Point defects determine various physical properties in solids. One of the most important properties is the optical property. For instance, ZnO is known to show green luminescence, which is seemingly attributed to point defects [1]. Another example is SrTiO$_3$, known to show blue-light emission at room temperature after Ar$^+$-irradiation, whose origin is presumably the emergence of oxygen vacancies [2]. In addition, we can investigate defects with deep states, which often degrade the device performance, from the photo-absorption or emission spectra. It is generally considered that absorption (emission) of a photon by a defect promotes (demotes) an electron to the excited (ground) state, most probably without altering the atomic configuration, based on the Franck-Condon principle [3]. This is a consequence of the fact that electrons are much lighter than nuclei. Thus, we can represent the optical transition by a vertical arrow in the configuration coordinate diagram, and its transition energy is given as an optical transition level or vertical transition level (VTL) with respect to the valence band maximum (VBM) or the conduction band minimum (CBM) [4, 5].

First-principles calculations have become powerful tools to understand and predict the defect-mediated optical transitions. In the calculations of extended systems with defects, these levels are almost always evaluated by a supercell approach nowadays, where a charged defect interacts with its periodic images and background charge, which erroneously modifies the total energies of charged defect supercells [6, 7]. Methods to correct the energies to the dilute limit are well established, as represented by the scheme proposed by Freysoldt, Neugebauer, and Van de Walle (FNV) [8], and its extension to anisotropic systems and/or relaxed geometries (eFNV) [9]. The correction energy of the eFNV scheme is written as

$$ E_{\text{cor}} = E_{\text{PC}} - q \Delta V_{\text{PC,q}/b|\text{far}} $$

where $E_{\text{PC}}$ is the point charge (PC) correction energy, $\Delta V_{\text{PC,q}/b|\text{far}}$ is the potential difference between defect-induced and PC potentials at a region outside of the defect in the supercell, and $q$ is the defect charge state. The second term is referred to as an alignment-like term, and is approximately equal to the Makov-Payne third-order correction $-2\varepsilon_{\text{PC}} Q Q q / 3L^3$ for cubic systems, where $Q$ is the second radial moment of the defect charge density, $\varepsilon$ is the dielectric constant in an isotropic medium, and $L$ is the dimension of the supercell [4, 8, 9]. Therefore, when the defect charge distribution is negligibly small compared to the supercell size, the alignment-like term is negligible as well. The PC correction energy and potential are evaluated using the static dielectric tensor on the assumption that a charged defect is screened by both electrons and ions. The charged defect formation energy in the dilute limit is accurately calculated using Eq. (1) as long as the defect charge is enclosed in a supercell [3].

However, the (e)FNV correction is not applicable to the calculation of the VTL, because the atomic configuration at the final state remains unchanged from the initial state. Although there have been numerous numbers of theoretical reports on the calculations of VTLs [11, 12], none has clearly specified the method to correct its finite supercell size effect. Therefore, we aimed to formulate a correction method for the VTLs within the total energy framework and systematically assess its accuracy with VTLs involving defects in prototypical non-metallic materials: MgO, GaN, cubic-BN (c-BN), and 3C-SiC.

A VTL from charge state $q$ to $q+1$ in the equilibrium configuration coordination $Q$ at charge state $q$, $Q(q)$, is denoted as $\mu(q/q+1; Q(q))$, which is calculated as

$$ \mu(q/q+1; Q(q)) = [E(q+1; Q(q)) - E(q; Q(q))] \pm \varepsilon_{\text{CBM}} + \Delta E_{\text{cor}} $$

(2)

or

$$ \mu(q/q+1; Q(q)) = [E(q+1; Q(q)) - E(q; Q(q))] \pm \varepsilon_{\text{VBM}} + \Delta E_{\text{cor}} $$

(3)

where $\varepsilon_{\text{CBM}}$ and $\varepsilon_{\text{VBM}}$ denote the energy levels of the CBM and VBM, respectively. Therefore, Eqs. (2) and (3) con-
sider vertical transitions involving the CBM and VBM, respectively. Since the VTL involves the energy difference between two charge states, the correction energy for the VTL, $\Delta E_{\text{cor}}$, corresponds to the difference of the correction energies for the final $(E_{\text{cor}}(q \pm 1; Q(q)))$ and initial $(E_{\text{cor}}(q; Q(q)))$ states.

Electrons are relaxed to their equilibrium state at the final state but the initial atomic positions remain unchanged. Therefore, we start by separating the correction energy into the electronic part, $E_{\text{cor}}$, and the ionic part, $E_{\text{cor}}$, as

$$E_{\text{cor}} = E_{\text{cor}}^{\text{el}} + E_{\text{cor}}^{\text{ion}}.$$  \hspace{1cm} (4)

From Eq. (4), $\Delta E_{\text{cor}}$ can be written as

$$\Delta E_{\text{cor}} = \left\{ E_{\text{cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{el}}(q; Q(q)) \right\} + \left\{ E_{\text{cor}}^{\text{ion}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{ion}}(q; Q(q)) \right\}. \hspace{1cm} (5)$$

Janak’s theorem [13] shows a relationship between the total energies and the defect-induced single-particle levels with the fractional charge $f, \varepsilon(f; Q(q))$, as follows

$$E(q \pm 1; Q(q)) - E(q; Q(q)) = \int_{q}^{q \pm 1} \varepsilon(f; Q(q))df.$$  \hspace{1cm} (6)

The cell size dependences should be the same at both sides of Eq. (6), so the correction term is written as

$$\Delta E_{\text{cor}} = E_{\text{cor}}(q \pm 1; Q(q)) - E_{\text{cor}}(q; Q(q)) = \int_{q}^{q \pm 1} \varepsilon_{\text{cor}}(f; Q(q))df,$$  \hspace{1cm} (7)

where $\varepsilon_{\text{cor}}(f; Q(q))$ is the correction to the single-particle level. Since the atomic positions are fixed, the ionic part of the correction to the defect eigenvalue is irrelevant for the charge state and, therefore, is taken out from the integration as

$$\Delta E_{\text{cor}} = \int_{q}^{q \pm 1} \varepsilon_{\text{cor}}^{\text{el}}(f; Q(q))df + \varepsilon_{\text{cor}}^{\text{ion}}(Q(q)).$$  \hspace{1cm} (8)

Conversely, the electronic part of the correction energy, $\int_{q}^{q \pm 1} \varepsilon_{\text{cor}}^{\text{el}}(f; Q(q))df$, depends on the charge state and corresponds to the difference of the correction energies, $E_{\text{cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{el}}(q; Q(q))$. Therefore, we obtain the following formula for $\Delta E_{\text{cor}}$,

$$\Delta E_{\text{cor}} = \left\{ E_{\text{cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{el}}(q; Q(q)) \right\} \mp \varepsilon_{\text{cor}}^{\text{ion}}(Q(q)).$$  \hspace{1cm} (9)

Since $\Delta V_{\text{PC/q]/bl}}$ in Eq. (1) includes both electronic and ionic contributions under relaxed atomic positions, we need a model or an assumption to estimate the respective alignment-like terms of the electronic and ionic parts, separately. In the cases of small polarons, one can estimate $\Delta V_{\text{PC/q]/bl}}$ of the electronic part from the charge distribution using squared wavefunctions of localized polaronic states, as has been reported by Kokott et al. [16], but such a method is not generally applicable to defects involving the removal and/or insertion of atoms.

We therefore first adopt the PC corrections, where the first bracket in Eq. (2) is calculated from the difference of the Madelung correction energies using an electronic (high-frequency) dielectric tensor. In the second term, we apply the correction scheme reported by Jain et al. [17] and Komsa et al. [7], where the correction to the eigenvalue of the defect-induced localized state is related to the total energy correction by $\varepsilon_{\text{corr}}^{\text{el}}(Q(q)) = -2E_{\text{corr}}^{\text{el}}(q; Q(q))/q$ [18].

To test our correction method, we investigate the supercell size dependence of the VTLs with respect to the CBM and VBM [Eqs. (2) and (3)] for donor- and acceptor-type defects, respectively. All the VTLs in this study were calculated with the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [19], and the Fock-exchange parameters were tuned to reproduce each experimental band gap [12, 20, 22]. We also confirmed that the formation energies of all the defects considered in this study were accurately corrected with eFNV (see Fig. S1 in Supplemental Material), which indicated these defects were mostly enclosed by relatively smaller, e.g., 64-atom supercells. Figure (a) and (b) shows both the corrected and uncorrected VTLs of the boron vacancy ($V_B$) in c-BN as a function of the supercell size. Without any corrections, one can see the VTLs strongly depended on the supercell size, and the absolute error was larger than 0.7 eV even with the largest 1000-atom supercell in our test set. Conversely, our PC correction scheme based on Eq. (9) drastically reduced the cell size dependences, and the absolute error was only 0.1 eV at the smallest 64-atom supercell. Such a small cell size dependence indicated the $V_B^{\text{rel}}$ and $V_B^{\text{el}}$ defect charge were very much localized. Indeed, their defect formation energies were satisfactorily corrected with the PC corrections as well.

We next applied the correction method to several systems to discuss the general tendency. Figure 2(a) shows the VTLs of (a) $V_{\text{Mg}}(1/2-)$, (b) $V_{\text{O}}(1/2)$, and (c) $V_{\text{Cu}}(2/1)$ in MgO, (d) $V_{\text{Ga}}(2/-3)$ and (e) $V_{\text{N}}(2/3)$ in GaN, (f) $V_{\text{N}}(2/3)$ and (g) $V_{\text{N}}(3/2)$ in c-BN, and (h) $V_{\text{C}}(1/2)$ in 3C-SiC as a function of the supercell size. Again, our PC corrections worked well with reasonable accuracy on average. Regarding cation vacancies [Figs. 2(a)]
the smallest supercells, as in the case of $V_{\text{Si}}$ in c-BN [Fig. 1]. In contrast, the VTLs of anion vacancies were not so well corrected especially at the smallest supercells [Fig. 2(b), (c), and (e)-(h)]; the worst case was $V_{\text{O}}(3/2)$ in c-BN with a deviation of 0.7 eV at the 64-atom supercell compared with the corrected VTL at the 1000-atom supercell [Fig. 2(g)]. This meant the PC corrections were not appropriate for the anion vacancies, which is consistent with the fact that their total energies were not corrected by the PC corrections (see Fig. S1 in Supplemental Material).

In this instance, consideration of a higher order contribution, namely an alignment-like term, is essential. As has been described, the problem is how to estimate the alignment-like terms of the electronic and ionic parts. Here, we introduce two assumptions: (i) Ionic screening does not modify the defect charge distribution, which means the ionic contribution to $\Delta V_{\text{PC,el}}(q)\mid_{\text{far}}$ is zero, and $\varepsilon_{\text{ion}}(Q(q))$ is estimated from the PC corrections; and (ii) The electronic part of $\Delta V_{\text{PC,el}}(q)\mid_{\text{far}}$ is unchanged by addition or removal of an electron. Therefore, one can derive the following relationship

$$E_{\text{cor}}^{\text{el}}(q \pm 1; Q(q)) - E_{\text{cor}}^{\text{el}}(q; Q(q)) =$$

$$\left[ E_{\text{PC,el}}^{\text{cor}}(q \pm 1; Q(q)) - E_{\text{PC,el}}^{\text{cor}}(q; Q(q)) \right] \mp \Delta V_{\text{PC,el}}(q)\mid_{\text{far}}. \quad (10)$$

Using these two approximations, $\Delta E_{\text{cor}}$ is given by

$$\Delta E_{\text{cor}} = \left[ E_{\text{PC,el}}^{\text{cor}}(q \pm 1; Q(q)) - E_{\text{PC,el}}^{\text{cor}}(q; Q(q)) \right]$$

$$\mp \varepsilon_{\text{ion}}(Q(q)) \mp \Delta V_{\text{PC,el}}(q)\mid_{\text{far}}. \quad (11)$$

We prefer to call the correction based on Eq. (11) the second-order defect charge corrections (SO corrections) since they effectively consider up to the second-order contributions to the Makov-Payne correction energy on the premise that the dipole-dipole interaction is negligibly small [7, 9, 10]. As shown in Figs. 1 and 2, the SO corrections successfully estimated the VTLs in the dilute limit even with relatively smaller supercells and worked better than the PC corrections in most cases. Notable examples were $V_{\text{Si}}(3/2)$ in c-BN [Fig. 2(g)] and $V_{\text{O}}(1/2)$ in 3C-SiC [Fig. 2(h)]; the PC corrections led to errors of 0.7 and 0.2 eV at the smallest supercells, respectively, while the errors were reduced to 0.1 and 0.0 eV by the SO corrections. Exceptions were $V_{\text{Ga}}(2/-3)$ in c-BN [Fig. 1(a)] and $V_{\text{Ga}}(2/-3)$ in GaN [Fig. 2(d)], where the SO corrections showed slightly larger errors than the PC corrections.

We now separately discuss the corrections to the electronic part, namely Eq. (10), and the ionic part, namely $\mp \varepsilon_{\text{ion}}(Q(q))$, of the corrections. One can see the VTLs corrected only with $\varepsilon_{\text{ion}}(Q(q))$ (shown as w/o $\varepsilon_{\text{ion}}^{\text{PC,el}}(Q(q))$ in the Figures) depended linearly on the supercell size in all the cases and provided even worse results than the uncorrected values in some cases [e.g., Fig. 2(c)]. This finding meant the electronic and ionic parts had a similar extent to each other, but with the opposite sign.

To see the overall performance of our correction methods, we aligned the VTLs calculated with the second smallest supercells (128 atoms for GaN and 216 atoms for the others) to the same scale in Fig. 3 such moderate size supercells are regularly adopted for practical defect calculations nowadays. Although the VTLs were reasonably well corrected even at the PC correction level, the SO corrections improved the ac-

![FIG. 2: Same as Fig. but of (a) $V_{\text{Si}}(1/-2)$, (b) $V_{\text{O}}(1/2)$, and (c) $V_{\text{O}}(2/-1)$ in MgO, (d) $V_{\text{Ga}}(2/-3)$ and (e) $V_{\text{N}}(2/-3)$ in GaN, (f) $V_{\text{N}}(2/3)$ and (g) $V_{\text{N}}(3/-2)$ in c-BN, and (h) $V_{\text{C}}(1/-2)$ in 3C-SiC.](image-url)
curacy and the errors were reduced to be within 0.1 eV in all the cases.

Another important merit to consider for the alignment-like term is that it removes the projector augmented wave (PAW) or pseudopotential radius dependences from the VTLs. Bruneval and co-workers have reported that the charged defect formation energies depend on the PAW or pseudopotential radii, because the standard of the electrostatic potential depends on the radii, and this modifies the total energy of a charged system \[23\]. The VTLs depend on these radii as well because the charge state is different by 1 or -1 between the final and initial states, but such an energy dependence is removed when an alignment-like term is considered since the potential at the final state is aligned to the initial state.

Finally, we would like to emphasize that our correction method is adaptive for evaluating any quantities involving different charge states at fixed geometry, as represented by the gKT-relevant quantity.

**Computational methods.** First-principles calculations were performed using the projector augmented wave method \[29\], as implemented in the Vienna Ab initio simulation package (VASP) \[30, 31\]. We used PAW data sets with radial cutoffs of 1.52, 1.40, 0.91, 1.31, 0.90, 0.74, and 0.86 \(\text{Å}\) for Mg, Ga, B, Si, O, N, and C, respectively. The Ga 3\(d\) electrons were treated as core electrons. In the supercell calculations, a \(2 \times 2 \times 2\) \(k\)-points mesh was applied to the 216-atom or smaller supercells, while \(\Gamma\)-only sampling was applied to the others, and spin polarization was considered in all the defect calculations. Note that all the VTLs considered did not involve partial occupation at the VBM, CBM or defect localized states.

**Acknowledgements.** Fruitful discussions with Naoki Tsunoda are deeply appreciated. This work was supported by the Grants-in-Aid for Scientific Research B (Grant No. 19H02416), PRESTO (Grant No. JPMJPR16N4), CREST (Grant No. JPMJCR17J2), and the Support Program for Starting Up Innovation Hub MI\(^2\)I from JST, Japan. The computing resources of ACCMS at Kyoto University and Research Institute for Information Technology at Kyushu University were used for part of this work.

T.G. and Y.K. contributed equally to this work.

---

[1] I. V. Rodnyi, P. A. and Khodyuk, Opt. Spectrosc. 111, 776 (2011).
[2] D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, and M. Takano, Nat. Mater. 4, 816 (2005).
[3] J. Franck and E. G. Dymond, Trans. Faraday Soc. 21, 536
Supplemental Material

Tomoya Gake\textsuperscript{1}, Yu Kumagai\textsuperscript{1,2}, and Fumiyasu Oba\textsuperscript{1,3}

\textsuperscript{1}Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan
\textsuperscript{2}PRESTO, Japan Science and Technology Agency, Tokyo 113-8656, Japan
\textsuperscript{3}Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba 305-0047, Japan.

July 15, 2019
Figure S1: Relative formation energies of (a) $V_{Mg}^-$, (b) $V_{O}^-$, and (c) $V_{O}^{2+}$ in MgO, (d) $V_{Ga}^{2-}$ and (e) $V_{Ga}^{2+}$ in GaN, (f) $V_{B}^{2-}$, (g) $V_{B}^{3-}$, (h) $V_{N}^{2+}$, and (i) $V_{N}^{3+}$ in c-BN, and (j) $V_{C}^+$ in 3C-SiC as a function of the supercell size. The energy zeros are set at the corrected values with the eFNV scheme for the largest supercells.
Figure S2: Relative single-particle energy levels corrected by adding $-2E_{\text{cor}}/q$, where $E_{\text{cor}}$ is the total energy correction and $q$ the charge state, of (a) $V_-^{\text{Mg}}$, (b) $V_+^{\text{O}}$, and (c) $V_2^{\text{O+}}$ in MgO, (d) $V_-^{\text{Ga}}$ and (e) $V_2^{\text{Ga+}}$ in GaN, (f) $V_-^{\text{B}}$, (g) $V_3^{\text{B-}}$, (h) $V_2^{\text{B+}}$, and (i) $V_3^{\text{N+}}$ in c-BN, and (j) $V_3^{\text{C+}}$ in 3C-SiC as a function of the supercell size. The energy zeros are set at the corrected values with the eFNV correction energies for the largest supercells.