Ab initio simulation of charged slabs at constant chemical potential

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We present a practical scheme for performing *ab initio* supercell calculations of charged slabs at constant electron chemical potential μ, rather than at constant number of electrons N_e. To this end, we define the chemical potential relative to a plane (or "reference electrode") at a finite distance from the slab (the distance should reflect the particular geometry of the situation being modeled). To avoid a net charge in the supercell, and thus make possible a standard supercell calculation, we restore the electroneutrality of the periodically repeated unit by means of a compensating charge, whose contribution to the total energy and potential is subtracted afterwards. The "constant μ" mode enables one to perform supercell calculation on slabs, where the slab is kept at a fixed potential relative to the reference electrode. We expect this to be useful in modeling many experimental situations, especially in electro-chemistry. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1379327]

I. INTRODUCTION

Density functional theory (DFT) in conjunction with *ab initio* self-consistent electronic structure calculations has proved to be a reliable tool in investigating various systems, in particular metallic surfaces. Since the DFT was formulated, there has been continuous interest in applying the formalism to study charged surfaces, or surfaces in an external electric field. The issues which have been addressed include the density of the induced surface charge and the (actual) position of the image plane,[1–7] field-induced reconstruction of a surface,[8,9] modeling of scanning tunneling microscopy (STM) measurements,[10–12] simulation of adatoms in the presence of external electric field,[13] changes of the vibrational frequencies of adsorbed molecules,[14] the study of metal–water interfaces,[15] and electrodes in an underpotential deposition experiment.[16]

Originally, DFT was formulated for systems with a fixed number of electrons N_e.[17] Soon after[18] it was realized that there exists an (equivalent) formulation of DFT in which the chemical potential of the electrons, μ, rather than their number, is one of the basic variables. In this case, the *grand potential* of the system considered as a functional of the electron density, $\Omega[\rho]$, attains a minimum at the correct ground state electron density, ρ_0, corresponding to a given μ,[19] rather than the *free energy* $F[\rho]$ at fixed N_e. The importance of this formalism lies in the fact that, in complex systems with strongly interacting parts, one cannot unambiguously assign a certain number of electrons to any particular part of the system, whereas the electron chemical potential μ is a global quantity and, hence, is uniquely defined.[20]

The difference between the canonical ("N_e=const") and grand canonical ("μ=const") description is easy to illustrate in the case of a charged metallic slab. Suppose we are interested in finding the equilibrium state of the system at variable charge and fixed temperature T and volume V. For instance, if the surface of the slab can adopt several alternative configurations, which one would be preferred at a given set of thermodynamic parameters? The following examples are illustrative of such a situation: surface reconstruction or deconstruction, reorientation of water molecules next to the metallic electrode in an electrochemical cell, adsorption/desorption of specific ions depending on the sign and magnitude of the charge of the metallic surface.

If the number of electrons is fixed in a system switching between possible alternatives, then N_e is a convenient variable, and the thermodynamic potential which should be compared for different configurations is the Helmholtz free energy $F(T,V,N_e)$. If, on the other hand, alternative configurations have the same chemical potential of electrons then μ is a more natural variable for describing the charge state of the system, and the grand potential $\Omega(T,V,\mu)$ is the relevant thermodynamic potential.[21] This is just the usual thermodynamic choice of extensive or intensive variables, e.g., pressure versus volume, or entropy versus temperature, where the most convenient variable is chosen depending on the particular problem under consideration.

A realization of the "N_e=const" mode for a metallic slab is, e.g., when an *isolated* slab is placed in an external electric field (as in the case of an isolated capacitor plate). The "μ=const" mode corresponds to a metallic slab which is a part of an electric circuit. There are numerous examples

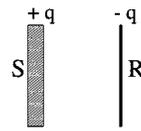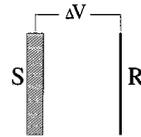| Mode	Scheme	Thermodynamic potential	Experimental realization
$N_e = $ const	S [+q] [−q] R	$F(T, V, N_e)$	Isolated capacitor
$\mu = $ const	S [ΔV] R	$\Omega(T, V, \mu)$	Electrochemistry (STM)

FIG. 1. The system under consideration S can be maintained either at constant charge ("$N_e = $ const" mode) or at constant potential drop ΔV relative to the reference electrode R ("$\mu = $ const" mode). In the first case the relevant thermodynamic potential is the Helmholtz free energy F, while in the second it is the grand potential Ω.

in different types of electrochemical experiments;[22] perhaps this is also relevant to STM measurements although, in this case, the system is not in equilibrium. We briefly summarize the above in Fig. 1.

Although the grand canonical DFT formalism is well established and in many cases is closer to an actual experimental situation, its practical implementation is less straightforward than that in the "$N_e = $ const" mode. Possibly, this explains why *ab initio* calculations of metallic surfaces have almost invariably been done at a constant number of electrons.[23]

Below we provide a practical scheme which allows for the implementation of the "$\mu = $ const" mode within a standard *ab initio* supercell calculation. This gives rise to a number of subtle issues regarding the definition of μ and the removal of the electrostatic divergence associated with charged systems in three dimensions, whose resolution is one of the principal goals of this article.

II. CHEMICAL POTENTIAL OF ELECTRONS

We would like to develop a scheme in which the electron chemical potential can be held fixed. However, μ is defined with respect to an energy zero, which can be arbitrarily chosen. This is a general property of the chemical potential: in specifying the chemical potential of a particle in a given state, one must choose the standard (or reference) state, where the particle is put after being removed from the system and where it is assigned zero energy. Although no physical property of the system is affected by the choice of the "particle reservoir," care should be taken to keep the "reservoir" unchanged during the simulation, and also to specify the same reservoir for systems which one is going to compare with each other. If we work with infinite slabs of definite orientation, at a given amount of vacuum, the chemical potential might be considered to be the energy required to re-

move an electron from the slab and put it at the "infinity," that is, sufficiently far in vacuum. For a neutral slab, this is simply the work function. The latter, however, is not defined for charged slabs, and we need to provide a generalized definition.

A. Uncharged slab

In the case of a neutral metallic surface, the electron chemical potential μ (defined as the first-order free energy change with respect to the electron number N_e) is related to the work function ϕ as[24]

$$\phi = V_\infty - \mu, \tag{1}$$

where V_∞ is the potential far away from the surface, well into the vacuum region. For finite slabs, V_∞ must be considered to be the value of the potential at a distance which is small compared to the macroscopic size of the slab, though large compared to any relevant microscopic distance, such as the lattice parameter.[25]

The work function measures the difference of potential between the Fermi level and the vacuum, and this difference depends on the surface dipole which varies with the face exposed. A way to display the dependence of the work function on the surface-dipole explicitly is to rewrite (1) as

$$\phi = (V_\infty - V_b) - (\mu - V_b) = D - \bar{\mu}, \tag{2}$$

where V_b is the average potential in the interior of the crystal. In this equation, $\bar{\mu}$ is the position of the Fermi level relative to V_b, and is the same for the metal regardless of the face exposed.[24] D is the surface-dipole potential, which is dependent on the surface orientation.[26] Thus the effect of changing the surface dipole is to change the electrostatic potential of the interior of the metal relative to the vacuum and so to shift the energies of the whole electron band including the Fermi level with respect to the potential at infinity. The chemical potential of electrons in different crystals must be measured relative to a common energy zero V_∞. This means that electrons in crystals with different exposed surfaces and different shapes have different chemical potentials.

In simulations of periodically repeated (neutral) slabs there is no field outside the slab and the computed work function is identical to that measured by a threshold experiment in which an electron is moved from the interior to a point just outside the crystal face. For a real crystal there is small change in potential between this point and "true infinity," that is, points whose distance from the crystal is large compared to crystal dimensions. This is the "true" vacuum potential. However, provided that the crystal is slab shaped with a thickness small compared its lateral dimensions, this correction is negligible. Within the current study we consider slabs of crystal with parallel faces of the same type.

B. Two metals in contact

Next, we consider two different metals Me_1 and Me_2 having different work functions ϕ_1 and ϕ_2 (Fig. 2). If the metals do not interact, their potentials are aligned so as to equalize the vacuum levels [Fig. 2(a)]. As soon as the electrons are allowed to flow from one metal to the other, their
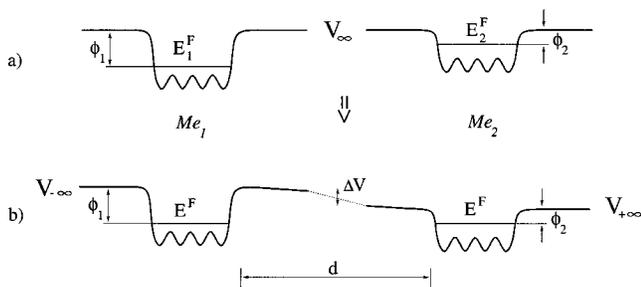
FIG. 2. Diagram showing two metals Me_1 and Me_2 before (a) and after (b) the electrons are allowed to equilibrate their Fermi levels E^F; ϕ denotes the work function, V_∞ indicates the potential far away from the surface, and $\Delta V = V_{-\infty} - V_{+\infty}$.

chemical potentials or, equivalently, their Fermi levels, equilibrate [Fig. 2(b)]. The resulting charge on each metal $+q$ and $-q$ gives rise to a constant electric field, $\mathcal{E}$, in the vacuum region between the surfaces of the two metals—the plates of a condenser. The surface charge per unit area, σ, which is related to q, and the field $\mathcal{E}$ are connected via

$$\sigma = \frac{\mathcal{E}}{4\pi} = -\frac{1}{4\pi}\frac{dV}{dz},$$

where V denotes the electrostatic potential, and the derivative dV/dz is taken sufficiently far away from the metallic surfaces, i.e., where the charge density becomes negligibly small.

We note that the surface charge is inversely proportional to the distance between the condenser plates d [Fig. 2(b)] with more charge being transferred if the plates are nearer together.

C. An isolated charged slab and the corresponding system with periodic boundaries

Figure 3(a) shows the potential of a charged symmetric slab of metal. Outside the slab the magnitude of the field is constant and its direction is opposite on the two sides of the slab. Taking $z=0$ at the center of the slab we have, in regions sufficiently far from the slab,

$$V = V_0 + 2\pi\sigma|z|, \tag{3}$$

which tends to infinity as $|z| \to \infty$. If we choose V_0 in Eq. (3) such that the potential is zero at $|z| = \Lambda$, then this is equivalent to placing reference electrodes at Λ and $-\Lambda$.

Figure 3(b) shows a periodic arrangement of slabs separated by a vacuum region. All replicas are subjected to the same local conditions, i.e., they are identical copies of a unique slab. The system is neutralized by placing a counter-charge $-\sigma$ per unit area on two-dimensional sheets $A, A', A'', \ldots$ Each periodic unit (metal/vacuum/metal) represents a symmetric condenser with capacitance $4\pi d$; the charge distribution and field on the two sides of the slab are symmetric provided that the slab is symmetric itself, and that it is placed in the center of the space between the charged sheets. The electric field near each slab in Fig. 3(b) is identical to the isolated charged slab in Fig. 3(a).

D. The idea of a reference electrode

In an electrode in an electrochemical cell the potential falls off from the metal surface to a constant value as the double layer is traversed. The charge on the electrode's surface depends on the potential difference between the metal and the solution far from the electrode, and on the capacitance of the double layer. In this setup, the control variable is the potential rather than the surface charge, and calculations should be carried out at constant chemical potential rather than constant charge.

In order to define the origin for the electron chemical potential, we set to zero the electrostatic potential at a distance $\pm\Lambda$ from the center of the slab:

$$V(\bar{r})\big|_{|z|=\Lambda} = 0. \tag{4}$$

This is equivalent to placing reference electrodes at these points. The electron chemical potential is then the difference between the potential at these points and the Fermi level [Fig. 3(a)]. This definition is compatible with the system with periodic boundaries shown in Fig. 3(b). However, since the potential is linear in the regions of low electron density, it is not necessary to have the cell boundaries at $\pm\Lambda$. In fact, if μ' is the chemical potential (Fermi level) corresponding to the periodic system shown in Fig. 3(b), where the choice of the energy zero is arbitrary, then the chemical potential consistent with (4) can be recovered as

$$\mu = \mu' - V(L_z/2) - (\Lambda - L_z/2)\frac{dV}{dz}\bigg|_{z>z_0}, \tag{5}$$

where z_0 is a point beyond which the electron density is negligible, and thus the potential is linear (obviously z_0
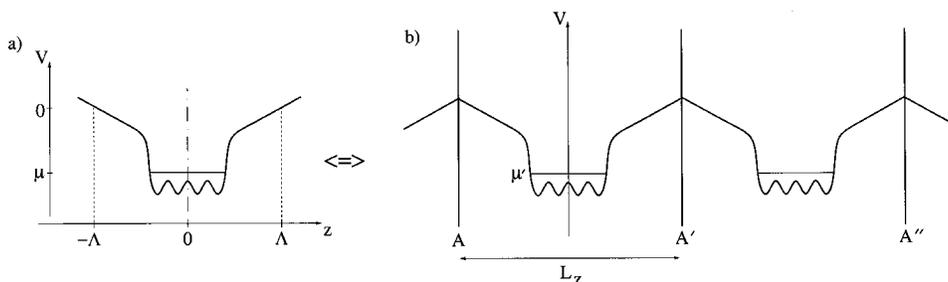

FIG. 3. The potential of an isolated, symmetric charged slab (a) can be reproduced by that of a periodically repeated neutral system consisting of slab and compensating charged planes A (b). The energy zero in (a), which defines μ, is chosen such that $V=0$ at $z=\pm\Lambda$. This is equivalent to placing the reference electrode at Λ. The choice of zero of the energy axis on (b) is not relevant, because the chemical potential μ' is related to μ in (a) by Eq. (5).

$\leq L_z/2$). This means that the size of the simulation cell L_z need not be as large as Λ. While the choice of Λ is dictated by the characteristics of the problem under consideration, e.g., the Debye–Hückel screening length of the electrolytic solution, the above reasoning suggests that, in practice, the first-principles calculations can be done for the periodic system shown in Fig. 3(b), by assuming that the reference electrode is placed at position A (i.e., $\Lambda = L_z/2$). Then, the results can be recalculated in a simple way for any particular value of Λ.

III. TWO SURFACE PHASES. WHICH IS MORE STABLE?

Suppose that the surface of a metal carrying a certain charge can assume a few different structures: how can we decide which one is preferred?

Here we must distinguish whether the surface is in the "$N_e = $ const" mode or in the "$\mu = $ const" mode. In the first case all states of the surface correspond to the same surface charge, and consequently to the same field. Therefore, to answer the question, we should minimize the Helmholtz free energy:[27]

$$F = F_e + E_{ii},$$

where F_e is the free energy of the electron subsystem (including their interaction with the ions)[28] and E_{ii} is the electrostatic ion–ion interaction energy.

In the second case, the system maintains the same μ, but the charge of the surface can differ from one state to another. As a consequence, the electric field near the surface can change, and this enters the overall energy balance. Note that the closer the reference electrode (i.e., the smaller the value of Λ), the larger the variation in the electric field should be: that is another illustration of why the position of the reference electrode becomes important in the "$\mu = $ const" mode.

In this case, to decide which of the states of the surface is more stable we have to compare the grand potentials:

$$\Omega = F - \mu N_e = F_e - \mu N_e + E_{ii}.$$

The surface can change state continually, rather than discretely; in this case we speak about the equilibrium state as a function of μ.

IV. PRACTICAL AND COMPUTATIONAL CONSIDERATIONS

In practice, *ab initio* calculations of solid surfaces are usually done within the supercell approach, in which the surface is represented with a slab, embedded in a vacuum region. The cell comprising the slab and the corresponding vacuum is periodically repeated, thus restoring the 3D periodicity of the system. Although the supercell approach is not the only possible way to calculate the electronic structure of the surfaces, and other methods have been devised,[4,7] the computational scheme presented here assumes that the *ab initio* calculations use the supercell approach as the most efficient at present.

In this case, treating charged surfaces becomes problematic because the net charge of the cell makes the electrostatic

potential and energy diverge. To circumvent this problem, a compensating charge must be introduced into the cell. In the "$N_e = $ const" mode, this does not introduce any additional complication, because the neutralizing charge distribution can be chosen in such a way that the free energy difference remains unaffected. For example, in Refs. 8 and 9 the charge was neutralized by placing sheets of charge in the vacuum region. The distribution of charge across the sheets was Gaussian. As long as the surface energies are compared at the same charge, then the Gaussian charge contributions to the total energy cancel out. Unfortunately, this is not the case of the "$\mu = $ const" mode, in which the states that are compared have different charges, and therefore the contribution of the neutralizing charge is different and must be treated explicitly.

The whole scheme of computation in the "$\mu = $ const" mode consists, then, of two steps: (1) Having introduced the compensating charge, the self-consistent electronic density, potential, and grand potential per supercell are calculated (Sec. IV A). (2) The properties of the isolated supercell are restored by removing the compensating charge and recalculating the potential and grand potential, so as to satisfy the appropriate boundary conditions (4) (Sec. IV B).

A. Grand potential calculation

To find the electron grand potential we use the method proposed in Ref. 29, which we briefly recall in the following, referring the reader to the original papers 29 and 30 for a more extensive discussion. The method has been implemented in the CPMD code[31] and since then has repeatedly been used for *ab initio* calculations of various types.

The method is related to Mermin's extension of the density functional theory (DFT) to finite temperatures, in the sense that the Helmholtz free energy functional

$$F[\rho_e] = \Omega[\rho_e] + \mu N_e + E_{ii} \qquad (6)$$

shares the stationary points with the Mermin functional.[18] In Eq. (6) ρ_e denotes the electron density, which integrates to N_e electrons, μ is the electron chemical potential, E_{ii} is the energy of the ion–ion electrostatic interaction, and the grand potential Ω is a functional defined at a finite temperature $T > 0$ in the following way:

$$\Omega[\rho_e] = -\frac{2}{\beta} \ln \det \left(1 + e^{-\beta(H - \mu)} \right)$$
$$- \int d\bar{r} \rho_e(\bar{r}) \left(\frac{V_H(\bar{r})}{2} + \frac{\delta \Omega_{xc}[\rho_e]}{\delta \rho_e(\bar{r})} \right) + \Omega_{xc}[\rho_e]. \qquad (7)$$

Here $\beta = 1/kT$, V_H is the Hartree potential, Ω_{xc} is the finite-temperature exchange-correlation grand potential functional (although in our calculations we shall use the zero temperature exchange-correlation functional), and H is the one-electron Hamiltonian:

$$H = -\tfrac{1}{2}\nabla^2 + V(\bar{r}).$$

The effective one-electron potential $V(\bar{r})$ is

$$V(\bar{r}) = V_H(\bar{r}) + V_{ext}(\bar{r}) + \frac{\delta \Omega_{xc}[\rho_e]}{\delta \rho_e(\bar{r})},$$

and V_{ext} is the external (ionic) potential.

In order to perform constant-μ calculations, at each self-consistent iteration we calculate the electron density as a sum of partial densities over Kohn–Sham orbitals with eigenvalues up to a given μ, thus rendering the electron density and the total number of electrons μ dependent. Correspondingly, we obtain the grand potential as a function of μ.

In practice, however, the self-consistent procedure at fixed μ turns out to converge more slowly than that at fixed N_e (as in standard DFT applications); the number of electrons N_e may initially undergo large fluctuations, although the procedure is always able eventually to find the self-consistent solution, which is fairly reproducible. We found that a simple way to speed up the calculation is to use the self-consistent density previously calculated for some value of μ—which is sufficiently close to the desired value, as an initial guess for the electron density. In this case, the procedure converges in only 10 to 15 iterations.

In this type of simulation, the total number of electrons is not an integer. This is permissible within a free energy functional: the interpretation is that the electron density is an average of all possible states in a grand canonical ensemble at the specified temperature and electron chemical potential. The states themselves, however, correspond to different but integral numbers of electrons each. The problem is that the usual exchange-correlation functionals do not distinguish states with integer and noninteger N_e, and therefore do not treat the latter as a superposition of the former.[32] A detailed discussion of this interesting issue is beyond the scope of the present article. A recent investigation of how well the density functional approach deals with noninteger numbers of electrons for both finite and extended systems can be found in Ref. 33.

B. Compensating charge correction

The compensating charge can have an arbitrary shape, for example the 2-D sheets of charge in Fig. 3(b). However, in many ways the simplest shape to implement is a uniform 3-D background charge.[34,35] In the case of localized charged defects, the uniform background contribution to the energy decays with the supercell size L as[36]

$$\Delta E_{es} = \frac{q^2 \alpha}{2L} + \frac{2\pi q Q}{3L^3} + O(L^{-5}), \tag{8}$$

where q is the net charge, α is the Madelung constant, and Q is the spherical quadrupole moment of the charge density distribution. Explicit subtraction of the background correction given by (8) allows for achieving a more rapid energy convergence with the supercell size.

Turning now to the case of charged slabs, one can similarly ask the question of how to determine the electrostatic energy and potential of the slab *without* any compensating charge, or with the compensating charge at a more distant reference electrode ($\pm \Lambda$), knowing the energy and potential of a slab *with* the compensating charge. In doing so, we employ the scheme suggested by Schultz,[37,38] which consists in decomposing a general charge density, $\rho(\bar{r})$, into the sum

$$\rho(\bar{r}) = \rho'(\bar{r}) + \rho_{lm}(\bar{r}), \tag{9}$$

where ρ' does not contain any moments (up to some value l), and ρ_{lm} matches moments of ρ and has an analytical form. The potential V', corresponding to $\rho'(\bar{r})$, can be calculated using periodic boundary conditions. The potential V_{lm}, related to ρ_{lm}, can be found by considering ρ_{lm} as an isolated charge in vacuum. Finally, the electrostatic potential V is obtained as

$$V(\bar{r}) = V'(\bar{r}) + V_{lm}(\bar{r}). \tag{10}$$

In this context the uniform background looks like a particular case of (9) for $l = 0$.

Note, correcting the potential by using (9) and (10) is only accurate to first order as it does not involve any redistribution of the electron density due to the changes of the potential. In other words, if V' and ρ' are calculated self-consistently within the DFT formalism, ρ' is the density which minimizes the total energy *only* for external potential V'. By adding V_{lm} non-self-consistently, we change the external potential, and ρ is no longer a variational density in the DFT sense. This has been recognized in Refs. 34 and 36, and a correction involving the electronic response function was proposed. However, provided that the cell is large enough compared to the slab thickness, the perturbation of the electron density in the slab is small and can be ignored in a first approximation. If the compensating charge can be placed in vacuum, then the removal of the neutralizing charge is exact, that is, it does not affect the ground state electron density.

Below we consider, first, a compensating charge of arbitrary shape (Sec. IV B 1) and, then, we address specifically the case of a uniform background (Sec. IV B 2).

1. Background of general shape

Consider a single slab placed in vacuum; the slab is infinite and periodic along the xy directions. The charge density $\rho(\bar{r})$ of the slab is not required to satisfy the neutrality condition. Our goal is to find the electrostatic energy E_{es} (per unit surface area) and the electrostatic potential $V(\bar{r})$ of the slab in the absence of any background density.

We embed the slab with some vacuum on both sides (sufficient to reach negligible electron density away from the slab) into a unit cell Ω_0 having dimensions A_0 and L_z ($\Omega_0 = A_0 L_z$), and introduce the background charge $\rho_b(z)$ which has an analytical form and restores the electroneutrality in the cell. The slab + background charge density, $\tilde{\rho}(\bar{r})$,

$$\tilde{\rho}(\bar{r}) = \rho(\bar{r}) + \rho_b(\bar{r}) \tag{11}$$

satisfies

$$\int_{\Omega_0} \tilde{\rho}(\bar{r}) d^3 r = 0.$$

Hereafter, we use the "tilde" to denote quantities that correspond to the cell *with* the compensating charge.

We do next the DFT calculation for the slab, from which we extract the self-consistent charge density $\tilde{\rho}(\bar{r})$ and the corresponding electrostatic energy $\tilde{E}_{es}$ (per unit cell Ω_0) and
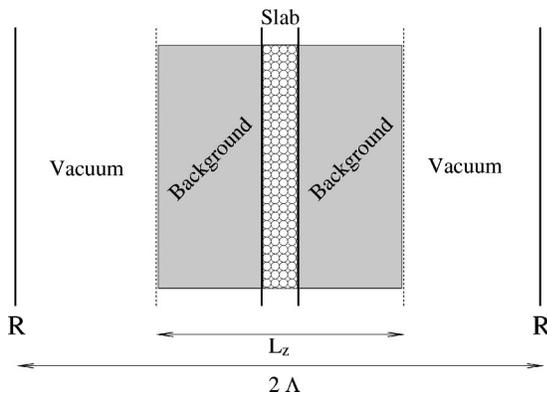
FIG. 4. A slab with a corresponding portion of background (compensating charge), representing a periodic unit in the supercell calculation, is placed into the vacuum. Both the slab and the strip of background are periodic in the x and y directions, but are not periodic in the z direction. The reference electrode R specifies the zero boundary conditions for the electrostatic potential of the slab.

electrostatic potential $\tilde{V}$. The latter is defined up to an additive constant, so we remove the ambiguity by setting its xy-average equal to zero in the middle of the vacuum [cell boundaries in Fig. 3(b)]:

$$\langle \tilde{V}(L_z/2) \rangle = \langle \tilde{V}(-L_z/2) \rangle = 0, \tag{12}$$

where

$$\langle \tilde{V}(z) \rangle = \frac{1}{A_0} \int_{A_0} \tilde{V}(\bar{r}) \, dx \, dy. \tag{13}$$

Now we take a single cell Ω_0 with the backgrounded slab out of the infinite periodic media and place it into the vacuum (Fig. 4). We assume that this procedure does not change either the electrostatic energy $\tilde{E}_{es}$ or the potential $\tilde{V}$ of the frame: the accuracy of such an assumption depends on the identity of the lowest nonzero multipole moment of the density $\tilde{\rho}(\bar{r})$. This is basically the same assumption as neglecting the interaction between periodic images in neutral supercell calculations.

The resulting system can be regarded as the superposition of two: the charged slab without background and the background itself. Correspondingly, for the electrostatic potential we have

$$\tilde{V}(\bar{r}) = V(\bar{r}) + V_b(\bar{r}), \tag{14}$$

where $V_b(\bar{r})$ is the electrostatic potential generated by the compensating charge $\rho_b(\bar{r})$.

To find $V_b(\bar{r})$, one needs to solve the Poisson equation with the charge density $\rho_b(\bar{r})$ and the boundary conditions for V_b consistent with (4), namely,

$$V_b(\bar{r})|_{z=\pm\Lambda} = \tilde{V}(\bar{r})|_{z=\pm\Lambda}. \tag{15}$$

Once $\tilde{V}$ at $z=\pm L_z/2$ is known, one can find its value at $z=\pm\Lambda$, $\Lambda \geqslant L_z/2$, by solving the corresponding Laplace equation; in practice however, this is an unnecessary complication: neglecting again any corrugation of the potential far

away from the slab and taking into account (12), we can assume that $\tilde{V}(\bar{r})|_{z=\pm\Lambda}=0$ [$\tilde{V}(\bar{z})=0$ everywhere between $L_z/2$ and Λ].

Similar to (14), we write the electrostatic energy $\tilde{E}_{es}$ of the backgrounded slab in the vacuum as:

$$\tilde{E}_{es} = E_{es} + E_{bc} + E_{bb}, \tag{16}$$

where E_{es} is the electrostatic energy of the slab without any background (i.e., the desired quantity), E_{bc} is the electrostatic energy of the background interaction with the charge density of the slab, and E_{bb} is the electrostatic energy of the background interaction with itself.

We take the term $\tilde{E}_{es}$ from the supercell calculations; E_{bb} can be easily found as soon as the background density ρ_b and potential V_b are known:

$$E_{bb} = \frac{1}{2A_0} \int_{-\infty}^{\infty} dz \int_{A_0} dx \, dy [V_b(\bar{r})\rho_b(\bar{r})]. \tag{17}$$

E_{bc} can be thought of in two ways: as an interaction of the background charge ρ_b with the slab potential V, or as an interaction of the slab charge ρ with the background potential V_b.

In the first case,

$$E_{bc} = \frac{1}{A_0} \int_{-\infty}^{\infty} dz \int_{A_0} dx \, dy [V(\bar{r})\rho_b(\bar{r})], \tag{18}$$

and in the second case,

$$E_{bc} = \frac{1}{A_0} \int_{-\infty}^{\infty} dz \int_{A_0} dx \, dy [V_b(\bar{r})\rho(\bar{r})], \tag{19}$$

The equivalence of the last two formulas is guaranteed by Green's theorem[39] and the boundary conditions for V and V_b: one can choose whichever formula is more convenient for any specific application.

2. Uniform background

By solving the Poisson equation for the uniform background potential in the cell with the boundary conditions $V_b(\pm\Lambda)=0$, and substituting the result into (14), we obtain that the artificial electrostatic potential due to the background can be eliminated by choosing

$$V(\bar{r}) = \tilde{V}(\bar{r}) + \frac{2\pi q}{A_0}$$
$$\times \begin{bmatrix} \Lambda + z, & z \leqslant -L_z/2, \\ -[z^2 - L_z\Lambda + (L_z/2)^2]/L_z, & -L_z/2 \leqslant z \leqslant L_z/2, \\ \Lambda - z, & z \geqslant L_z/2, \end{bmatrix}$$
$$\tag{20}$$

where $\tilde{V}$ is the potential taken from the supercell calculation with the background, and q is the uncompensated charge per simulation cell, which is positive if electrons are in excess. Note that $\tilde{V}(\bar{r})=0$ if $|z|>L_z/2$.

As an example, we plot in Fig. 5 the self-consistent xy-averaged electronic density and effective potential (before and after the correction) for the Pt(110) unreconstructed sur-

J. Chem. Phys., Vol. 115, No. 4, 22 July 2001

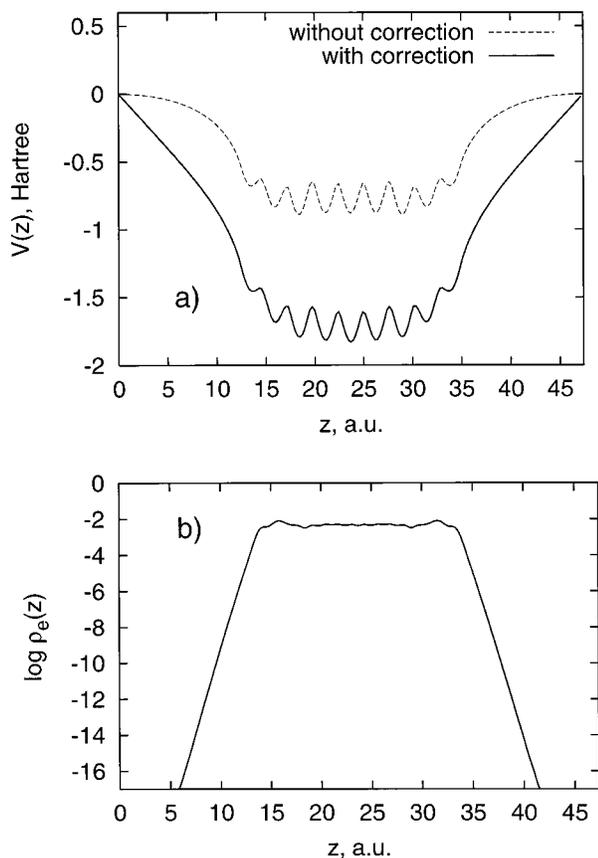Simulation of charged slabs   1667

FIG. 5. Pt(110) unreconstructed surface: (a) the effective potential before (dashed line) and after applying the background correction (solid line); and (b) electronic density, obtained as a result of the self-consistent DFT calculations and averaged in the xy directions (note the logarithmic scale for the density). The slab is charged positively and contains 159 valence electrons instead of 160 per 16-atom unit cell, which corresponds to the surface charge σ as large as $-0.25\bar{e}$ per surface atom, or $-0.023\bar{e}/\text{Å}^2$. The boundary condition for the charged slab potential is chosen to be zero at the supercell boundary ($\Lambda = L_z/2$). The linear behavior of the potential far from the charged slab is what one expects in the absence of any distributed charge.

face. The calculations are done for periodically repeated eight layer slabs separated with vacuum of thickness equal to ten interlayer spacings of the bulk platinum. The slab is positively charged (1 electron out of 160 valence electrons per unit cell is missing, i.e., $q=-1$), which corresponds to surface charge $\sigma=-0.25\bar{e}$ per surface atom, or $-0.023\bar{e}/\text{Å}^2$. This is actually a rather large charge. We have chosen such a plot to demonstrate that the corrected potential becomes linear in the region where the electronic density is negligible.

Another feature visible in Fig. 5 is the small curvature of the average potential inside the slab. This is an artifact, as one does not expect any electric field inside a metal, and is a consequence of the non-self-consistent character of the correction mentioned above: the electronic response to the removal of the background charge has been neglected.

Similarly, substituting the uniform background density ρ_b and its corresponding electrostatic potential V_b, into expressions (17)–(19), and using (16), we arrive at the following alternative forms of the correction to the electrostatic energy per unit cell surface area:
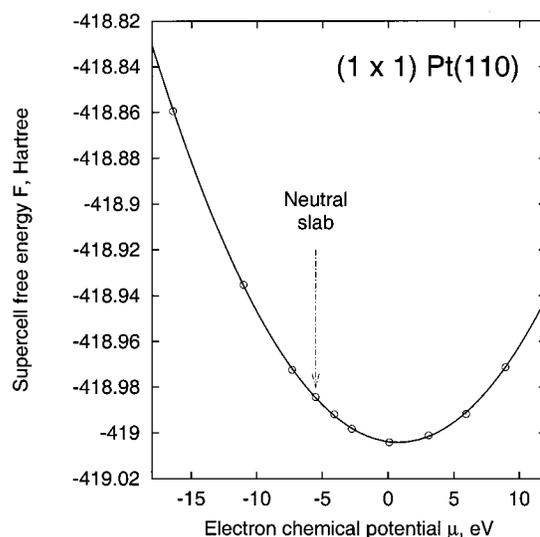

FIG. 6. Pt(110) unreconstructed surface: Helmholtz free energy F per 16-atom supercell as a function of the electron chemical potential μ after applying the background correction. The result of the self-consistent DFT calculations are shown with open circles, the solid line represents the fifth-order polynomial fit of the DFT results. Position of the neutral slab is marked with the arrow: chemical potential of the electrons in this case is the negative of the work function (5.53 eV). The boundary condition for the charged slab potential is chosen to be zero at the supercell boundary ($\Lambda = L_z/2$). The figure demonstrates that the minimum of the free energy nearly coincides with $\mu=0$.

$$E_{es} = \widetilde{E}_{es} + \frac{q}{A_0} \langle \widetilde{V} \rangle_{\Omega_0} + \frac{\pi q^2}{A_0^2} \left(\Lambda - \frac{L_z}{3} \right), \qquad (21)$$

$$E_{es} = \widetilde{E}_{es} - \frac{2\pi}{\Omega_0} \frac{q}{A_0} \widetilde{\rho}_{2z} + \frac{\pi q^2}{A_0^2} \left(\Lambda - \frac{L_z}{3} \right), \qquad (22)$$

where $\langle \widetilde{V} \rangle_{\Omega_0}$ is the average electrostatic potential obtained in the supercell calculation,

$$\langle \widetilde{V} \rangle_{\Omega_0} = \frac{1}{\Omega_0} \int_{\Omega_0} \widetilde{V}(\bar{r}) \, d^3r, \qquad (23)$$

and $\widetilde{\rho}_{2z}$ is the second moment of density $\widetilde{\rho}$ in the z direction:

$$\widetilde{\rho}_{2z} = \int_{\Omega_0} z^2 \widetilde{\rho}(\bar{r}) \, d^3r. \qquad (24)$$

Both equations express the necessary correction in terms of tilde quantities which are the output of the supercell calculation of the slab with the background. Equation (22) seems more convenient for a theoretical analysis of the formula, whereas Eq. (21) is better for practical calculations.

As a test of internal consistency of the above correction, we plot in Fig. 6 the Helmholtz free energy of the slab representing the (1×1) unreconstructed Pt(110) surface as a function of the chemical potential of electrons. The $F(\mu)$ curve reaches the minimum very close the $\mu=0$ point: this agrees with the following general thermodynamic relation:

$$\left(\frac{\partial F}{\partial \mu} \right)_{V,T,V_{ext}} = \left(\frac{\partial F}{\partial N_e} \right)_{V,T,V_{ext}} \times \left(\frac{\partial N_e}{\partial \mu} \right)_{V,T,V_{ext}} = \mu \left(\frac{\partial N_e}{\partial \mu} \right)_{V,T,V_{ext}},$$

where the partial derivatives are calculated at constant temperature T, volume V, and external potential V_{ext} (i.e., the ionic positions are fixed).

The removal of the background charge also implies corrections to the *forces* acting on the ions. In case of the uniform background, the z-component of the force which ion i experiences should be corrected as

$$F_z^i = \widetilde{F}_z^i + \frac{4\pi q}{\Omega_0} Q^i z^i, \tag{25}$$

where Q^i and z^i are the charge of the ion (expressed in units of electron charge e, i.e., $Q^i < 0$) and its z-coordinate. The correction vanishes with increasing the cell size as L_z^{-1}. For comparison, the corresponding correction in the case of localized charged defects in a cubic supercell given in Ref. 36 should decay as L^{-3}, where L is the cube size. However, this formula must be used with caution, as the (opposite) polarization of the electronic cloud due to the background may partly cancel the correction (25).

V. REAL ELECTRODES

As we have shown above, the "$\mu = $ const" mode of calculation becomes necessary if electrons are maintained at a constant chemical potential, which is the case in most experiments. However, if the experimental conditions are such that the change of the electric field near the surface (i.e., the surface charge), due to possible changes in the surface, is negligible, the "$N_e = $ const" mode is still a good approximation. The distinction between "$\mu = $ const" and "$N_e = $ const" disappears as Λ tends to infinity, but can be important otherwise.

Perhaps, one of the most important areas in which the "$\mu = $ const" mode is relevant is electrochemistry. Although the distance between the charged electrodes is macroscopic, the electric field is confined to a small distance away from the electrode (within the so-called double layer) due to the screening of the electrode charge by ions dissolved in the electrolyte. In this case, one can choose Λ as a typical screening length in a particular electrolyte, which depends on the electrolyte composition.[40] Therefore, it becomes very easy to model the dependence of some surface effect on the electrolyte concentration by tuning the effective screening length Λ (see Ref. 41 for a recent review of models of the double layer).

The final comment is on the perturbation of the electron density by the removal of the neutralizing charge. This is the main limitation of the scheme described here, especially for a uniform background charge, because it restricts the magnitude of the surface charge which is meaningful to consider. Fortunately, even for the uniform background case, the effect is not very large because $dV_b(z)/dz = 0$ in the center of the slab; it becomes increasingly steeper near the cell boundaries, i.e., in the vacuum. Therefore, one can afford to consider higher fields for pure slabs than for slabs with adsorbed molecules, as the latter are in regions where there is a larger correction to the field. Introducing the compensating charge in such a way that it does not overlap with the charge density of the slab and adsorbed molecules seems to be a better solution to the problem. Then, no additional electric field acts on the electrons of the slab. For example, charged plates were placed in the vacuum region in Refs. 8, 9, and 12. In cases when this is not possible (for example, if the space between the electrodes is filled with ions and water), the use of a uniform background charge with the approximate correction described here may be a better option.

However, in some special situations (especially in the electrochemical environment), where the screening occurs in the immediate vicinity of the charged surface, it might be useful to model the screening effect by an explicit distribution of background charge, or even to optimize its shape. The scheme considered in the current article is perfectly suitable for that purpose.

VI. CONCLUSIONS

(1) Alternative configurations of a system (such as different surface reconstructions) can be compared either at the same charge or at the same electron chemical potential. The second case corresponds to an experiment in which the system is maintained at constant potential drop relative to the reference electrode. The relevant thermodynamic potential in this case is the grand potential Ω rather than the free energy F.

(2) In practical terms, the difference becomes important if the distance corresponding to the potential drop is microscopic, which is true in the case of electrochemical phenomena. This distance, therefore, enters into the definition of the electron chemical potential μ.

(3) The approach presented here allows for performing calculations in the "constant μ" mode, without abandoning the standard *ab initio* supercell schemes. The physical quantities are thus obtained with no additional computational effort, as compared to the "constant N_e" mode.

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[21] Strictly speaking, the "μ=const" mode corresponds to the semi-grand canonical ensemble (the grand canonical ensemble with respect to electrons, and the canonical ensemble with respect to nuclei), i.e., the number of nuclei (ions) in the system is fixed. That coincides with the standard DFT definition of the electron chemical potential μ as the partial derivative of the total energy with respect to the number of electrons *at fixed external potential*; the latter is the Coulomb potential due to nuclei (ions).

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[23] The only exception which we are aware of is the work by Bohnen and Kolb (Ref. 9) in which the authors, studying the reconstruction of the Au(100) surface in an electrochemical environment, calculated first the total energy curves in the "N_e=const" mode and then compared the energies at the same voltage rather than at the same charge, using the experimentally obtained capacitance of the double layer as a function of the applied voltage.

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[25] The work function is the energy required to remove an electron from an infinite slab of definite orientation and put it at "infinity." An apparent paradox arises if we do not consider the infinite nature of the slab, for it appears that we can remove an electron from one face, and pay an energy ϕ, and insert it through a different face, and gain an energy ϕ'. In other words, it would appear that we could extract useful work of magnitude $\phi' - \phi$ from the system by undergoing a cyclic process. The resolution of this paradox is that, in performing this cyclic process, we implicitly assume a finite slab in which a common V_∞ must be assumed for both faces. In this sense, the chemical potential (the energy required to remove an electron and put it at this common infinity) becomes a true bulk quantity, independent of the face exposed.

[26] The property that the work function can be effectively separated into the bulk and surface contributions can even be used in practice in *ab initio* calculations to improve the convergence of the work function with respect to the slab thickness [C. J. Fall, N. Binggeli, and A. Baldereschi, J. Phys.: Condens. Matter **11**, 2689 (1999)].

[27] A note on the terminology should be added here. Speaking about the Helmholtz free energy F, we imply the free energy with respect to the electronic subsystem, characterized by a certain electron temperature T_e (denoted in the paper with T), whereas the ionic positions are perhaps somehow optimized and then fixed, which means that we refer to the zero ionic temperature, and thus the Helmholtz free energy is in fact the free energy for the electronic subsystem, but just the total energy for the ionic subsystem. Similarly, the grand potential Ω is again the grand potential with respect to electrons, but the total energy with respect to ions (Ref. 28). Such a "mixed" description of the system is possible in the Born–Oppenheimer approximation because of a separation of time scales between nuclear and electronic degrees of freedom. We can exploit the separation to compute the Helmholtz free energy for the electrons as a function of nuclear positions for given number of electrons N_e and electronic temperature T_e, or to compute the grand potential Ω for the electrons as a function of T_e and the chemical potential of electrons μ at again fixed arbitrary positions of nuclei.

[28] We use hereafter the term *ions* to denote the ionic cores, i.e., the nucleus plus core electrons. This terminology is common in *ab initio* pseudopotential calculations, where the core electrons are integrated into the ionic core, and thus not considered explicitly. It should not be confused with the *real ions*, i.e., *anions or cations*, present in electrolytic solutions, e.g., $SO_4^=$.

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