

## Dipole correction for surface supercell calculations

Lennart Bengtsson

*Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden*

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When performing density-functional calculations of surfaces using a plane-wave pseudopotential code, it is necessary to embed a slab with two surfaces in a periodic supercell. In many situations, it is desirable to study an asymmetric slab with a net surface dipole density. The periodic boundary conditions imposed on the electrostatic potential then give rise to an artificial electric field across the slab. We present a dipole correction that cancels the artificial field, and show how this correction can be incorporated in the density-functional theory total-energy expression. The results are supported by total-energy calculations of water-molecule layers. [S0163-1829(99)02019-6]

### I. INTRODUCTION

In recent years, density-functional theory (DFT) combined with local- or semilocal approximations of the exchange-correlation energy has become a widely used theoretical model for the calculational study of atomic and electronic structure of surfaces. Examples of applications for which the local-density approximation or the generalized-gradient approximation (GGA) yields results with useful accuracy include surface reconstruction,<sup>1</sup> interactions with adatoms,<sup>2</sup> and calculation of surface energies.<sup>3</sup> Most of these calculations are based on pseudopotentials and a plane-wave basis set. The plane-wave basis is well suited for surface systems for a number of reasons: The basis set is independent of ionic positions and gives, thus, an unbiased description of the surface, including bulk and vacuum regions. Because no Pulay corrections are needed, accurate ionic forces can be calculated efficiently. Moreover, it is possible to improve the quality of the basis set in a systematic manner by adjusting the plane-wave cutoff energy. With the advent of ultrasoft pseudopotentials<sup>4</sup> even traditionally “hard” elements like first-row atoms and transition metals can be handled efficiently.

The plane-wave basis set assumes a supercell geometry that is periodic in all three directions. In order to study a surface, a slab with two surfaces is embedded with vacuum regions in a supercell. The number of slab layers is chosen so that the surface-surface interaction is small, and similarly the vacuum region should be large enough so that the interaction between neighboring slabs is negligible.

In many situations it is desirable to study an asymmetric slab with a nonvanishing surface-dipole density. An example is a slab with adatoms on one side. The electrostatic potentials on the two sides of the slab will then be different at the cell boundary. However, plane-wave methods impose periodic boundary conditions on the electrostatic potential, so an artificial uniform electric field is introduced in the supercell in order to cancel the potential jump at the boundary. One way to circumvent this problem when studying surface-adatom systems is to put adatoms on both sides of the slab, so that the net dipole moment is zero. Unfortunately, this procedure introduces undesirable adatom interaction effects across the slab and across the vacuum region, and to coun-

teract them the number of slab layers and the size of the vacuum region must be increased. A better solution was suggested by Neugebauer and Scheffler.<sup>5</sup> They introduced a dipole field that compensated the artificial field in the supercell. By treating this field as external, they derived an incorrect expression for the electrostatic energy, however.

In this paper, we derive a dipole correction that compensates for the artificial dipole field within the context of a periodic supercell calculation. It consists of two parts: a compensating ramp-shaped potential that cancels the artificial field, and an energy correction term. The proposed correction formulas are supported by test calculations on layers of water molecules. The results show that the dipole correction gives accurate values for both total energy and forces.

The paper is organized as follows: In Sec. II we derive correction formulas for the electrostatic potential and the total energy, which compensate for the artificial field in the vacuum region. We also show how these corrections can be incorporated into the DFT total-energy expression in a form that is easy to implement in existing DFT codes. We present results from prototype calculations in Sec. III and end with a concluding discussion in Sec. IV.

### II. THEORY

#### A. Dipole correction

By calculating the electrostatic potential and the total energy for an isolated slab and comparing the results with a supercell calculation with periodic boundary conditions, we are now going to derive correction formulas that compensate for the artificial field in the vacuum region in the supercell.

Consider an isolated slab-shaped density distribution  $\rho(\mathbf{r})$  that is normal to the  $z$  axis. We assume that the density is periodic in the  $x$  and  $y$  directions. When calculating the electrostatic potential that is generated by  $\rho(\mathbf{r})$ , it is convenient to separate the charge density into a laterally averaged quantity and a remainder:

$$\rho(\mathbf{r}) = \rho_{\text{av}}(z) + \rho'(\mathbf{r}) \quad \text{where} \quad \int \int \rho'(\mathbf{r}) dx dy = 0 \quad \forall z. \quad (1)$$

The decomposition allows us to write down the following expressions for the electrostatic potentials  $V_{\text{av}}(z)$  and  $V'(z, \mathbf{G}_{\parallel})$  that are generated by  $\rho_{\text{av}}$  and  $\rho'$ , respectively:

$$V_{\text{av}}(z) = -2\pi \int_{-\infty}^{\infty} \rho_{\text{av}}(z') |z - z'| dz' \quad (2)$$

and

$$V'(z, \mathbf{G}_{\parallel}) = \begin{cases} \frac{2\pi}{|\mathbf{G}_{\parallel}|} \int_{-\infty}^{\infty} \rho'(z', \mathbf{G}_{\parallel}) e^{-|z-z'|\|\mathbf{G}_{\parallel}\|} dz', & \mathbf{G}_{\parallel} \neq \mathbf{0} \\ 0, & \mathbf{G}_{\parallel} = \mathbf{0} \end{cases} \quad (3)$$

Here,  $\mathbf{G}_{\parallel}$  is a lattice vector of the two-dimensional reciprocal lattice that is parallel to the slab. Outside the slab Eq. (2) simplifies to  $V_{\text{av}} = 2\pi m$  (above) or  $-2\pi m$  (below), where

$$m = \int_{-\infty}^{\infty} \rho_{\text{av}}(z') z' dz' \quad (4)$$

is the surface dipole density of the slab. The other potential  $V'$  decays exponentially for large  $|z|$  and the decay constant is given by  $1/G_{\parallel, \text{min}}$ . For a square lattice,  $1/G_{\parallel, \text{min}} = L/(2\pi)$ , where  $L \times L$  is the dimension of the periodic cell in the  $xy$  plane.

Now assume that the slab is put in a box of height  $z_m$  with periodic boundary conditions also in the  $z$  direction. Let  $V_{\text{av, per}}$  and  $V'_{\text{per}}$  be periodic solutions of Poisson's equation in the box, with source terms  $\rho_{\text{av}}$  and  $\rho'$ , respectively. Because  $V'(\mathbf{r})$  decays exponentially away from the surface, the error made when imposing periodic boundary conditions on  $V'$  should be small, so  $V'_{\text{per}}(\mathbf{r}) \approx V'(\mathbf{r})$ . On the other hand, a linear term has emerged in the laterally averaged part of the potential:

$$V_{\text{av, per}}(z) = V_{\text{av}}(z) - 4\pi m \left( \frac{z}{z_m} - \frac{1}{2} \right) \quad (5)$$

in order to satisfy  $V_{\text{av, per}}(0) = V_{\text{av, per}}(z_m)$ . An approximation for the Hartree potential of the isolated slab is thus

$$V(\mathbf{r}) \approx V_{\text{per}}(\mathbf{r}) + V_{\text{dip}}(z), \quad (6)$$

where  $V_{\text{per}} = V_{\text{av, per}} + V'_{\text{per}}$  and the dipole correction is

$$V_{\text{dip}}(z) = 4\pi m \left( \frac{z}{z_m} - \frac{1}{2} \right), \quad 0 < z < z_m. \quad (7)$$

The dipole correction introduces a jump in the potential  $V(\mathbf{r})$ . The discontinuity should of course be placed within the vacuum region of the supercell.

The added potential  $V_{\text{dip}}$  affects the energy of the supercell  $\Omega$ . Because the Hartree energy is given by

$$E_H = \frac{1}{2} \int_{\Omega} \rho(\mathbf{r}) V(\mathbf{r}) d^3 r, \quad (8)$$

it follows that the energy associated with the dipole-potential correction is

$$E_{\text{dip}} = \frac{1}{2} \int_{\Omega} \rho(\mathbf{r}) V_{\text{dip}}(z) d^3 r. \quad (9)$$

The potential term  $V_{\text{dip}}$  corresponds to an electric field  $E_z = -4\pi m/z_m$ . The field has internal origin, because it is proportional to the surface-dipole density of the slab. Note that the energy shift caused by an applied external field is twice the amount in Eq. (9). The potential correction in Eq. (7) was first proposed by Neugebauer and Scheffler.<sup>5</sup> However, because they assumed that the applied field was external, they did not provide a correct expression for the Hartree energy.

## B. Total energy within DFT

In the previous section we derived correction formulas for the electrostatic potential and the Hartree energy. We will now proceed with deriving expressions for the DFT total energy and effective potential that include the dipole correction terms.

Within DFT the electronic density is constructed from occupied one-particle states  $\{\psi_i\}$ :

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2, \quad (10)$$

where we for simplicity omit the  $k$ -point index and assume that all bands are filled. The ground-state energy of the system is then obtained by minimizing the following energy functional with respect to the one-particle states  $\{\psi_i\}$ :

$$E[\{\psi_i\}, \{\mathbf{R}_j\}] = \sum_i \langle \psi_i | T | \psi_i \rangle + E_H + E_{\text{XC}}. \quad (11)$$

The terms appearing in Eq. (11) are kinetic energy, Hartree energy and exchange-correlation energy, respectively. The total charge density  $\rho(\mathbf{r})$  is the sum of the electronic part  $\rho^e(\mathbf{r}) = -en(\mathbf{r})$  and the ionic part  $\rho^i(\mathbf{r}) = e \sum_j Z_j \delta(\mathbf{r} - \mathbf{R}_j)$ , where  $Z_j$  is the atomic number of atom  $j$  and  $\mathbf{R}_j$  is its position. It follows that the Hartree energy of the isolated slab can be written as

$$\begin{aligned} E_H &= \frac{1}{2} \int_{\Omega} (\rho^i + \rho^e) (V_{\text{per}} + V_{\text{dip}}) d^3 r \\ &= E_{\text{dipc}} + \int_{\Omega} \rho^e(\mathbf{r}) [V_{\text{per}}^i(\mathbf{r}) + V_{\text{dip}}(\mathbf{r})] d^3 r + E_{e-e} + E_{i-i}, \end{aligned} \quad (12)$$

where the ‘‘dipole correction energy’’

$$E_{\text{dipc}} = \frac{1}{2} \int_{\Omega} [\rho^i(\mathbf{r}) - \rho^e(\mathbf{r})] V_{\text{dip}}(\mathbf{r}) d^3 r, \quad (13)$$

and

$$E_{e-e} = \frac{1}{2} \int_{\Omega} \int \frac{\rho^e(\mathbf{r}) \rho^e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' d^3 r. \quad (14)$$

The last term  $E_{i-i}$  in Eq. (12) is the Madelung energy of the ions. We arrive at the following dipole-corrected expression for the total energy:

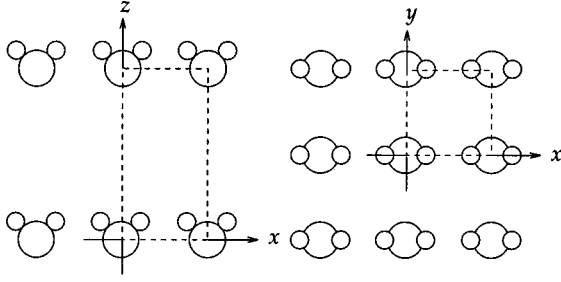


FIG. 1. Orientation of the water molecules within the two-dimensional layer. The extent of the supercell is drawn with dashed lines. The distance between neighboring molecules is 3 Å and the spacing between different layers is 6 Å.

$$\begin{aligned}
 E[\{\psi_i\}, \{\mathbf{R}_j\}] &= \sum_i \langle \psi_i | T | \psi_i \rangle \\
 &+ \int_{\Omega} [V_{\text{per}}^i(\mathbf{r}) + V_{\text{dip}}(\mathbf{r})] \rho^e(\mathbf{r}) d^3 r \\
 &+ E_{e-e} + E_{i-i} + E_{\text{XC}} + E_{\text{dipc}}. \quad (15)
 \end{aligned}$$

The corresponding one-electron Hamiltonian operator  $H$  is the functional derivative of the total energy with respect to the electronic density  $n(\mathbf{r})$ :

$$H = T + V_{\text{per}}^e + V_{\text{per}}^i + V_{\text{dip}} + V_{\text{XC}}, \quad (16)$$

where  $V_{\text{XC}} = \delta E_{\text{XC}} / \delta n$  is the exchange-correlation potential.

The modifications necessary to include the dipole correction in a DFT code is thus very straightforward.  $V_{\text{dip}}$  should be added to the ionic potential and the total energy should include the extra term  $E_{\text{dipc}}$ . Because  $V_{\text{dip}}$  is present in the one-electron Hamiltonian, it affects the one-electron states and thus also the electronic density. It is therefore necessary to determine the surface dipole density  $m$  in a self-consistent way. The fact that  $E_{\text{dip}}$  defined in Eq. (9) differs from  $E_{\text{dipc}}$  in Eq. (13) is explained by the presence of  $V_{\text{dip}}$  in the second term of Eq. (15).

### C. Corrected Hellman-Feynman forces

Because both the ionic charge density  $\rho^i$  and the dipole moment  $m$  depends on the ionic positions, a careful derivation of the ionic forces is needed. According to the Hellman-Feynman theorem the ionic forces may be calculated as if the ions were embedded in a classical charge distribution  $\rho^e(\mathbf{r})$ . More specifically, the force  $\mathbf{F}^I$  on atom  $I$  at position  $\mathbf{R}_I$  is given by  $\mathbf{F}^I = -\nabla_{\mathbf{R}_I} E_H$ , where  $E_H$  is the Hartree energy from Eq. (12). Expressing  $\mathbf{F}^I$  as

$$\begin{aligned}
 \mathbf{F}^I &= -\frac{1}{2} \int (\nabla_{\mathbf{R}_I} \rho^i) V_{\text{dip}} d^3 r - \frac{1}{2} \int (\rho^i + \rho^e) \nabla_{\mathbf{R}_I} V_{\text{dip}} d^3 r \\
 &- \int \rho^e \nabla_{\mathbf{R}_I} V_{\text{per}}^i d^3 r - \nabla_{\mathbf{R}_I} E_{i-i} \quad (17)
 \end{aligned}$$

and simplifying the first two terms using

$$\begin{aligned}
 \int (\nabla_{\mathbf{R}_I} \rho^i) V_{\text{dip}} d^3 r &= -e Z_I \int \delta'(\mathbf{r} - \mathbf{R}_I) V_{\text{dip}} d^3 r \\
 &= e Z_I \nabla_{\mathbf{r}} V_{\text{dip}}(\mathbf{R}_I) = Z_I \frac{4\pi m e}{z_m} \hat{z} \quad (18)
 \end{aligned}$$

and ( $A$  is the area of the supercell in the  $xy$  plane)

$$\nabla_{\mathbf{R}_I} V_{\text{dip}} = 4\pi \left( \frac{z}{z_m} - \frac{1}{2} \right) \nabla_{\mathbf{R}_I} m, \quad (19)$$

$$\nabla_{\mathbf{R}_I} m = \frac{1}{A} \nabla_{\mathbf{R}_I} \int (\rho^i + \rho^e) z d^3 r = \frac{1}{A} \nabla_{\mathbf{R}_I} \sum_j e Z_j \mathbf{R}_j \cdot \hat{z} = \frac{e Z_I \hat{z}}{A} z, \quad (20)$$

we get the following expression for the ionic force:

$$\mathbf{F}^I = -Z_I \frac{4\pi m e}{z_m} \hat{z} - \int \rho^e(\mathbf{r}) \nabla_{\mathbf{R}_I} V_{\text{per}}^i(\mathbf{r}) d^3 r - \nabla_{\mathbf{R}_I} E_{i-i}. \quad (21)$$

The first term is the force from the dipole correction field exerted on ion  $I$ , and the last two terms comprise the usual DFT expression for the force.

## III. RESULTS

In order to demonstrate the accuracy of the proposed dipole-correction formula, we present results from a DFT-GGA calculation on a two-dimensional layer of water molecules (see Fig. 1.) This system was chosen because the water molecules have a large internal dipole moment, so the electrostatic potentials on either side of the molecule layer differ by several volts. It follows that the dipole correction field in a supercell calculation for this system will be large ( $\sim 1$  V/Å) and may affect the total energies if no dipole corrections are included.

The plane-wave pseudopotential code DACAPO was used for the total-energy calculations.<sup>6</sup> The interactions between the valence electrons and the ions were represented with ultrasoft pseudopotentials.<sup>4</sup> Although the hydrogen  $1s$  and oxygen  $2p$  orbitals are highly localized around the ion cores, these potentials give accurate total energies with a plane-wave cutoff energy of only 25 Ry.

We performed calculations both with and without dipole

TABLE I. Calculated total energies for a water molecule within a two-dimensional layer, using various dipole corrections. The double-cell result for the total energy is used as reference.

	Total energy (eV)	$\Delta E$ (eV)
No correction	-467.0192	-0.10
Correction from Eq. (13)	-466.8994	0.02
Correction from Ref. 1	-466.8142	0.10
Double cell, per layer	-466.9191	0.00

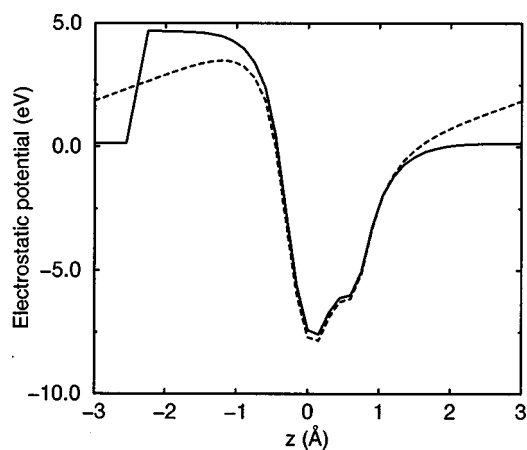


FIG. 2. Laterally averaged electrostatic potential for the electrons in the supercell, with (solid-curve) and without (dashed-curve) dipole correction.

corrections, and in order to verify the energy-correction formula in Eq. (13) we also made a calculation for a larger supercell containing two molecule layers oriented so that the net dipole moment in the cell was zero and no dipole correction was needed. The results are presented in Table I. As shown in Table I, omitting the dipole correction results in an error in the total energy of 0.1 eV/molecule for this system. With corrections included the error is only 0.02 eV. The correction formula suggested by Neugebauer and Scheffler overcorrects the energy by a factor of 2, so its applicability is questionable. Dipole-corrected forces differ from the ones calculated in the larger supercell by at most 0.04 eV/Å. Without correction the error is approximately 0.2 eV/Å. In Fig. 2 we present the laterally averaged electrostatic potential  $-eV(z)$  across the molecule layer. The applied dipole layer, visible as a potential jump in the graph, exactly cancels the artificial field in the vacuum region. The figure also shows that work functions are ill defined if the dipole correction is

not included, because then the vacuum levels cannot be identified.

#### IV. CONCLUSION

By adding dipole corrections to the electrostatic potential and the total energy, it is possible to embed a slab with an intrinsic dipole moment in a periodic supercell without forcing the electrostatic potential to be periodic as well. For example, this possibility is important for surface-atom calculations and when calculating work functions. The energy associated with the dipole correction field differs from the energy shift caused by an external applied electric field by a factor of  $\frac{1}{2}$ , which is explained by the fact that the dipole correction field has internal origin. The proposed formula is supported by DFT-GGA calculations on layers of water molecules. The results show that the dipole-corrected total energy from a supercell containing only one layer agrees with the energy for a larger symmetric supercell containing two oppositely directed layers.

Although we have focused on slabs with intrinsic dipole moments, we should mention that the dipole correction may be useful also for other surface systems that are embedded in periodic supercells. One important example is finding the linear response of a surface to an external electric field. Because the external field induces a dipole moment in the slab, dipole corrections are needed in order to obtain the proper induced electric field outside the slab.

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