

Finite-Size Supercell Correction for Charged Defects at Surfaces and Interfaces

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(Received 19 November 2012; revised manuscript received 18 January 2013; published 28 February 2013)

A finite-size supercell correction scheme is introduced for the formation energy of charged defects at surfaces and interfaces. **The scheme combines classical electrostatics with the dielectric profile and the electrostatic potential extracted from the electronic-structure calculation.** Spurious electrostatic interactions are removed while retaining the dielectric and quantum-mechanical features of the system of interest, which may have no interface (bulk), a single interface or surface, or two interfaces. **A pertinent extrapolation scheme validates the proposed corrections.** Applications to the charged Cl vacancy at the surface of NaCl and to the dangling bond at the Si(100) surface show that the corrected formation energies are largely **independent of the supercell dimensions and of the size of the vacuum region.**

DOI: 10.1103/PhysRevLett.110.095505

PACS numbers: 61.72.J-, 68.35.Dv, 71.15.-m, 73.20.Hb

First-principles calculations of charged defects in supercells subject to periodic boundary conditions are plagued by a strong dependence on the supercell size. This is caused by the long-ranged Coulomb interactions between the periodic images of the localized charges. **To probe the properties of an isolated defect, several correction schemes have been proposed [1–4] and shown to work fairly well in the bulk [5].** With the rapid advancement of nanoscale science, it has become increasingly important to be able to access properties of defects in low-dimensional systems, where the presence of surfaces and interfaces cannot be neglected. However, defects subject to such inhomogeneous dielectric environments have so far received little attention. When isolated charged defects at surfaces or interfaces are modeled, spuriously repeated charges due to the supercell periodicity add to physical image charges arising from the spatial variations in the dielectric constant [6,7]. In previous theoretical studies, bulk models were used and the physical image-charge interactions treated *a posteriori* within classical electrostatics [8,9]. However, such descriptions yield artificial divergences [8] and neglect quantum-mechanical effects resulting from the proximity of the interface [9]. Other approaches recover the correct electrostatics by modifying the Poisson solver [10–13], but are limited to systems surrounded by vacuum.

To appreciate the importance of finite-size supercell errors in inhomogeneous dielectric environments, we calculate formation energies of a charged Cl vacancy at the NaCl surface without applying any finite-size correction upon variation of the supercell dimensions (Fig. 1). Formation energies obtained in this way correspond to the periodically repeated supercell system in which the defect charge is compensated by a uniform background and are here referred to as uncorrected. In particular, such **uncorrected formation energies are found to diverge linearly with the size of the vacuum region w_{vac} .** At variance, the

uncorrected formation energy might appear converged with increasing lateral dimensions but the value obtained does not correspond to the correct formation energy, as can be inferred from the comparison with the corrected formation energies obtained in the following of the present work. A supercell correction scheme for inhomogeneous systems encompasses several difficulties. It is imperative to compensate the defect charge to prevent the energy of the periodically repeated system from diverging. However, the uniform background charge generally used in bulk systems leads to effects which are unclear in inhomogeneous

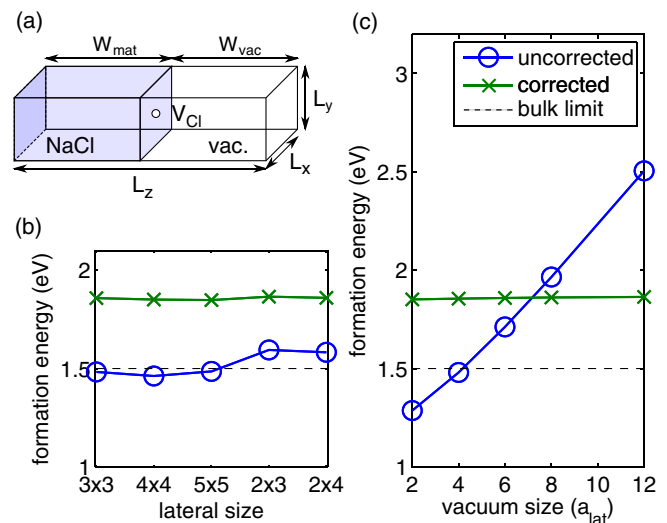


FIG. 1 (color online). (a) System geometry used for modeling a Cl vacancy in the +1 charge state at the surface of NaCl, with adopted notation. **Uncorrected and corrected formation energies** vs (b) lateral width of the supercell with fixed $w_{\text{mat}} = 2$ and $w_{\text{vac}} = 2$ and (c) size of the vacuum region with fixed $w_{\text{mat}} = 2$ and $L_x \times L_y = 3 \times 3$. Distances are given in units of $a_{\text{lat}} = 5.66 \text{ \AA}$.

systems. Furthermore, the indetermination of the potential by a constant in supercell calculations causes alignment problems, which are emphasized in the presence of a net charge and a varying dielectric constant in the supercell [5].

In this Letter, we describe an *a posteriori* correction scheme for the formation energies of charged defects in systems showing a spatially varying dielectric constant along one dimension, such as surfaces and interfaces. The proposed scheme relies on the dielectric constant profile extracted from the electronic-structure calculation. The corrected results are validated against extrapolated values obtained through a properly designed procedure. The scheme reproduces the corrections given by Freysoldt *et al.* [3,14] in the case of bulk defects. The scheme is here illustrated (i) for the +1 charged Cl vacancy located at various distances from the surface within a NaCl slab and (ii) for a -1 charged Si dangling bond at the H-passivated Si(001) surface.

We correct the formation energy of a defect with charge q accounting for the variation in electrostatic energy going from periodic to open boundary conditions:

$$E_{\text{corr}} = E_{\text{isolated}} - E_{\text{periodic}} + q\Delta V, \quad (1)$$

where the last term is an alignment term [3]. We obtain the electrostatic energies E_{isolated} and E_{periodic} for a chosen model defect charge distribution $\rho(\mathbf{r})$ by solving for the corresponding model electrostatic potential $V(\mathbf{r})$ subject to the respective boundary conditions: $E = \frac{1}{2} \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$. The shift ΔV is taken such that the model potential and the electrostatic potential in the electronic-structure calculations agree far from the defect [3]. Inclusion of the alignment term ensures that the form of model charge distribution $\rho(\mathbf{r})$ is generally not critical [3,5]. We here use a Gaussian charge distribution.

In the periodic case, the potential is the solution of the Poisson equation

$$\nabla \cdot [\epsilon(\mathbf{r})\nabla V(\mathbf{r})] = -\rho(\mathbf{r}), \quad (2)$$

$$\epsilon(\mathbf{r})\nabla^2 V(\mathbf{r}) + \nabla\epsilon(\mathbf{r}) \cdot \nabla V(\mathbf{r}) = -\rho(\mathbf{r}). \quad (3)$$

We limit our study to systems for which the dielectric constant depends only on z . The second term on the left-hand side then simplifies to $\frac{\partial}{\partial z}\epsilon(z)\frac{\partial}{\partial z}V(\mathbf{r})$. An efficient numerical solution of this equation can be achieved in Fourier space, where $V(\mathbf{G})$ is found through the solution of one-dimensional linear systems at fixed G_x and G_y [15]. The average potential over the supercell is set to zero in correspondence with the convention adopted in electronic structure calculations.

The isolated system corresponds to the targeted dielectric environment of the defect for which we would like to have the correct formation energy. Our scheme can accommodate several possibilities, namely the absence of any nearby surface (bulk), the presence of a single surface or interface,

and the occurrence of two nearby interfaces as, e.g., in a finite slab. For all of these situations, the electrostatic energy E_{isolated} for a Gaussian charge distribution can easily be calculated from elementary electrostatics [15–19].

We validate our correction scheme through extrapolation to the limit of infinitely large supercell. The extrapolation needs to be designed properly depending on the targeted dielectric environment. For instance, for an isolated charge at a single interface, all dimensions (width of the cell and thicknesses of both interface components) need to be scaled concomitantly, i.e., $L \rightarrow \alpha L$ for L_x , L_y , L_z , and w (for definitions cf. Fig. 1). The extrapolation is demonstrated in Fig. 2 for a model slab system where half of the supercell contains a material with dielectric constant $\epsilon = 4$ and the other half, vacuum. A Gaussian charge distribution is placed in the middle of the slab or at the surface. The extrapolated values of the electrostatic energy calculated at finite dimensions (E_{periodic}) are found to agree very well with the respective results of E_{isolated} for the bulk and for an isolated surface, thereby demonstrating the consistency between the calculations of E_{isolated} and E_{periodic} . A proper extrapolation procedure is critical for avoiding the divergence of the electrostatic energy, as is found when scaling in only one or two dimensions (Fig. 2). Indeed, for such scaling conditions, the electrostatic energy approaches that of an infinite plane or wire of charges as the background charge is progressively diluted.

To demonstrate the performance of the correction scheme, it is here applied to the charged chlorine vacancy defect in a NaCl slab in vacuum. In bulk NaCl, this defect is a well-known color center (*F* center) [20]. It is also

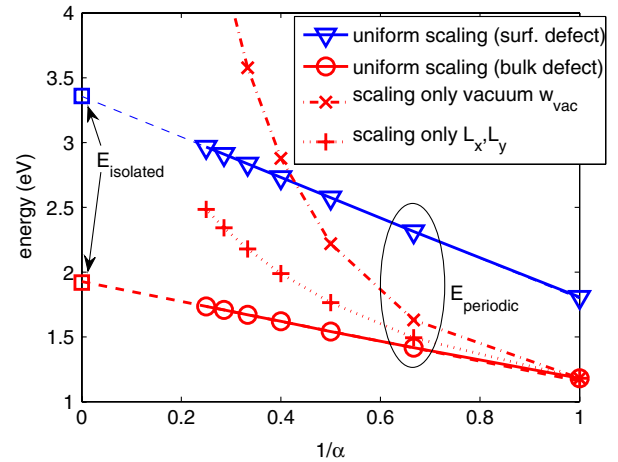


FIG. 2 (color online). Electrostatic energies for a Gaussian charge distribution at the surface (triangles) and in the middle (circles) of a material slab with dielectric constant ($\epsilon = 4$), as obtained by uniformly scaling all dimensions in the supercell. The values corresponding to the isolated systems are obtained separately (squares) and can be compared to the linear extrapolations (dashed lines) fitted to the last four points. Scaling only the vacuum region (crosses) or only the lateral dimension (pluses) of the supercell leads to divergences.

stable at the surface and has been observed in scanning-tunneling-microscopy experiments [6]. For simulation, a typical system geometry is depicted in Fig. 3(a). The NaCl(100) surface is nonpolar and shows little geometric reconstruction. Furthermore, the isolated Cl vacancy in its +1 charge state has a very localized defect state, which is well represented by a Gaussian charge distribution [cf. Fig. 3(a)]. **Structural relaxation has been disregarded in the present study to avoid strain effects.**

The electronic-structure calculations are based on the **Perdew–Burke–Ernzerhof** functional within density functional theory (DFT) [21]. We use plane wave basis sets in conjunction with a normconserving Na and an ultrasoft Cl pseudopotential, as implemented in the QUANTUM-ESPRESSO package [22]. The plane wave cutoffs are fixed at 30 Ry for the wave functions and at 200 Ry for the charge density [23,24]. Unless otherwise noted, the system dimensions are given in units of the NaCl lattice constant $a_{\text{lat}} = 5.66 \text{ \AA}$. The adopted k -point densities correspond to that of a 8×8 mesh in the lateral directions of the Brillouin zone of a single unit cell, whereas the

z -direction is sampled at the sole Γ -point. The (undefected) slab is constructed to be symmetric for reflection in the z direction. For reference, the formation energy of an unrelaxed Cl vacancy in the +1 charge state in bulk is found to be 1.50 eV by extrapolation [15], in good agreement with previous results [25].

The dielectric-constant profile across the NaCl slab is obtained through the direct application of a constant electric field [Fig. 3(b)] [14,26]. The calculated profile is found to be rather abrupt converging rapidly within the slab to the bulk value of the dielectric constant ($\epsilon = 2.45$). This value is small enough to give strong interactions with the periodic images, yet large enough to provide sufficient dielectric contrast with respect to the vacuum ($\epsilon = 1$). Thus, this system represents a stringent benchmark for our correction scheme. **In our model calculation of E_{periodic} , we employ a dielectric-constant profile given by an error-function form which accurately matches the profile found in the DFT calculation.** The electrostatic potentials in the DFT and in the model calculations agree very well far from the defect, as shown in Fig. 3(c). The good agreement between the potentials, within both the slab and vacuum regions of the supercell, indicates that the model $\epsilon(z)$ is properly constructed. In general, the potentials are allowed to differ by a constant shift ΔV , but this shift is small when the model charge distribution agrees well with the defect charge density [Fig. 3(a)].

In Fig. 4(a), we show uncorrected and corrected formation energies for a defect (i) in the middle and (ii) at the surface of the slab. A scaling of all involved dimensions is

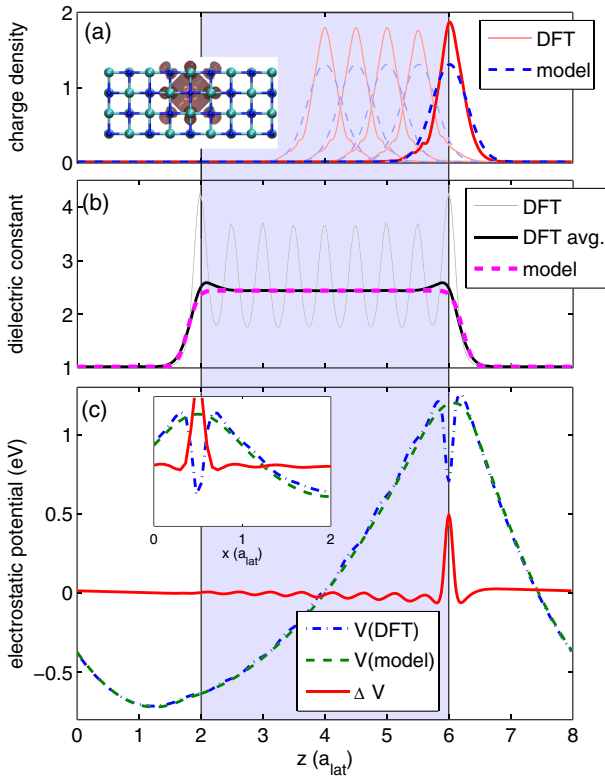


FIG. 3 (color online). (a) Plane-averaged distributions of the model charge and of the Cl vacancy defect charge as found in the DFT calculation compared for various defect positions in a NaCl slab. Inset: geometry of the slab and isosurface of the defect wave function. (b) Plane-averaged and unit-cell averaged dielectric constant profiles as obtained in the DFT calculation compared to the adopted model profile. (c) Electrostatic potentials from the DFT and from the model calculation along with their difference. Inset: potentials along the lateral direction.

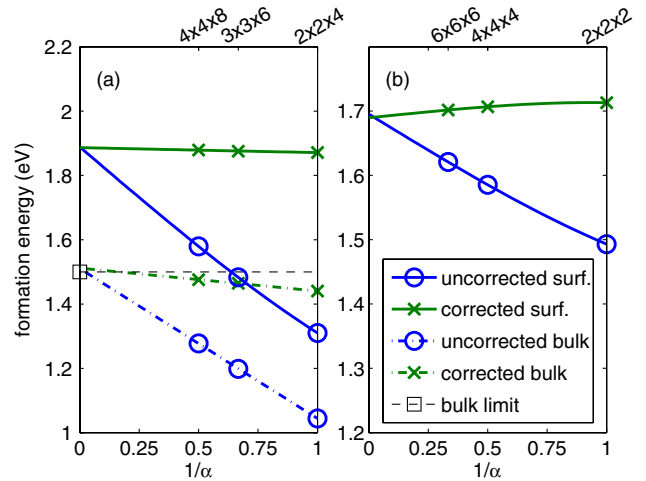


FIG. 4 (color online). **Formation energies** calculated within DFT without (circles, blue) and with (crosses, green) the correction as a function of inverse system size for: (a) A chlorine vacancy defect in the +1 charge state in the middle (dash-dotted) and at the surface (solid line) of a NaCl slab. (b) A Si dangling bond in the -1 charge state at the H-passivated Si(001)-(2 × 1) surface. The supercell sizes used are given at the top. In all cases, half of the cell consists of vacuum. In (a), the result from a separate bulk calculation is also shown (square).

performed to ensure that the respective limits correspond to the values of the bulk and of the isolated surface (cf. Fig. 1). One notes that the uncorrected and corrected formation energies extrapolate to identical values [27], namely 1.50 eV for the bulk and 1.89 eV for the surface. The corrected formation energies are rather constant, being within 0.05 eV from the extrapolated values even for the smallest considered system. In the latter case, this residual error is one order of magnitude smaller than the correction itself which is ~ 0.5 eV for both positions of the defect. Furthermore, **for the defect in the middle of the slab, the extrapolated value agrees with the formation energy obtained separately from a bulk calculation.** All these observations corroborate the validity of the proposed correction scheme.

The corrections lead to the same formation energies independently of the shape of the supercell. We focus here on a Cl vacancy at the surface of the slab. When **only the lateral size of the supercell is changed** [Fig. 1(b)], the applied corrections yield formation energies differing by less than 0.02 eV from the extrapolated value of 1.89 eV for the isolated surface (Fig. 4). The uncorrected results thus misleadingly stabilize around a formation energy of ~ 1.5 eV. In fact, scaling beyond the regime studied here would reveal **the diverging energetics pertaining to an infinitely long charged wire** (cf. model in Fig. 2). We also consider the corrections when **the size of the vacuum region is increased** [Fig. 1(c)]. In this case, **the diverging behavior which appears as the system approaches a plane of charges** is particularly striking and, nevertheless, is effectively eliminated through the corrections.

While the DFT supercell calculations are performed for a slab, the present correction scheme can yield formation energies pertaining to various dielectric environments such as the bulk, the isolated surface, or an isolated slab. The corrected formation energies corresponding to these three kinds of dielectric environments are illustrated in Fig. 5 for various defect positions. Defects in the middle of the slab can be used for modeling the bulk and the corrections indeed recover the bulk formation energy (1.50 eV) within 30 meV. The supercell calculations can also be used to achieve formation energies for charged defects at isolated surfaces. The method gives the formation energy of the defect as its distance d from the surface is varied and reproduces the correct $1/d$ dependence at large d . Alternatively, one could be interested in obtaining formation energies pertaining to an isolated slab. The corrections would thus be used to eliminate the effects of the periodic boundary conditions in the supercell calculation. In this case, the uncorrected formation energies capture well the general dependence on defect position but severely underestimate the corrected results.

Finally, we demonstrate the general applicability of our scheme by applying the correction scheme to a silicon dangling bond in the -1 charge state at the otherwise

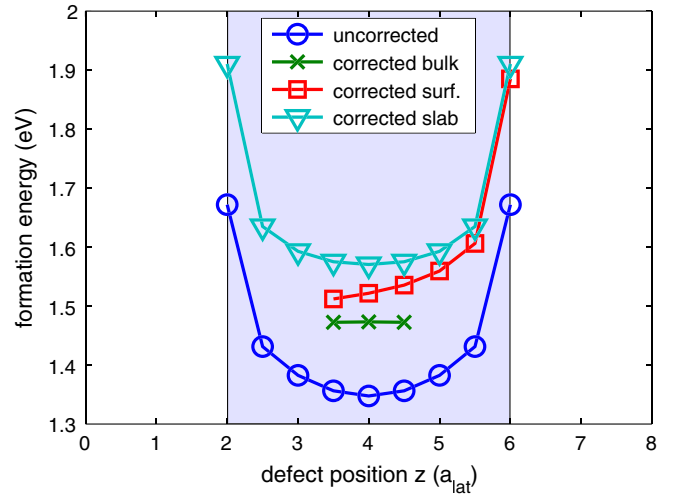


FIG. 5 (color online). Uncorrected (circles, blue) and corrected formation energies as a function of the defect position within the slab. The uncorrected system corresponds to a slab in a periodic supercell. The applied electrostatic corrections depend on the targeted dielectric environment, which can be the bulk (crosses, green), a single surface (squares, red), or a slab with two surfaces (triangles, cyan).

hydrogen passivated Si(001)-(2 \times 1) surface [28,29]. Computational details are given in the Supplemental Material [15]. This system severely challenges the correction scheme as it features a covalent-bonded material with a small band gap, a complex surface structure, a high dielectric-constant contrast, and a more extended defect wave function. As can be inferred from the extrapolation study in Fig. 4(b), the correction performs very well also in this challenging case. The robustness of our scheme mainly rests on a proper description of the underlying electrostatics. Insofar the defect charge is well localized within the supercell, the electrostatics is correctly captured and our correction scheme is reliable.

In summary, we have developed a finite-size supercell correction scheme for removing spurious electrostatic interactions of charged defects in the proximity of surfaces and interfaces while preserving the physically relevant electrostatic and quantum-mechanical effects. This is achieved through a scheme which extracts model parameters self-consistently from the electronic-structure calculation. The scheme generally applies to any charged species at surfaces and interfaces. An extension of the scheme to more complex dielectric environments, such as for embedded clusters or nanodots, can be envisaged along the same lines.

We acknowledge fruitful discussions with A.V. Krashennnikov. Financial support is acknowledged from the Swiss National Science Foundation (Grants No. 200020-119733/1, 200020-134600, and 206021-128743). We used computational resources of CSCS, CSEA-EPFL, and CSC.

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