Fundamental Resolution of Difficulties in the Theory of Charged Point Defects in Semiconductors

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Fundamental resolution of difficulties in the theory of charged point defects in semiconductors

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A defect's formation energy is a key theoretical quantity that allows the calculation of equilibrium defect concentrations in solids and aids in identification of defects that control the properties of materials and device performance, efficiency, and reliability. The theory of formation energies is rigorous only for neutral defects, but the Coulomb potentials of charged defects require additional *ad-hoc* numerical procedures. Here we invoke statistical mechanics to derive a revised theory of charged-defect formation energies, which eliminates the need for *ad-hoc* numerical procedures. Calculations become straightforward and transparent. We present calculations demonstrating the significance of the revised theory for defect formation energies and thermodynamic transition levels.

Point defects, such as impurities, vacancies, and self-interstitials, control the properties of materials and are widely used to engineer custom properties in nanostructures and devices and functionalize two-dimensional materials [1–6]. Defects introduce localized levels in the energy gap of semiconductors through which they control device performance, efficiency, and reliability [7]. Native defects such as vacancies, self-interstitials, and antisite defects often act as unintended dopants or compensate intentionally introduced dopants [8–10]. In addition, native defects as well as contaminant impurities limit the efficiency of light-emitting diodes [11], cause degradation of power devices [7], and play key roles in structural transformations of two-dimensional materials [12, 13].

First-principles calculations for defects [14] contribute significantly to understanding material properties and improving device performance, efficiency and reliability. A key theoretical quantity for a defect is the formation energy for each charge state, which determines the species concentration under equilibrium conditions [10, 15, 16]. The formation energies also determine the defect's thermodynamic transition energy levels, which are related to the localized eigen levels in the gap. Even in the absence of equilibrium, defect formation energies along with the resulting transition levels provide guidance as to which defects are most likely to form, which aids in defect identification [7]. More recently, calculations of cross sections for carrier capture have become possible, aiding in defect identification [11, 17] The emergence of oxide semiconductors and related heterostructure and superlattice devices [18] have added renewed emphasis on the need for reliable calculations of defect properties, as oxygen vacancies are one of several degrees of freedom that determine structural, electronic, and magnetic properties [19–22].

In this Letter, we show that the conventional definition of formation energies for charged defects cannot be reconciled with statistical mechanics. We demonstrate that this is the fundamental reason for the well-known difficulties associated with the long-range Coulomb interactions, which are typically remedied using *ad-hoc* numerical procedures. We then use the principles of statistical mechanics to derive a revised definition of charged-defect formation energies that naturally and rigorously eliminates the difficulties. We also report calculations of formation energies that demonstrate the efficiency and significance of the revised theory.

We start with a critical overview of the existing theory of formation energies, which are fundamentally thermodynamic quantities. As such, they are not, in principle, defined for an isolated defect in an otherwise infinite crystal. For example, for neutral vacancies in a monatomic crystal such as Si, one envisions creating large numbers of well-separated neutral vacancies. The removed atoms are placed on the surfaces, extending the bulk crystal, which serves as the reservoir that defines the chemical potential $\mu_{\text{Si}} = E^N/N$ for Si atoms. The resulting formula for the formation energy is,

$$E_0^{\text{form}} = (E_0^{N-1} + \mu_{\text{Si}}) - E^N, \tag{1}$$

where the superscripts on the right indicate the number of atoms in the supercell. In calculation, the supercell plays the role of the average volume per vacancy. A converged calculation means that the well-separated limit is achieved and corresponds to a single vacancy in an otherwise perfect crystal (limit of infinite supercell. The first formation-energy calculations were in fact done in this limit [23].

For charged defects, the standard theory places a charged defect in a supercell, assuming that the extra or missing electron(s) come from or go to an electron reservoir with chemical potential μ_e that is equated with the Fermi energy [10, 15],

$$E_q^{\text{form}}(\mu_e) = (E_q^{N-1} + \mu_{\text{Si}} + q\mu_e) - E^N, \tag{2}$$

where q is the vacancy charge in units of an electron charge. This definition, however, has a serious inherent difficulty: The Coulomb interactions of an infinite periodic array of charged defects introduce a divergence. This divergence is usually removed by a uniform compensating charge ("jellium") [24] or by compensating charges at the supercell boundary [25]. The jellium model, however, only removes the divergence, but does not change the local electrostatic potential, i.e., the

Coulombic tails remain intact. As a result, convergence with respect to supercell size is very slow if not impossible, for both the atomic relaxations and the values of the formation energies [24]. These uncertainties are particularly large for complex oxides [19–22, 26]. Several competing schemes have been proposed and debated to deal with the convergence issue [25, 27–31]. A review has been given by Komsa et al. [32]. A comprehensive study of defects in ZnO [26] illustrates the difficulties of dealing with charged states.

Equation (2), however, is merely an Ansatz, a generalization of Eq. (1) that cannot be derived from or reconciled with the principles of statistical mechanics. More specifically, the statistical definition of formation energies of neutral vacancies, which underlies Eq. (1), cannot be applied to charged vacancies: One cannot envision a process where large numbers of well-separated *charged* vacancies are created, leaving the crystal supercharged. Furthermore, in Eq. (2), the nature of the electron reservoir is not transparent as there are no energy states at the Fermi energy. We conclude that *the charged-defect formation energy is not that of a charged defect in an otherwise infinite crystal*, as assumed by the standard theory.

We shall construct a revised, rigorous theory of charged-defect formation energies using statistical mechanics, motivated by the following considerations. A crystal containing charged defects is in fact electrically neutral. Physically, in the absence of dopants, defects become charged by trading electrons with the energy bands, not with the abstract Fermi energy, where there exist no energy levels. Thus, the average volume per defect, which corresponds to a supercell, is always neutral in one of three ways: it contains a) a nominally neutral defect, b) a nominally positively-charged defect plus one or more electrons in the conduction bands, normalized in the supercell, or c) a nominally negatively-charged defect plus one or more holes in the valence bands, again normalized in the supercell. We conclude that the supercell for a charged defect should be made neutral not by an artificial uniform compensating background, but by placing compensating free carrier(s) in the pertinent energy bands. *Both the divergence and the lack of convergence caused by Coulomb tails in the standard theory are eliminated at a fundamental level.*

We will now formulate the above as a rigorous mathematical theory. The statistical definition of the formation energy E_q^{form} is the average energy cost per charged vacancy to create a large number N_q^V of isolated charged vacancies. For positively-charged defects ($q > 0$), with q in units of an electron charge, $N_q^V q$ electrons are removed from defect levels and *placed in the energy bands*; for negatively-charged defects ($q < 0$), $N_q^V q$ electrons are removed from the energy bands and placed in defect levels. Statistical mechanics applied to a large solid tells us that the creation of charged defects alters the neutrality condition, which leads to a change $\delta\mu_e$ to the Fermi energy and a concomitant change $\delta f(E)$ to the Fermi-Dirac distribution function $f(E) = 1/[1 + e^{(E-\mu_e)/k_B T}]$. We then have

$$\int_{-\infty}^{\infty} g(E)\delta f(E)dE = N_q^V q \tag{3}$$

and

$$\int_{-\infty}^{\infty} Eg(E)\delta f(E)dE = N_q^V q\mu_e \tag{4}$$

where $g(E)$ is the density of band states, assumed to remain undisturbed. These equations demonstrate that the energy bands are the physical electron reservoir and why the Fermi energy serves as the electron chemical potential *even though the electrons are not physically there*. Instead, the $N_q^V q$ electrons are *physically* in the energy bands and, on average, ensure that the nominal volume per vacancy is neutral. It is then evident that it is best to place the "missing" electron(s) of a positively-charged defect at the bottom of the conduction bands. In principle, one could place an electron high in the conduction bands or place two electrons in the conduction bands and one hole in the valence bands and do a statistical average, but such configurations would contribute minimally to the partition function and can be neglected.

We conclude that, for $q > 0$, Eq. (2) must be replaced by

$$\tilde{E}_q^{\text{form}}(\mu_e) = \tilde{E}_q^{N-1} + q(\mu_e - E_c) + \mu_{\text{Si}} - E^N. \tag{5}$$

Here $\tilde{E}_q^{N-1}$ is the supercell total energy in the naturally neutral supercell as just desscribed. The term $q(\mu_e - E_c)$ reflects the fact that ionized electrons are placed at the bottom of the conduction band *only for the purpose of providing the correct screening of the charged defect*, while statistically their energy should be counted as if they are placed at the Fermi energy as per Eq. (4). The band gap error in a density functional theory (DFT) calculation is cancelled out between $\tilde{E}_q^{N-1}$ and qE_c. A similar expression holds for $q < 0$:

$$\tilde{E}_q^{\text{form}}(\mu_e) = \tilde{E}_q^{N-1} + q(\mu_e - E_v) + \mu_{\text{Si}} - E^N. \tag{6}$$

Here the extra electron(s) are compensated by hole(s) at the top of the valence bands.

Both Eqs. (5) and (6) hold if the crystal contains only vacancies. If dopants are present, the supercell must contain one or more dopant atoms, well-separated from the vacancy. For each charge state, one must calculate the formation energy using a neutral supercell with compensating electrons or holes in either a dopant level or the pertinent energy band and carry out a statistical average. A generalization of the above equations is straightforward. Such calculations, however, require large supercells that are currently impractical. The effect of dopants on the formation energies can be neglectd, except for their role in the determination of the Fermi energy [33, 34]. Finally, a generalization of the above equations to a compound semiconductor and other defects is straightforward. For example, for an AB compound, for the formation of a A-vacancy, μ_{Si} in the above equations is replaced by μ_A, which is not uniquely determined as discussed in Refs. 10 and 15 and elsewhere (see also below where the theory is applied to vacancies in ZnO).

In the new scheme of calculating formation energies in naturally neutral supercells, the average volume per defect corresponds to the total concentration of all charge states. It is this average volume that corresponds to the supercell used for calculations of the formation energy of each charge state as described in the present paper. Nevertheless, we are generally interested in the dilute limit, when the concentration of charged defects, e.g., vacancies, is given by

$$N_q^V = N_{\text{solid}} g_q e^{-E_q^{\text{form}}/k_B T}, \tag{7}$$

where N_{solid} is the number of pertinent lattice sites in the solid and g_q is the electronic degeneracy of the defect [the degeneracy factor is usually omitted; a derivation of Eq. (7) is given in Supplementary Information]. In this limit, one must use a large enough supercell so that the defects in neighboring supercells do not interact, i.e., one must converge the calculation of formation energies with repect to supercell size.

The naturally neutral supercells for charged defect states in the present theory eliminate in principle the problems introduced by the Coulomb interactions of charged defects in the conventional approach. The rate of convergence of course always depends on the particular defect and host. When the supercell is small, a Burstein-Moss-like increase in the band gap may be present, but the effect disappears if the calculation is converged with respect to supercell size.

We now present results for a vacancy in Si, which has served as a prototype system [24, 35, 36]. A vacancy in Si introduces four dangling bonds that hybridize and form an s-like state within the valence bands and three p-like deep levels in the energy gap[37]. Two electrons occupy gap states when the vacancy is neutral. Four charged states, $++$, $+$, $-$, and $--$ are possible. Calculations have been carried out using the plane-wave-based DFT package Quantum Espresso [38] with the Perdew-Burke-Ernzerhof (PBE) [39] form of generalized-gradient approximation (GGA) exchange-correlation potential and the ultrasoft pseudopotential [40]. Supercells containing 64-, 216-, and 512-atom are used, each of which has one vacancy. Norm-conserving pseudopotentials are used. As our purpose here is not necessarily to perform the most accurate calculations, but to compare the conventional and new method for calculating charged-defect formation energies, we used only the Γ point to approximate the $\mathbf{k}$-point sum over the Brillouin zone. The energy cutoff for the plane waves is 50 Ry. The Fermi energy is set to be at the valence band top. The relaxed structures have the same symmetry as found in Ref. 35. The calculations for charged defects proceed precisely as in the case of neutral defects, except that electrons in the conduction band or holes in the valence are introduced by "constrained DFT" as implemented in Quantum Espresso [38] and VASP [41, 42].

Figure 1 shows the formation energy for each charge state as a function of supercell size. We include the values for neutral vacancies for completeness, even though the theory for them remains unchanged. The results obtained by the conventional approach shown in Fig. 1 do not include any Madelung or finite-supercell corrections in order to highlight the difference in screening by band electrons/holes, which makes the supercell truly neutral, and the conventional uniform background ("jellium"), which leaves the Coulombic tails intact because no physical electron or hole is introduced in the supercell. As expected, the difference between conventional calculations (dashed lines) and the present theory (solid lines), carried out at the same level of accuracy, increases with the charge on the vacancy site, especially for negative charge states. The "negative-U" effect [43, 44], which manifests as a much smaller difference between the formation energies of the neutral and the V^{+} states, is reproduced. For the largest supercell (512 atoms) this energy difference is 0.08 eV.

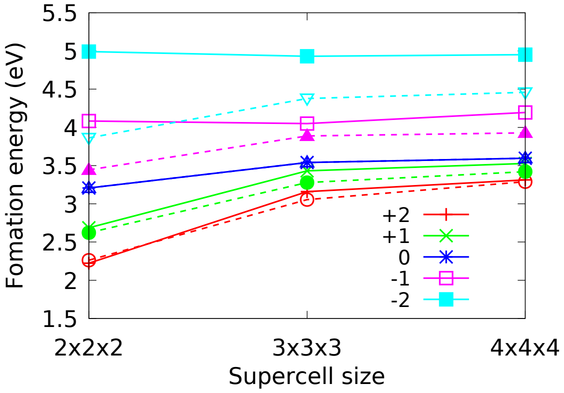

FIG. 1. Formation energies as functions of supercell size for different charge states. Solid lines are calculations using the present theory (screening by band electrons); dashed lines are calculations using the conventional approach based on a compensating uniform charged background ("jellium")

The necessity of replacing the conventional approach with the revised theory is more vividly demonstrated in the calculation of the formation energies of oxygen vacancies in ZnO. Defects in ZnO were investigated extensively using the conventional method by Oba et al. [26], who tested different exchange-correlation functionals and finite-supercell correction schemes. At the PBE level of DFT, the energy gap is very small compared with the experimental value, whereby the calculation of defect energy levels is not very meaningful. Using a hybrid functional, on the other hand, Oba et al. find that the oxygen vacancy is a negative-U center, i.e., the formation energy of the neutral vacancy with two electrons in the gap is lower than the formation energy of the $+1$ charged vacancy. As a result, the $+1$ charge state would not form under equilibrium conditions for any position of the Fermi energy. The calculated formation energy of the V^{++}state, however, including finite-supercell corrections, is highly negative, -3.5 eV.

We have performed calculations for the oxygen vacancy in ZnO as follows. Both the lattice structural relaxation and the defect formation energies are calculated using the HSE06 functional as implemented in VASP [41, 42], which mixes the PBE exchange part with 37.5% of Hartree-Fock exchange in short range to match the experiment band gap. The HSE06 calculation was performed using 520 eV cutoff and only the Γ point for a 9.86 Å× 11.38 Å× 10.61 Å supercell containing 96 atoms. The Projector Augmented Wave (PAW) method [45] was used. The formation energies were calculated for various charge states under oxygen poor (or zinc rich) condition, in which the chemical potential for Zn is given by its bulk Zn value $\mu_{\text{Zn[bulk]}}$, and the chemical potential for oxygen reaches its lowest value $\mu_{\text{O}} = E_{\text{[ZnO]}} - \mu_{\text{Zn[bulk]}}$ [46]. Compared to the conventional jellium approach, the present method using screening by electrons in the conduction band leads to *significantly reduced atomic displacements near the vacancy site*, which is consistent with the fact that the screening by two electrons in the conduction band significantly reduces the total perturbation. Specifically, in a perfect wurtzite crystal, there are two Zn-Zn nearest-neighbor interatomic distances, 3.17 Å and 3.19 Å. Consider the $+2$ charge state for which the difference between the two methods is the greatest. In the jellium model, the Zn-Zn distances at the O vacancy site are 4.10 Å and 4.15 Å, respectively, while the present theory yields 3.60 Å and 3.64 Å. Also, the two methods lead to large differences in the vacancy formation energies for the $+2$ charge state, -2.3 eV compared with -3.65 eV (the latter number is obtained at our level of accuracy and compares well with the numerically more accurate value -3.5 reported by Oba et al.). The formation energies for the three charged states 0, $+1$, and $+2$ using the present method are 0.69 eV, -0.77 eV, and -2.30 eV, respectively, as shown in Fig. 2, compared with 0.93 eV, -1.30 eV, and -3.65 eV using the conventional approach. It is notable that, as seen in Fig. 2, the two transition levels almost collapse into a single level near $E_v + 1.5$ eV. The effective Hubbard U is essentially zero.

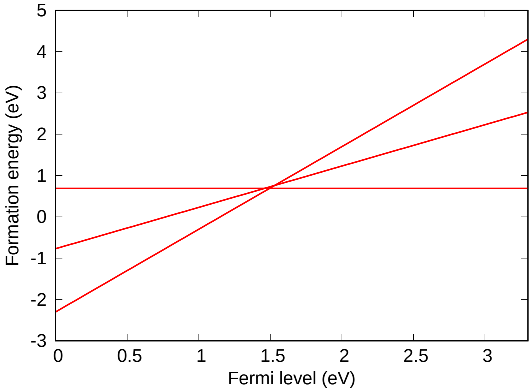

FIG. 2. Formation energy of oxygen vacancy in ZnO under oxygen-poor conditions. The $+2/0$ transition occurs at 1.5 eV above the valence band maximum.

In addition to the large differences in formation energies between the conventional and new theories, there is one more notable feature that distinguishes the new theory. A neutral defect has localized states in the band gap that correspond to eigenvalues ϵ^d of the pertinent one-electron Hamiltonian. These levels shift slightly with changing occupations so they are properly designated as ϵ^d_q. The thermodynamic transition levels, on the other hand, correspond to the positions $E^d_{q/0}$ of the Fermi energy where $E^{\text{form}}_q(\mu_e)$ and $E^{\text{form}}_0(\mu_e)$ are equal. Since the dependene of E^{form}_q on μ_e is linear as in Eqs. (5)-(6), the $q/0$ transition level is given by

$$q\mu_e = E^{\text{form}}_0(0) - E^{\text{form}}_q(0) = \tilde{E}^{N-1}_0 - \tilde{E}^{N-1}_q. \qquad (8)$$

At low temperatures approaching 0 K, the transition level $E^d_{q/0}$ for positive q values must be below the unoccupied defect energy level ϵ^d_q. Otherwise we may have the paradoxical situation where the Fermi energy is above a mostly unoccupied defect level when the charge-q state is energetically favored over the neutral state. This condition provides a physical constraint on the formation energies,

$$E^{\text{form}}_q(0) - E^{\text{form}}_0(0) > -q\epsilon^d_q. \qquad (9)$$

A similar constraint can be derived for negative q values.

For ZnO, using the conventional jellium screening we find $\epsilon^d_{+2} = 2.13$ eV for the lowest unoccupied defect level of the $+2$ charge state. Thus the physical constraint for the formation energies is $E^{\text{form}}_{+2}(0) - E^{\text{form}}_0(0) > -4.26$ eV. Evidently, the conventionally calculated formation energies of $E^{\text{form}}_0(0) = 0.93$ eV and $E^{\text{form}}_{+2}(0) = -3.65$ eV violate this condition. On the other hand, with $\epsilon^d_{+2} = 1.59$ eV calculated using the new theory, we get $E^{\text{form}}_{+2}(0) - E^{\text{form}}_0(0) > -3.18$ eV, so Eq. (9) is satisfied by $E^{\text{form}}_0(0) = 0.69$ eV and $E^{\text{form}}_{+2}(0) = -2.30$ eV for the new theory.

In summary, we have shown that difficulties introduced by Coulombic potentials in the standard theory of charged-defect formation energies, which are remedied by *ad-hoc* numerical procedures, can be overcome by reformulating the theory using rigorous statistical mechanics. We then demonstrated that supercells containing charged defects are neutral because the "missing" electrons are physically in the conduction bands and "extra" electrons are compensated by holes in the valence bands. Thus, *long-range Coulombic potentials are inherently absent*. We reported calculations showing that the numerical results are significantly different in the two approaches. We expect that significant differences would persist if one were to push both calculations to convergence with respect to supercell size. If the supercell size is small, the errors of the two methods arise from different sources. The conventional method leaves the Coulomb tail intact whereas the new method confines the band electron in an unphysically small volume to keep the supercell neutral. Fully converged calculations are not always practical and the question of corrections to unconverged calculations is too complex to address here. Nevertheless, anchored on rigorous statistical mechanics, the new theory places calculations of charged-defect properties on a more solid footing.

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