 3D defect charge transition level calculations.

2. COMPUTATION METHODS

The calculations were conducted based on spin-polarized density functional theory with GGA-PBE functional\(^\text{39}\) and projector augmented wave (PAW) potential,\(^\text{40}\) as implemented in the VASP code.\(^\text{41}\) An energy cutoff of 400 eV was used. A reciprocal space was sampled with \(5 \times 3 \times 1, 3 \times 2 \times 1, 2 \times 1 \times 1\), and \(1 \times 1 \times 1\) Monkhorst–Pack \(k\)-point mesh for the \(3 \times 3 \times 3, 6 \times 6\) supercells, respectively. All atoms were relaxed until the Hellman–Feynman force on each atom was less than 0.01 eV/Å and the energy convergence criterion was \(10^{-6}\) eV. To validate our proposed rescale scheme, charged \(V_N\) supercells were calculated by the HSE06 functional and compared with the PBE derived data.

During the calculations, we redefined the lattice of the h-BN primitive cell into an orthogonal form using VASPKIT, a pre- and post-processing program for the VASP code,\(^\text{42}\) as shown in Figure 1, to take advantage of the correction scheme proposed by Freysoldt, Neugebauer, and Van de Walle (FNV).\(^\text{14}\) The optimized unit cell lattice is \(a = 2.51\ \text{Å}, b = 4.35\ \text{Å}\), and with an SVS of 7.50 Å. When point defects were introduced into the h-BN host, we calculated \(3 \times 3, 3 \times 4 \times 4, 5 \times 5 \times 5\), and \(6 \times 6\) supercells with linearly scaled vacuum thickness, implying that all the supercells were scaled uniformly in both the \(x\)-\(y\) plane and the \(z\) direction by which the formation energies would converge linearly to a finite value.\(^\text{14}\) Again, it is of particular importance and necessary to uniformly enlarge the vacuum size to maintain the converged defect transition level.
The formation energy of an isolated charged defect in the 2D h-BN monolayer is defined as

$$E_{ff}^{\alpha}[X^\alpha] = E_{finite}^{\alpha}[X^\alpha] + E_{correct}$$

(1)

where $E_{ff}^{\alpha}[X^\alpha]$ and $E_{finite}^{\alpha}[X^\alpha]$ are the defect formation energies of the infinite and finite h-BN supercells containing a defect in charge state $q$, respectively, and $E_{correct}$ is a correction term by the FNV method \(^{14}\) or extrapolating \(^{-1}\) and is different from the 3D defect case. Specially, $E_{correct}$ can be obtained by uniformly extending the supercells in the case of extrapolating, which is not necessary in the 3D case. In contrast, if $E_{correct}$ is obtained by posteriori correction with FNV method, then the Poisson equation should be solved by particularly considering the distribution of the dielectric function in the vacuum direction of the model. The very detailed description about the charged defect formation energy, especially the correction term, is in the Supporting Information.

The charge transition level (CTL) is determined by \(^{7,8}\)

$$E_{CTL}^{\alpha} = E(q; E_f = 0) - E(q'; E_f = 0)$$

(2)

where $E(q; E_f = 0)$ and $E(q'; E_f = 0)$ represent the formation energies for the states of charge $q$ and $q'$, respectively. The energy difference between the transition level and band edges determines the donor/acceptor ionization energy, denoted as

$$ID = CBM - E_{CTL}^{\alpha}$$

(3)

and

$$IA = E_{CTL}^{\alpha} - VBM$$

(4)

respectively, which can be used to directly judge the depth of a certain defect energy level.

3. RESULTS AND DISCUSSIONS

First, the FNV method \(^{14}\) was used to calculate the $E_{correct}$ term in eq 1 in which the method of the alignment term $\Delta V_{\alpha}^{\alpha} = \Delta E_f$ in eq S5 is required to well converge to a constant in the region far from the defect (i.e., in the vacuum region), as seen in Figure 2 (blue line). For the sake of simplicity, only the alignment plot of the charged boron vacancy defect ($V_b^{+}$ and $V_b^{-}$) is illustrated as an example.

Then, we calculated the formation energies of different defects in all supercell sizes, and the results are shown in Figure 3. It is observed that all the formation energies vary linearly with the inverse scale sizes, similar to those in refs 10, 11, and 43, owing to the uniformly cell-enlarged method. Besides, almost all the formation energies are converged well. That is to say, for a given defect type under a certain charge state, the formation energies barely vary among different supercell sizes. These well-converged formation energies imply that all the vacuum sizes in different supercells are the exact (or very close to the) SVSs \(^{11}\) considering that all the vacuum sizes are obtained by uniformly enlarged supercells. Thus, we deduce that the SVS can be uniformly enlarged as well. To further verify this speculation, we also uniformly scale and obtain the SVSs of all supercells (with different shapes) in ref 11 based on the normalized vacuum thickness of the 10 x 10 supercell. The derived SVSs (Table 1, last row) are close to those reported in ref 11 with an average error of less than 2.8%. This indicates that the scalability of SVS is reliable, which has not been proposed by previous reports. The finding manifests that we can choose a relatively smaller supercell to test the SVS by fixing the $x$-$y$ size and varying the $z$ (vacuum) thickness before starting a calculation with a larger supercell; thus, it is time-saving.

Compared with the extrapolated values (the dotted line at $1/\alpha = 0$), which is the most accurate method up till now, one can find that only the results of $\pm 1$ and some $\pm 2$ charge states are well corrected by the FNV method. This implies that the FNV method would work better in lower charge states than higher charge cases, similar to those reported in refs 14 and 43. However, it is still acceptable considering the general higher formation energies at higher charge states.

Based on the similar defect formation energies between the two functionals \(^{16}\), we propose that the calculated CTL by the PBE functional can be rescaled to the HSE functional scale using the scheme plotted in Figure 4. The band gap and ionic potentials (energy difference between vacuum and VBM) of the h-BN unit cell were first calculated by PBE and HSE functionals to obtain the band edge offsets ($\Delta E_V$ and $\Delta E_C$), and our calculated gap and IP values agree very well with previous reports \(^{44}\). As illustrated, the band offsets differ...
we will discuss the CTL of native point defects in h-BN.

several atoms) to determine the band edge positions, which

functional calculation for the pristine bulk material (only

defect con

acceptor ionization energies were rescaled as well, i.e.,

positions were considered in our scheme. Furthermore, the

V

and

E

PBE-scale CTL, i.e.,

calculations involved for the charged defect calculation are only

di

ferences between both the band gap value and band edge

is obtained by adding

ΔE

V

are marked as

Schematic of the rescaling scheme used in this paper. The

Figure 4. Schematic of the rescaling scheme used in this paper. The

charge transition level calculated within the semilocal PBE and the

hybrid HSE functional are marked as

PBE

and

HSE

respectively, aligned to the vacuum level. ΔE

PBE

and ΔE

HSE

are shifts of the VBM and

CBM between the two functionals, respectively. IP represents the

ionic potential, i.e., energy difference between the vacuum level and

VBM, while ID and IA represent the donor and acceptor ionization

energies (eqs 3 and 4), respectively. The rescaled HSE transition level is

obtained by adding

ΔE

V

to PBE calculation (PBE(1/0)).

distinctly from each other (∆E

V

is 0.78 eV while ∆E

C

is 0.25 eV).

So, the previously proposed CTL rescaling methods by

roughly adding half (all) of ∆E

IP

VBM

are not so robust. In our

work, the HSE-scale CTL is obtained by adding the ∆E

V

to the

PBE-scale CTL, i.e., E

HSE

(1/0) = E

PBE

(1/0) + ∆E

V

That is to say, the
differences between both the band gap value and band edge positions were considered in our scheme. Furthermore, the donor (acceptor) ionization energies were rescaled as well, i.e., ID

HSE

= ID

PBE

+ ∆EC

(IA

HSE

= IA

PBE

+ ∆EA).

So, all the calculations involved for the charged defect calculation are only PBE functional (rather than HSE) for supercells with different defect configurations or charge states as well as an HSE functional calculation for the pristine bulk material (only several atoms) to determine the band edge positions, which saves much time compared with the standard HSE defect calculation procedures. Based on the method described above, we will discuss the CTL of native point defects in h-BN.

Additionally, to verify the reliability of our rescaled method, we took the VN system as a benchmark check to conduct practical HSE calculations.

3.1. Discussions on VN. After full relaxation, the B-B distances around VN under a neutral or −1 charge state are decreased from 2.51 to 2.07 and 2.29 Å, respectively, owing to the electrostatic attraction between the boron atoms. The most stable charge states (MSCSs) for VN defect are VN−1, VN0, VN+1, and VN+2 when the Fermi energy is swept from VBM to CBM, as shown in Figure S1, in which both the rescaled and practical HSE CTL results are illustrated. Note that the HSE CTLs (both rescaled or practical) can be obtained just by referencing the HSE-calculated VBM as the zero points of the x axis. For instance, the rescaled E

HSE

VN−1 = 2/ + 1) and E

HSE

VN0 = 0/0) lie ~0.4, ~2.8, and ~4.8 eV above the VBM, respectively, and their corresponding practical HSE CTLs are 0.2, 2.6, and 4.6 eV, respectively. All the CTLs in our rescaled results are overestimated only ~0.2 eV within the error range mentioned in ref 18. Specially, the E

HSE

VN+2 = (0/0) (~2.8 eV) is comparable to a value of ~3.5 eV in ref 37 where a bulk phase of BN was calculated. The errors of formation energies are found to vary from 0.1 to 0.5 eV under different charge states within the same error range in ref 16, confirming that our rescaled results are reliable. To expediently judge the depth of donor or acceptor nature, the donor ionization energies (ID

HSE

; eq 3) with the rescaled (practical) HSE method for VN−1/0 and E

HSE

VN+2/0 are calculated to be 5.3 (5.5) and 2.8 (3.0) eV, respectively. Likewise, the acceptor ionization energy (IA

HSE

; eq 4) for E

HSE

VN+1/0 is 4.8 (4.6) eV, indicating that all of the donors (acceptors) are deep and do not effectively contribute conductivity but expect to be recombination centers. Note that the formation energy of VN in the whole electron chemical potential range under N-rich (or poor) limitation is high enough to hinder the defects to be introduced. However, with relative lower formation energy, VN0 in p-type h-BN under N-poor limitation may be non-negligible to affect the properties of h-BN.

3.2. Discussions on VB. As shown in Figure 6, the MSCSs for VB defect are VB−1, VB0, VB+1, and VB+2 as well. The N-N distances around VB in all charge states increase significantly, respect to that of pristine h-BN, i.e., from 2.51 to 2.65 Å, due to the Coulomb repulsion between nitrogen atoms around the

Table 1. SVS (in Å) for Different Lateral Supercell Sizes Based on the Orthogonal Unit Cell (Labeled as OC, Shown in Figure 1) or the Standard h-BN Primitive Cell (from Ref 11, Labeled as PC)a

<table>
<thead>
<tr>
<th>lattice size</th>
<th>SVS in this paper (OC) (Å)</th>
<th>uniformly scaled SVS using data in ref 11 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.5</td>
<td>16.35</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>20.82</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>25.44</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>30.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“*The uniformly scaled SVSs of different supercells are also shown.

Figure 5. Calculated formation energies of an isolated VN in the h-BN monolayer in different charge states as a function of the Fermi level range from VBM to CBM for (a) N-rich and for (b) N-poor limitation conditions. The rescaled and practical HSE results are labeled as the blue and green lines, respectively.

ACS Applied Materials & Interfaces www.acsami.org

ACS Appl. Mater. Interfaces 2020, 12, 17055–17061

10.1021/acsami.9b23431

https://dx.doi.org/10.1021/acsami.9b23431

17058
Figure 6. Calculated formation energies of the isolated native defects of $V_B$, $V_N$, $N_B$, and $B_N$ in the h-BN monolayer for their stable charge states as a function of the Fermi level in (a) N-rich and (b) N-poor limitation conditions. The rescaled HSE CTLs can be obtained by referencing the zero-point of the $x$ axis to the HSE VBM. The PBE and HSE gaps are labeled as blue and green colors, respectively.

Figure 7. Stable charge states and CTLs of the isolated native defects of $V_B$, $V_N$, $N_B$, and $B_N$ in the h-BN monolayer, and the PBE (HSE) conduction and valence band are labeled as blue (green) colors. The practical HSE CTLs are illustrated in the first column. By referencing HSE VBM to zero point, the CTLs can be rescaled from PBE to HSE values.

different native point defects. By referencing HSE VBM to zero point, the CTLs can be rescaled from PBE to HSE values. As seen in Figure 7, $V_B$ and $B_N$ show a much deep acceptor nature in the n-type doping h-BN monolayer. The only relative shallow singlet acceptor is $V_N$. All kinds of defects show a deep multiorbital nature with rescaled HSE results. Thus, these levels are too high to be thermally ionized at device-operating temperatures. As a result, we expect that the unintentionally doped h-BN monolayer exhibiting either n- or p-type behavior cannot be attributed to the native defects.

4. CONCLUSIONS

In this paper, we proposed a simplified scheme to rescale the charge transition levels from the semilocal PBE to the hybrid HSE functional, which not only significantly improves the accuracy of the PBE CTL results but also saves much time during the calculations of charged defects. We also found that the special vacuum size in the 2D slab model is uniformly scalable, as well as the scalability is supercell shape-independent, which provides a time-saving method to obtain the SVS for a larger supercell by testing it out with a smaller supercell. Based on our proposed scheme, we have systematically investigated the charged native point defects of $V_{NC}$, $V_{NB}$, $N_{BC}$, and $B_{NC}$ in the h-BN monolayer, and the reliability of this rescaled method was verified by choosing the $V_B$ system as a benchmark check to carry out authentic HSE calculations. The results show that the native point defects cannot be efficient dopants (electrons or holes) in a single-layer h-BN but act as recombination centers by which the electrical conductivity in h-BN monolayer-based electronic devices can be suppressed in the presence of the native defects.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b23431.

The details for the correction of charged defect formation energy about 2D materials (PDF)

AUTHOR INFORMATION

Corresponding Authors
Zhao Ding — College of Big data and Information Engineering, Guizhou University, Guiyang 550025, China; Semiconductor
Power Device Reliability Engineering Center of Ministry of Education, Guiyang 550205, China; Email: zdining@gzu.edu.cn

Zhaofu Zhang — Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, United Kingdom; orcid.org/0000-0002-1406-1256; Email: zz389@cam.ac.uk

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.9b23431

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work is supported by the National Natural Science Foundation of China (grant nos. 61564002 and 11664005), the Joint Foundation of Guizhou Normal University (grant no. 7341), the Scientific and Technological Cooperation Projects of Guizhou Province, China (grant no. [2013]7019), the Guizhou Normal University Innovation and Entrepreneurship Education Research Center Foundation (grant no. 0418010), and the Key laboratory of Low Dimensional Condensed Matter Physics of Higher Educational Institution of Guizhou Province, Guizhou Normal University, Guiyang 550205, China

REFERENCES


