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Multilayer lattice relaxation at metal surfaces: A total-energy minimization

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Relaxation at simple metal surfaces is studied via minimization of the total energy of a semi-infinite crystal. The expression for the total energy depends explicitly on the ionic positions, and is based on the use of pseudopotential theory and linear response. Electron screening is treated self-consistently including exchange and correlation effects. From a systematic investigation of the energetics underlying metal surface relaxation, for the low-index surfaces of bcc Na and fcc Al it is concluded that to achieve quantitative surface structural predictions requires the use of the full total-energy expression for the semi-infinite solid. Such an expression must maintain the three-dimensional nature of the system and account properly for the inhomogeneous surface electron density and the self-consistent response of the electron system to the ionic positions (screening). Multilayer relaxation is shown to be essential for quantitative structural predictions and the origins of the phenomena are discussed in detail demonstrating the relative effects of electrostatic terms and band-structure contributions. The results exhibit damped oscillatory multilayer relaxations (the relaxation being particularly pronounced for the open faces) with a period equal to the bulk layer stacking period and agree well with available structural determinations obtained via the analysis of experimental data.

I. INTRODUCTION

Knowledge of the surface crystallographic structure of metals, i.e., the location of atoms at the surface and in the near-surface region, is of fundamental importance for investigation and elucidation of various metal surface properties and surface phenomena. This problem is of particular interest since the surface structure of metals is expected, and indeed is observed,[1-5] to deviate (both relaxation and reconstruction) from the truncated bulk atomic arrangement due to changes in atomic coordination and electron distribution in the surface region. Consequently, major efforts have been devoted in recent years to the development of experimental probes, and associated theoretical analysis and data-reduction methods, for the determination of structures of clean surfaces and in the presence of adsorbed species [e.g., low-energy electron diffraction (LEED),[1(a),1(b)] ion scattering,[1(c)] surface extended x-ray absorption fine structure[6,7] (SEXAFS), glancing-angle x-ray scattering,[8] and stimulated-desorption ion angular distributions[9] (SDIAD), to name a few]. However, the interpretation of these experiments involves analysis models which, in addition to the structural variables, contain a host of nonstructural parameters (inner potential, energy-dependent projectile mean free path, scattering phase shifts, dynamical response functions, vibrational mean-square amplitudes, vibrational correlations, etc.). The optimization of the fit between the data and the corresponding analysis model requires variation of both the structural and nonstructural parameters (which may be interrelated). In addition, the analysis is often complex and time consuming due to the wide range of possible values for the structural parameters, often hindering an exhaustive search except for certain simple systems. Thus it is both timely and important to develop surface structure theories of *predictive* capability to guide data analysis. Moreover, such theories (and their interplay with experiments) provide a fundamental understanding of the microscopic origins of the structure.

The development of such structure-predictive theories, however, is hindered by difficulties in carrying out a self-consistent energy minimization for the coupled system of ions and conduction electrons. Semiempirical methods, based on lattice static calculations with pair potentials derived semiempirically or using bulk pseudopotential pairwise interaction, are known often to yield results which contradict experiments, and their inadequacy has been discussed elsewhere.[10] These observations have led recently[10] to the development of a simple electrostatic model in which structural minimization of the total energy of a semi-infinite metal predicted, semiquantitatively, multilayer surface relaxation in both fcc and bcc materials, dependent upon surface crystallographic orientation and other material parameters. The existence of multilayer relaxation phenomena has since been verified by several careful examinations of LEED and ion scattering experiments for several systems [e.g., Al(110),[2] Cu(110),[3] V(100),[4] Re($01\bar{1}1$)[5]]. Nevertheless, the electrostatic model,[10] while containing certain essential ingredients (i.e., contributions to the force on ions in the surface layers due to the delocalized, inhomogeneous, valence-electron distribution and due to the electrostatic interaction between ions), did not allow for self-consistency of the combined electron-ion system. It is therefore a "frozen profile" model in which the electronic response to variations in ionic positions is not included. The objective of the present study is to alleviate this problem by formulating and implementing a theory which allows for a self-consistent structure determination.[11] In the course of development of the theory we also provide a systematic and critical analysis of the various contributions to the energetics of surface relaxation. The theoretical model is described in Sec. II and draws upon, when necessary, the detailed discussion of the electron response model given in the preceeding paper[12] (which will be referred to as Paper I). The relaxation algorithm is described in Sec. III. Analysis of various models and sample results for the low-index faces of fcc and bcc materials (Al and Na) and comparisons to other studies and to experimental results are discussed in Sec. IV.

II. THEORETICAL MODEL

A prerequisite for a self-consistent energy minimization structure determination scheme is an expression for the total energy of the system, which depends explicitly on the ionic positions. In this study we consider surface normal relaxation, i.e., changes in layer spacings (no reconstruction, i.e., lateral, intraplane structural modifications are considered). Thus the position vector of the ith ion in layer n is given by

$$\vec{r}_{n,i} \equiv (\vec{R}_i + \Delta\vec{R}_n, z_n^\lambda) , \tag{1a}$$

where

$$z_n^\lambda = z_0 + (n - \tfrac{1}{2} + \lambda_n)d, \quad n = 1,2,\ldots . \tag{1b}$$

$\vec{R}_i$ is a two-dimensional (2D) vector in the surface plane ($\vec{R}_i = l_i\vec{a}_1 + m_i\vec{a}_2$, where $\vec{a}_1$ and $\vec{a}_2$ are the primitive translation vector of the 2D mesh) and $\Delta\vec{R}_n$ specifies the origin of the 2D mesh of layer n,

$$\Delta\vec{R}_n = [n \pmod{n_R}]\Delta\vec{R} , \tag{1c}$$

where n_R is the repeat period of the layer stacking sequence and $\Delta\vec{R}$ is the registry shift between adjacent layers (see Table I). The bulk layer spacing is denoted by d and $\lambda_n d$ is the deviation of the z coordinate of the nth layer from its truncated bulk position (the superscript λ on z_n^λ serves to emphasize this dependence on λ_n). The constant z_0 specifies the position of the "jellium edge" (our choice of $z_0 = 3\pi/8k_F$, where $\hbar k_F$ is the Fermi momentum is dictated by notational convenience in discussing the electron response; see also Paper I).

We begin by writing the Hamiltonian for the conduction electrons in the presence of the ions as

$$H = H^0 + \sum_{n>0}\sum_i w_n^\lambda(\,|\vec{R} - \vec{R}_i - \Delta\vec{R}_n\,|, z) , \tag{2}$$

where H^0 is the Hamiltonian for the interacting electrons in the presence of a neutralizing positive background charge density

$$e\rho^+(z) = e\Omega_0^{-1}\Theta(z - z_0) ,$$

with $\Omega_0 = 4\pi r_s^3/3$ (i.e., the volume per conduction electron in the bulk metal) and $\Theta(z)$ is the Heaviside step function. The ground-state electronic energy and density of the "jellium" model Hamiltonian[13] are E^0 and $\rho^0(z)$, respectively. The second term in Eq. (2) is the potential associated with the replacement of the neutralizing positive background with discrete ions represented by ionic pseudopotentials

$$w_n^\lambda(R,z) = V_p(R, z - z_n^\lambda) - \frac{1}{N_A\Omega_0}\int_{z_n^-}^{z_n^+} d^2R' \int dz' V_C(\,|\vec{R} - \vec{R}'\,|, z - z') , \tag{3}$$

where $z_n^\pm = z_0 + (n - \frac{1}{2})d \pm \frac{1}{2}d$, N_A is the number of ions in a layer ($N_A \to \infty$), V_c is the Coulomb potential

$$V_C(R,z) = -e^2/(R^2 + z^2)^{1/2} , \tag{4}$$

and $V_p(R,z)$ is the ionic pseudopotential. In our calculations we use the local form of the Heine-Abarenkov model pseudopotential,

TABLE I. Input parameters: r_s is the electron density parameter, Z is the valence, r_c and u_c are the pseudopotential core radius and level parameters, a is the lattice constant, A_0 and d are the 2D unit-cell area and bulk interlayer distance, $\vec{b}_1$ and $\vec{b}_2$ are the 2D reciprocal-lattice primitive translation vectors, n_R is the repeat period of the layer stacking sequence, and $\Delta\vec{R}$ is the shift in the origin of the 2D lattice of adjacent layers. For fcc Al, we have $r_s = 2.064a_0$, $Z = 3$, $r_c = 1.388a_0$, $u_c = 0.3894$, and $a = (16\pi Z/3)^{1/3}r_s$. For bcc Na, we have $r_s = 3.931a_0$, $Z = 1$, $r_c = 2.076a_0$, $u_c = 0.3079$, and $a = (8\pi Z/3)^{1/3}r_s$.

Metal	Surface	A_0	d	$\vec{b}_1$	$\vec{b}_2$	n_R	$\Delta\vec{R}$
fcc Al	(001)	$\frac{a^2}{2}$	$\frac{a}{2}$	$\frac{2\pi}{a}(\bar{1}\bar{1}0)$	$\frac{2\pi}{a}(\bar{1}10)$	2	$\frac{a}{2}(100)$
	(110)	$\frac{a^2}{\sqrt{2}}$	$\frac{a}{2\sqrt{2}}$	$\frac{2\pi}{a}(001)$	$\frac{2\pi}{a}(1\bar{1}0)$	2	$\frac{a}{4}(1\bar{1}2)$
	(111)	$\frac{\sqrt{3}a^2}{4}$	$\frac{a}{\sqrt{3}}$	$\frac{4\pi}{3a}(\bar{1}2\bar{1})$	$\frac{4\pi}{3a}(\bar{1}\bar{1}2)$	3	$\frac{a}{6}(\bar{2}11)$
bcc Na	(001)	a^2	$\frac{a}{2}$	$\frac{2\pi}{a}(100)$	$\frac{2\pi}{a}(010)$	2	$\frac{a}{2}(110)$
	(110)	$\frac{a^2}{\sqrt{2}}$	$\frac{a}{\sqrt{2}}$	$\frac{\pi}{a}(\bar{1}10)$	$\frac{2\pi}{a}(1\bar{1}0)$	2	$\frac{a}{2}(001)$
	(111)	$\sqrt{3}a^2$	$\frac{a}{2\sqrt{3}}$	$\frac{2\pi}{a}(\bar{1}2\bar{1})$	$\frac{2\pi}{a}(\bar{1}\bar{1}2)$	3	$\frac{a}{3}(\bar{2}11)$

$$V_p(R,z)=\begin{cases}ZV_C(R,z), & R^2+z^2>r_c^2\\ -Ze^2u_c/r_c, & R^2+z^2\le r_c^2\,.\end{cases} \tag{5}$$

where Z is the valence of the ion and r_c,u_c are the pseudopotential parameters (chosen[14] to fit physical bulk properties such as lattice constant, bulk modulus, phonon spectrum, etc.).

The total energy E_T per 2D unit cell, obtained via the coupling-constant integration method (see Paper I) can be written as

$$\begin{aligned}E_T(\lambda_1,\lambda_2,\ldots)=&E^0/N_A+\int d^2R\int dz\,\rho^0(z)\sum_{n>0}w_n^\lambda(R,z)\\&+\tfrac{1}{2}\int d^2R\int dz\sum_{n>0}\rho_n^\lambda(R,z)\sum_{m>0}\sum_j w_m^\lambda(|\vec{\mathrm{R}}-\vec{\mathrm{R}}_j+\Delta\vec{\mathrm{R}}_{n-m}|,z)\\&+\tfrac{1}{2}\sum_{n>0}\sum_{m>0}\sum_j{}'[-Z^2V_C(|\vec{\mathrm{R}}_j-\Delta\vec{\mathrm{R}}_{n-m}|,z_n^\lambda-z_m^\lambda)]\,,\end{aligned}\tag{6}$$

where $\rho_n^\lambda(R,z)$ is the induced (screening) electron density due to the potential $w_n^\lambda(R,z)$. The last term in Eq. (6) is the Coulomb interaction energy between the ions (the primed sum over j omits the term with $\vec{\mathrm{R}}_j=0$ when $n=m$). The induced electron density ρ_n^λ is taken to be linearly related to the potential w_n^λ, as expressed by the coupled integral equations

$$\begin{aligned}\rho_n^\lambda(R,z)&=\int d^2R'\int dz'\alpha_0(|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|;z,z')[w_n^\lambda(R',z')+\phi_n^\lambda(R',z')]\,,\\\phi_n^\lambda(R,z)&=\int d^2R'\int dz'g(|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|;z,z')\rho_n^\lambda(R',z')V_C(|\vec{\mathrm{R}}-\vec{\mathrm{R}}'|,z-z')\,.\end{aligned}\tag{7}$$

In our calculation we use the infinite barrier response model developed in Paper I, i.e., α_0 is the random-phase-approximation (RPA) response function for electrons confined to the half-space $z\ge0$. Exchange and correlation contributions are included through the function g (see Paper I, Sec. II B).

Using the expression for w_n^λ given in Eq. (3) we rewrite the total energy as

$$\begin{aligned}E_T(\lambda_1,\lambda_2,\ldots)=&\left[E^0/N_A-A_0\int dz\,\rho^0(z)\int dz'\rho^+(z')\int d^2R\;V_C(R,z-z')\right]\\&+\sum_{n>0}\left[\tfrac{1}{2}\sum_{m>0}\sum_j{}'[-Z^2V_C(|\vec{\mathrm{R}}_j-\Delta\vec{\mathrm{R}}_{n-m}|,z_n^\lambda-z_m^\lambda)]+\int dz\,\rho^+(z)\int d^2R\;ZV_C(R,z-z_n^\lambda)\right]\\&+\sum_{n>0}\int dz[\rho^0(z)-\rho^+(z)]\int d^2R\;ZV_C(R,z-z_n^\lambda)\\&+\sum_{n>0}\int dz\,\rho^0(z)\int d^2R[V_p(R,z-z_n^\lambda)-ZV_C(R,z-z_n^\lambda)]\\&+\tfrac{1}{2}\sum_{n>0}\sum_{m>0}\sum_j\int d^2R\int dz\,\rho_n^\lambda(R,z)w_m^\lambda(|\vec{\mathrm{R}}-\vec{\mathrm{R}}_j+\Delta\vec{\mathrm{R}}_{n-m}|,z)\\=&E_0'+E_M\{\lambda\}+E_{\mathrm{DL}}\{\lambda\}+E_H\{\lambda\}+E_{\mathrm{BS}}\{\lambda\}\,.\end{aligned}\tag{8}$$

The term denoted as E_0' in Eq. (8), which does not depend on ionic positions, consists of the ground-state energy of the jellium system,[13] from which the electrostatic energy of the interaction of the ground-state electron density ρ^0 with the positive background ρ^+ has been subtracted. The second term, $E_M\{\lambda\}$, is the Madelung energy, i.e., the electrostatic energy of positive point ions in the presence of a neutralizing negative background. The third term, $E_{\mathrm{DL}}\{\lambda\}$, is the interaction of point ions with the difference $\rho^0(z)-\rho^+(z)$ between the jellium ground-state electron density and the step-truncated uniform bulk density. This term will be called the "dipole layer" (DL) energy. The fourth term, $E_H\{\lambda\}$, is the Hartree contribution, i.e., the difference between the interactions of the jellium electron density ρ^0 with ionic pseudopotentials V_p, and with point ions. The combined contributions from E_{DL} and E_H constitute the first-order correction to the total energy due to the replacement of the positive background by a lattice of ions represented by pseudopotentials. The second-order correction to the total energy, $E_{\mathrm{BS}}\{\lambda\}$, is the last term in Eq. (8) and is referred to as the band-structure (BS) energy. Note that while E_{DL} and E_H depend only on the positions of individual layers with no dependence on intralayer structure, E_M and E_{BS} depend on the relative positions of layers and their registry and on intralayer structure. In the band-structure energy E_{BS}, these dependencies are due to the interaction of the induced electron density associated with the pseudopotential at a given lattice site with the pseudopotentials located at other sites. In addition, E_{BS} contains contributions from the electron density associated with a given site interacting with the ionic pseudopotential located at that site. Owing to the symmetry breaking in the surface normal direction, in the surface region these on-site interactions depend on the z coordinate of the site, and approach a constant value away from the surface. In addition, the intersite contributions to $E_{\rm BS}$ depend separately on the z coordinates of the ion pairs. Thus, unlike in the bulk, $E_M+E_{\rm BS}$ cannot be written as a sum over pair potentials depending only on the relative positions of pairs of ions (see Paper I).

To find the equilibrium configuration the total energy $E_T(\lambda_1,\lambda_2,\ldots)$ is minimized with respect to the layer relaxation parameters $\{\lambda_n\}$. We assume that in the relaxed configuration bulk arrangement is maintained beyond a certain number of layers n_s (i.e., $\lambda_n=0$ for $n>n_s$). The number of layers allowed to relax, n_s, is determined via investigation of convergence of the results versus n_s. The minimization conditions are

$$F(l)=0 \text{ for } l=1,2,\ldots,n_s \tag{9a}$$

and

$$\sum_{m=1}^{n_s}\Phi(l,m)\delta\lambda_m>0 \text{ for } l=1,2,\ldots,n_s\ , \tag{9b}$$

where $\{\delta\lambda_m\}$ are small but otherwise arbitrary and the force $F(l)$ is obtained from $E_T(\lambda_1,\lambda_2,\ldots)$ via

$$F(l)=-\frac{\partial E_T}{\partial\lambda_l}\equiv F_M(l)+F_{\rm DL}(l)+F_H(l)+F_{\rm BS}(l) \tag{9c}$$

and

$$\Phi(l,m)=\frac{\partial^2E_T}{\partial\lambda_l\partial\lambda_m}\equiv\Phi_M(l,m)+\Phi_{\rm DL}(l,m)+\Phi_H(l,m)+\Phi_{\rm BS}(l,m)\ , \tag{9d}$$

where the subscripts on the F's and Φ's specify the contributions obtained from the corresponding terms in the total-energy expression, Eq. (8).

Prior to a discussion of the relaxation algorithm we discuss in the following the evaluation of the various terms in Eqs. (8) and (9). Those readers who are not interested in such details should skip to Secs. III and IV.

A. Madelung energy E_M

With the use of the identities

$$(R^2+z^2)^{-1/2}=\frac{1}{2\pi}\int d^2K\frac{e^{-K|z|}}{K}e^{i\vec{K}\cdot\vec{R}}\ , \tag{10}$$

where $\vec{K}$ is a 2D reciprocal-space vector, and

$$\sum_i e^{i\vec{K}\cdot\vec{R}_i}=\frac{(2\pi)^2}{A_0}\sum_{\vec{G}}\delta(\vec{K}-\vec{G})\ , \tag{11}$$

where A_0 is the 2D unit-cell area and $\vec{G}$ is a 2D reciprocal-lattice vector:

$$\vec{G}=l\vec{b}_1+m\vec{b}_2\ ,$$

where $\vec{b}_1$ and $\vec{b}_2$ are the primitive translation vectors of the 2D reciprocal mesh, the Madelung energy E_M can be written as

$$\begin{aligned}E_M={}&(Ze)^2\frac{2\pi}{A_0}\sum_{\vec{G}}{}'\tfrac{1}{2}\sum_{n,m>0}(e^{i\vec{G}\cdot\Delta\vec{R}})^{n-m}\frac{e^{-G|z_n^\lambda-z_m^\lambda|}}{G}\\&+(Ze)^2\frac{1}{2\pi}\int d^2K\frac{(2\pi)^2}{A_0}\delta(\vec{K})\sum_{n,m>0}\left[\frac{e^{-K|z_n^\lambda-z_m^\lambda|}}{K}-\frac{2}{d}\int_{z_m^-}^{z_m^+}dz'\frac{e^{-K|z_n^\lambda-z'|}}{K}\right]-(Ze)^2\frac{1}{2\pi}\int d^2K\tfrac{1}{2}\sum_{n>0}K^{-1}\ ,\end{aligned} \tag{12}$$

where the prime on the sum over $\vec{G}$ omits $\vec{G}=\vec{0}$. Using Eq. (12) in the definitions (9c) and (9d) we obtain (for details see Ref. 10)

$$\begin{aligned}F_M(l)=(Ze)^2\frac{2\pi}{A_0}d\Bigg[&-2\lambda_l+\sum_{n=1}^{n_s}(1-\delta_{l,n})\sum_{\vec{G}}{}'(e^{i\vec{G}\cdot\Delta\vec{R}})^{l-n}\operatorname{sgn}(l-n)\exp(-Gd\,|\,l+\lambda_l-n-\lambda_n\,|\,)\\&-\sum_{\vec{G}}{}'\exp[Gd(l+\lambda_l-n_s)](1-e^{-n_RGd})^{-1}\sum_{m=1}^{n_R}(e^{i\vec{G}\cdot\Delta\vec{R}})^{l-m-n_s}e^{-Gdm}\Bigg]\end{aligned} \tag{13}$$

and

$$\begin{aligned}\Phi_M(l,m)=(Ze)^2\frac{2\pi}{A_0}\Bigg[&(\delta_{l,m}-1)\sum_{\vec{G}}{}'(e^{i\vec{G}\cdot\Delta\vec{R}})^{l-m}Gd\exp(-Gd\,|\,l+\lambda_l-m-\lambda_m\,|\,)\\&+\delta_{l,m}\Bigg[2+\sum_{\vec{G}}{}'Gd\exp[Gd(l+\lambda_l-n_s)](1-e^{n_RGd})^{-1}\sum_{m=1}^{n_R}(e^{i\vec{G}\cdot\Delta\vec{R}})^{l-n_s-m}e^{-Gdm}\\&+\sum_{\vec{G}}{}'\sum_{n=1}^{n_s}(1-\delta_{n,l})(e^{i\vec{G}\cdot\Delta\vec{R}})^{l-n}Gd\exp(-Gd\,|\,l+\lambda_l-n-\lambda_n\,|\,)\Bigg]\Bigg]\ .\end{aligned} \tag{14}$$

B. Dipole layer energy $E_{\rm DL}$

Substituting the expression for $E_{\rm DL}$ [third term in Eq. (8)] in the definitions (9c) and (9d) we obtain

$$F_{\rm DL}(l)=2\pi Ze^2 d\int dz[\rho^0(z)-\rho^+(z)]{\rm sgn}(z-z_l^\lambda) \tag{15}$$

and

$$\Phi_{\rm DL}(l,m)=4\pi Ze^2 d^2\delta_{l,m}[\rho^0(z_l^\lambda)-\rho^+(z_l^\lambda)]\ , \tag{16}$$

where $\rho^0(z)$ is taken from the calculations of Lang and Kohn[13] (three-point Lagrange interpolation is used to obtain ρ^0 for the appropriate value of r_s) and the integration is performed numerically.

C. Hartree energy E_H

Substituting Eqs. (4) and (5) for V_c and V_p in the fourth term in Eq. (8) and performing the d^2R integration yields

$$E_H=-2\pi Ze^2\sum_{n>0}\int_{z_n^\lambda-r_c}^{z_n^\lambda+r_c}dz\,\rho^0(z)\left[\frac{u_c}{2r_c}[r_c^2-(z-z_n^\lambda)^2]-r_c+|z-z_n^\lambda|\right]\ , \tag{17}$$

which, when used in Eqs. (9c) and (9d), yields

$$F_H(l)=2\pi Ze^2 d\int_{z_l^\lambda-r_c}^{z_l^\lambda+r_c}dz\,\rho^0(z)\left[\frac{u_c}{r_c}(z-z_l^\lambda)-{\rm sgn}(z-z_l^\lambda)\right]\ , \tag{18}$$

$$\Phi_H(l,m)=-2\pi Ze^2 d^2\delta_{l,m}\left[2\rho^0(z_l^\lambda)+(u_c-1)[\rho^0(z_l^\lambda+r_c)+\rho^0(z_l^\lambda-r_c)]-\frac{u_c}{r_c}\int_{z_l-r_c}^{z_l^\lambda+r_c}dz\,\rho^0(z)\right]\ . \tag{19}$$

D. Band-structure energy $E_{\rm BS}$

Evaluation of the band-structure energy requires a self-consistent solution for the induced electron density ρ_n^λ [see Eqs. (7)]. In the response model developed in Paper I

$$\rho_n^\lambda(r,z)=0 \text{ for } z<0\ . \tag{20}$$

Thus we can specify symmetrized quantities

$$w_{ns}^\lambda(R,z)=w_n^\lambda(R,|z|) \text{ and } \rho_{ns}^\lambda(R,z)=\rho_n^\lambda(R,|z|) \tag{21}$$

and their three-dimensional (3D) Fourier transforms $w_{ns}^\lambda(Q,q_z)$, $\rho_{ns}^\lambda(Q,q_z)$, where $\vec{q}=(\vec{Q},q_z)$ is a 3D reciprocal-space vector and $\vec{Q}$ is a 2D vector in the surface plane. $\rho_{ns}^\lambda(Q,q_z)$ is obtained as a function of q_z for specified Q, n, and λ_n as the solution of a single one-dimensional integral equation, as discussed in detail in Paper I. This symmetrization allows us to evaluate $E_{\rm BS}$ entirely in reciprocal space. We obtain

$$E_{\rm BS}=\frac{1}{4A_0}\sum_{n,m>0}\sum_{\vec{G}}(e^{i\vec{G}\cdot\Delta\vec{R}})^{n-m}\frac{1}{2\pi}\times\int dq_z\rho_{ns}^\lambda(G,q_z)w_{ms}^\lambda(G,q_z)\ . \tag{22}$$

Since the sums over layers converge slowly as $|n-m|$ increases, we define an unrelaxed sublattice potential

$$W_{ms}(G,q_z)=\widetilde{\sum_{n(m)}}w_{ns}(G,q_z),\quad m=1,2,\ldots,n_R \tag{23a}$$

and the corresponding induced electron density

$$P_{ms}(G,q_z)=\widetilde{\sum_{n(m)}}\rho_{ns}(G,q_z),\quad m=1,2,\ldots,n_R \tag{23b}$$

where $\widetilde{\sum}_{n(m)}$ means summations over the sequence $n=m$, $m+n_R$, $m+2n_R,\ldots,$ where n_R is the layer stacking sequence period. We denote $w_{ns}^\lambda(G,q_z)$ and $\rho_{ns}^\lambda(G,q_z)$ with $\lambda_n=0$ by $w_{ns}(G,q_z)$ and $\rho_{ns}(G,q_z)$, respectively, in Eqs. (23). We also define layer difference quantities

$$\Delta w_{ns}^\lambda(G,q_z)=w_{ns}^\lambda(G,q_z)-w_{ns}(G,q_z) \tag{24a}$$

and

$$\Delta\rho_{ns}^\lambda(G,q_z)=\rho_{ns}^\lambda(G,q_z)-\rho_{ns}(G,q_z)\ . \tag{24b}$$

Since $w_{ns}(G,q_z)$ does not involve the variable λ_n, $W_{ms}(G,q_z)$ can be evaluated analytically, and $P_{ms}(G,q_z)$ and $\Delta\rho_{ns}^\lambda$ are obtained from $W_{ms}(G,q_z)$ and Δw_{ns}^λ in the same manner that ρ_{ns}^λ is obtained from w_{ns}^λ by solving the integral equation. The expressions for $w_{ns}^\lambda(G,q_z)$ and $W_{ms}(G,q_z)$ are derived in the Appendix.

Finally, using the above definitions in Eq. (22) we write the band-structure energy as

$$E_{\rm BS}=E_{\rm BS}^{(0)}+\sum_{n=1}^{n_s}\Delta E_{\rm BS}^{(1)}(n,\lambda_n)+\tfrac{1}{2}\sum_{n,m=1}^{n_s}\Delta E_{\rm BS}^{(2)}(n,\lambda_n;m,\lambda_m)\ , \tag{25}$$

where

$$E^{(0)}_{\mathrm{BS}}=\frac{1}{4A_0}\sum_{\vec{\mathrm{G}}}\sum_{n,m=1}^{n_R}(e^{i\vec{\mathrm{G}}\cdot\Delta\vec{\mathrm{R}}})^{n-m}\frac{1}{2\pi}\int dq_z W_{ms}(G,q_z)P_{ns}(G,q_z)\ , \tag{26a}$$

$$\Delta E^{(1)}_{\mathrm{BS}}(n,\lambda_n)=\frac{1}{4A_0}\sum_{\vec{\mathrm{G}}}\sum_{m=1}^{n_R}(e^{i\vec{\mathrm{G}}\cdot\Delta\vec{\mathrm{R}}})^{n-m}\frac{1}{2\pi}\int dq_z[W_{ms}(G,q_z)\Delta\rho^{\lambda}_{ns}(G,q_z)+\Delta w^{\lambda}_{ns}(G,q_z)P_{ms}(G,q_z)]\ , \tag{26b}$$

$$\Delta E^{(2)}_{\mathrm{BS}}(n,\lambda_n;m,\lambda_m)=\frac{1}{4A_0}\sum_{\vec{\mathrm{G}}}(e^{i\vec{\mathrm{G}}\cdot\Delta\vec{\mathrm{R}}})^{n-m}\frac{1}{2\pi}\int dq_z[\Delta w^{\lambda}_{ms}(G,q_z)\Delta\rho^{\lambda}_{ns}(G,q_z)+\Delta w^{\lambda}_{ns}(G,q_z)\Delta\rho^{\lambda}_{ms}(G,q_z)]\ . \tag{26c}$$

Using Eqs. (25) and (26) in Eqs. (9c) and (9d) we obtain

$$F_{\mathrm{BS}}(l)=\frac{-\partial}{\partial\lambda_l}\Delta E^{(1)}_{\mathrm{BS}}(l,\lambda_l)-\sum_{n=1}^{n_s}(1-\delta_{n,l})\frac{\partial}{\partial\lambda_l}\Delta E^{(2)}_{\mathrm{BS}}(l,\lambda_l;n,\lambda_n)-\frac{1}{2}\frac{\partial}{\partial\lambda_l}\Delta E^{(2)}_{\mathrm{BS}}(l,\lambda_l;l,\lambda_l) \tag{27}$$

and

$$\Phi_{\mathrm{BS}}(l,m)=\delta_{lm}\left[\frac{\partial^2}{\partial\lambda_l^2}\Delta E^{(1)}_{\mathrm{BS}}(l,\lambda_l)+\frac{1}{2}\frac{\partial^2}{\partial\lambda_l^2}\Delta E^{(2)}_{\mathrm{BS}}(l,\lambda_l;l,\lambda_l)\right]+(1-\delta_{lm})\frac{\partial^2}{\partial\lambda_l\partial\lambda_m}\Delta E^{(2)}_{\mathrm{BS}}(l,\lambda_l;m,\lambda_m)\ . \tag{28}$$

Note that $\Delta E^{(2)}_{\mathrm{BS}}(l,\lambda_l;l,\lambda_l)$ is actually a function of only one variable, namely λ_l.

The derivatives of $\Delta E^{(1)}_{\mathrm{BS}}$ and $\Delta E^{(2)}_{\mathrm{BS}}$ are obtained numerically as follows:

(i) Evaluate these functions for judiciously chosen values of the λ's.

(ii) Fit with cubic or bicubic spline functions.

(iii) Obtain F_{BS} and Φ_{BS} by taking derivatives of the spline functions.

(iv) Relax the layers (by the algorithm described in Sec. III).

(v) Calculate the energies for additional values of λ's around the relaxed positions obtained in step (iv) [as necessary to obtain an accurate spline fit near the λ's determined in (iv)].

(vi) Repeat steps (ii)—(v) until convergence is obtained.

III. RELAXATION ALGORITHM

The conditions for total-energy minimization, with respect to the structural parameters (layer spacings for the case of normal relaxation), are given in Eqs. (9). We define the transpose of the n_s-dimensional (column) force vector as a $1\times n_s$ matrix $\underline{F}^T(\underline{\Lambda})\equiv(F(1),\ldots,F(n_s))$ and that of the relaxation parameter vector as $\underline{\Lambda}^T\equiv(\lambda_1,\ldots,\lambda_{n_s})$. The matrix elements of the energy second-derivative matrix $\underline{\Phi}(\underline{\Lambda})$ are given as $[\underline{\Phi}(\underline{\Lambda})]_{lm}=\Phi(l,m)$, where $\Phi(l,m)$ is defined in Eq. (9d). The relaxation algorithm consists of the following steps:

(i) Evaluate $\underline{F}(\underline{\Lambda}_i)$ and $\underline{\Phi}(\underline{\Lambda}_i)$ for a given value of $\underline{\Lambda}_i$.

(ii) Find the direction of steepest descent in the relaxation parameter space according to

$$\underline{Y}_i=\underline{\Phi}^{-1}(\underline{\Lambda}_i)\underline{F}(\underline{\Lambda}_i)\ . \tag{29}$$

(iii) Minimize the total energy with respect to displacements in the relaxation parameter space along the vector $\underline{\Lambda}_i+s\zeta\underline{Y}_i$, where the scalar $\zeta>0$ is found from the requirement

$$\underline{Y}_i^T\underline{F}(\underline{\Lambda}_i+s\zeta\underline{Y}_i)\simeq 0 \tag{30}$$

and $s=\mathrm{sgn}[\underline{Y}_i^T\underline{F}(\underline{\Lambda}_i)]$. This ensures that the extremum is a minimum.

(iv) Increment $\underline{\Lambda}_i$ according to $\underline{\Lambda}_{i+1}=\underline{\Lambda}_i+s\zeta\underline{Y}_i$ and repeat (i)—(iii) until $\underline{Y}_i=\underline{0}$, in Eq. (29).

IV. MODELS AND RESULTS

A. Models

In order to investigate systematically the energetics of surface relaxation and to facilitate comparison with other studies we distinguish several models which will be introduced in order of increasing complexity and realism.

(a) In the most primitive model the system consists of point ions in the presence of uniform truncated bulk electron density. This model will be referred to as the point ion, truncated bulk (PITB) model. The total energy [see Eq. (8)] of this model is given by

$$E_T^{\mathrm{PITB}}\{\lambda\}=E'_0+E_M\{\lambda\}\ . \tag{31}$$

(b) Replacing the uniform truncated bulk electron density by the ground-state electron density of the jellium system, $\rho^0(z)$, yields the dipole-layer (DL) model in which the total energy given in Eq. (31) is supplemented by the dipole-layer contribution E_{DL}:

$$E_T^{\mathrm{DL}}\{\lambda\}=E'_0+E_M\{\lambda\}+E_{\mathrm{DL}}\{\lambda\}\ . \tag{32}$$

(c) Adding the Hartree energy E_H to E_T^{DL} [Eq. (32)] constitutes the dipole-layer, Hartree (DLH) model,

$$E_T^{\mathrm{DLH}}\{\lambda\}=E'_0+E_M\{\lambda\}+E_{\mathrm{DL}}\{\lambda\}+E_H\{\lambda\}\ . \tag{33}$$

In this model the total energy is computed to first order in the ionic pseudopotentials. This model is the electrostatic model investigated previously,[10] sometimes referred to as the "frozen-profile" model, since it does not include the response of the electrons to the presence of the ions.

(d) The next level of approximation is to include the $\vec{\mathrm{G}}=0$ contribution to the band-structure energy E_{BS} [see Eq. (22)]. This is equivalent to a one-dimensional treatment of the electron response obtained by averaging the ionic potentials over the layers. We include results for this dipole-layer, Hartree, band structure, $\vec{G}=0$ (DLHBS0) model since this reduction in the dimensionality of the electron response has been employed in several previous studies.[15,16] The total energy of this model is given by

$$E_T^{\mathrm{DLHBS0}}\{\lambda\}=E_T^{\mathrm{DLH}}\{\lambda\}+E_{\mathrm{BS},\,\vec{G}=\vec{0}}\{\lambda\} \,. \tag{34}$$

(e) Finally, the model in which all contributions to second order in the ionic pseudopotentials are included is the DLHBS model. The total energy of this model is given by Eq. (8). This model retains the full three-dimensional nature of the system.

B. Results

Prior to a discussion of our results, we specify in Table I the material input parameters used in the calculations along with face-dependent crystallographic information. The parameters of the simplified Heine-Abarenkov pseudopotentials [Eq. (5)] were taken after Ref. 14, where they have been chosen to fit the material lattice parameter and bulk modulus. We have verified that with this choice of pseudopotential parameters the cohesive energy agrees to within 0.3% with experimental values. In addition, they have been used[14] in calculations of vacancy formation energies and volumes, yielding results in good agreement with experiments. Results for interlayer distance relaxation, $\Delta_{l,l+1}=(\lambda_{l+1}-\lambda_l)\times 100\%$, expressed in percent change of the interlayer distance from the bulk layer spacing value d, for the low-index faces of Na(bcc) and Al(fcc) as obtained via the various models, are given in Tables II–IV. Negative and positive values of $\Delta_{l,l+1}$ correspond, respectively, to interlayer distance contraction and expansion. To demonstrate the effect of the number n_s of layers which are allowed to relax on the equilibrium structure we include results for several n_s values. In Tables II and III the results corresponding to the larger n_s value are those for which convergence with respect to increasing n_s has been obtained, with the exception of the results for Na(111), which are given in detail in Table IV. Results of previous calculations[10,15,17–19] and those obtained via the analysis of experimental data are included in Tables II and III. In comparing to previous calculations it should be noted that with the exception of the electrostatic model,[10] all others have considered single-layer relaxation only. Also the inclusion of multilayer relaxation in the analysis of experimental data is a recent development.[2–5] From the inspection of the results in Tables II and III we note the tendency for larger relaxations at the more open faces [fcc (110) and bcc (111)]. The necessity of allowing multilayer relaxation in each system and for all the theoretical models considered is clearly demonstrated. The multilayer relaxation results exhibit damped oscillatory relaxations; the period of the oscillations is equal to the period of the layer stacking sequence n_R (see Table I).

The principal origin of the multilayer oscillatory relaxation lies in the 3D crystallinity of the system, i.e., in the intralayer structure and the registry shift between layers, and in the relation between intralayer structure and interlayer spacing. Thus the less-open surfaces show smaller relaxations because the ions are more densely packed

TABLE II. Summary of the surface relaxation results for the low-index surfaces of Na obtained using the PITB, DLH, DLHBS0, and DLHBS models (see text); available experimental results and the results of other calculations are given in the columns labeled Expt. and Other, respectively. The results are presented as the percent change from the bulk value, $\Delta_{l,l+1}$ of the spacing between the layers numbered l and $l+1$. Negative (positive) values of $\Delta_{l,l+1}$ indicate contraction (expansion) of the layer spacing. n_s is the number of layers which were allowed to relax (the results of other calculations, in the last column, are all for single-layer relaxation).

n_s	Model	PITB	DLH	DLHBS0	DLHBS	Expt.	Other
					[Na(100)]		
1	Δ_{12}	-7.0	-1.4	1.2	-3.6		$\Delta_{12}=-2$ (Ref. 18)
4	Δ_{12}	-10.8	-1.9	-0.4	-2.7		$\Delta_{12}=+1$ (Ref. 15)
	Δ_{23}	4.0	0.7	1.2	0.7		
	Δ_{34}	-1.2	-0.3	0.4	-1.0		
	Δ_{45}	0.2	0.1	0.4	0.8		
					[Na(110)]		
1	Δ_{12}	-0.7	-0.3	1.0	-0.1		$\Delta_{12}=0$ (Ref. 18)
3	Δ_{12}	-0.7	-0.2	0.1	-0.2	$\Delta_{12}=0$ (Ref. 20)	$\Delta_{12}=-5$ (Ref. 15)
	Δ_{23}	0.0	-0.1	0.2	0.1		
	Δ_{34}	$--0.0$	-0.0	0.8	0.0		
					[Na(111)]		
1	Δ_{12}	-34	-13	-10	-20		$\Delta_{12}=-12.5$ (Ref. 15)
6	Δ_{12}	-63	2	4	-8		
	Δ_{23}	-10	-32	-32	-29		
	Δ_{34}	46	25	24	23		
	Δ_{45}	-30	-1	0	-2		
	Δ_{56}	5	-11	-12	-11		
	Δ_{67}	3	6	10	8		

TABLE III. Summary of the surface relaxation results for the low-index surfaces of Al. See the caption of Table II.

n_s	Model	PITB	DLH	DLHBS0	DLHBS	Expt.	Other
					[Al(100)]		
1	Δ_{12}	-2.1	0.3	1.0	-0.7		$\Delta_{12}=-7.5$ (Ref. 15)
3	Δ_{12}	-2.4	0.4	1.0	0.0	$\Delta_{12}=0$ [Ref. 1(a)]	$\Delta_{12}=-4.6$ (Ref. 17)
	Δ_{23}	0.3	0.0	0.7	-0.0		
	Δ_{34}	-0.0	-0.0	-0.1	-0.0		
					[Al(110)]		
1	Δ_{12}	-11	-4	-5	-14		$\Delta_{12}<-15$ (Ref. 15)
4	Δ_{12}	-26	-12	-14	-10	$\Delta_{12}=-8.4\pm0.8$ (Ref. 2)	$\Delta_{12}=2.0$ (Ref. 19)
	Δ_{23}	15	8	9	4	$\Delta_{23}=4.9\pm1$ (Ref. 2)	
	Δ_{34}	-7	-4	-2	-3	$\Delta_{34}=-1.6\pm1.1$ (Ref. 2)	
	Δ_{45}	2	1	2	0		$\Delta_{12}=-16$ (Ref. 17)
					[Al(111)]		
1	Δ_{12}	-0.4	0.8	1.9	1.8	$\Delta_{12}=0.9\pm0.5$ (Ref. 21)	$\Delta_{12}=1$ (Ref. 15)
3	Δ_{12}	-0.4	0.9	0.7	1.6	$\Delta_{12}=2.5$ [Ref. 1(a)]	$\Delta_{12}=-1.6$ (Ref. 17)
	Δ_{23}	0.0	-0.1	-0.1	0.1		
	Δ_{34}	-0.0	0.0	0.1	0.0		

within the layer, i.e., the resulting potential has less variation both parallel and perpendicular to the surface plane since the layers are neutrally charged (ions plus negative background slab), and because the layer spacing is larger. These effects of crystallinity appear in the Madelung and band-structure contributions: The Madelung force between adjacent unrelaxed (100) and (110) layers ($n_R=2$) is attractive while the force between next-nearest-neighbor layers is repulsive; for (111) surfaces ($n_R=3$) the interlayer forces oscillate with a period of three layers. The Madelung contribution is larger; the band-structure terms reduce (screen) the Madelung interactions, but since the electron response is affected by the presence of the surface, this screening is complicated and gives rise to forces

TABLE IV. The effect of incrementing the number of layers allowed to relax, n_s, on the interlayer spacings for Na(111). See also the caption of Table II.

n_s	Model	PITB	DL	DLH	DLHBS0	DLHBS
			[Na(111)]			
1	Δ_{12}	-34	-42	-13	-10	-20
2	Δ_{12}	-56	-57	-9	-5	-10
	Δ_{23}	15	10	-2	-5	-10
3	Δ_{12}	-49	-45	0	1	-8
	Δ_{23}	-6	-32	-24	-27	-26
	Δ_{34}	15	30	13	20	17
4	Δ_{12}	-56	-58	-3	1	-10
	Δ_{23}	-14	-42	-26	-29	-25
	Δ_{34}	40	65	23	25	22
	Δ_{45}	-17	-23	-7	-5	-7
6	Δ_{12}	-63	-63	2	4	-8
	Δ_{23}	-10	-42	-32	-32	-29
	Δ_{34}	46	73	25	24	23
	Δ_{45}	-30	-33	-1	0	-2
	Δ_{56}	5	-5	-11	-12	-11
	Δ_{67}	3	10	6	10	8
9	Δ_{12}	-67	-69	3		
	Δ_{23}	-10	-43	-35		
	Δ_{34}	53	84	27		
	Δ_{45}	-40	-46	-0		
	Δ_{56}	6	-7	-15		
	Δ_{67}	18	34	12		
	Δ_{78}	-18	-23	-1		
	Δ_{89}	6	4	-5		
	Δ_{910}	0	2	3		

TABLE V. Change in surface energy ΔE_{SR} (Ry/2D unit cell) resulting from surface relaxation in the DLHBS model. The value in parentheses is the result for single-layer relaxation.

Na			Al		
(100)	(110)	(111)	(100)	(110)	(111)
-2.7×10^{-4}	-1.3×10^{-6}	-3.7×10^{-3}	-3.4×10^{-4}	-3.4×10^{-2}	-3.2×10^{-3}
(-2.2×10^{-4})	(-1.6×10^{-7})	(-2.5×10^{-3})	(-6.8×10^{-5})	(-2.6×10^{-2})	(-3.1×10^{-3})

which are not simply related to the interlayer distances.

The dipole layer and Hartree energy terms also give rise to oscillatory forces on the layers. However, these forces come from single-ion potentials, i.e., potentials which depend on the position of an individual ion with respect to the bulk through the interaction with the jellium electron and positive background densities $\rho^0(z)$ and $\rho^+(z)$ (see also the discussion of single-ion potentials in Paper I). These forces, $F_{\rm DL}$ and F_H, are significant only for the topmost layer and, although they do oscillate due to the Friedel oscillations in $\rho^0(z)$, they approach zero rapidly as the z coordinate of the layer increases. The principle effect of the dipole layer and Hartree contributions is to limit the displacement of the first layer with respect to the bulk.

To show the effect of incrementing n_s we choose the system of Na(111) which of all the systems studied exhibits the largest relaxations. We first note that in this system, even with $n_s=9$, the layer spacings in the bottom of the surface region have not converged to the bulk value. However, increasing n_s from 6 to 9 does not substantially change the first three $(n_R=3)$ layer spacings. We conclude that if n_s is a multiple of n_R, then the first n_s-n_R layer spacings so obtained are reasonably close to the equilibrium values even though n_s is not large enough to obtain convergence of the deeper layer spacings to the bulk value. For this reason, and because the inclusion of the band-structure energy is relatively costly in computer time, we have limited n_s to 6 in the DLHBS0 and DLHBS model calculations for this Na(111) system. In addition, it is improbable that analysis of experimental data will be able to accurately determine the layer spacings of such deeper layers.

Also included in Table IV are results for the DL model, which are not included in Tables II and III. Note that the results of the DL model, which is an electrostatic model describing a system of point ions embedded in the Lang-Kohn electron density $\rho^0(z)$, qualitatively resemble the PITB model results, while the DLH model results are qualitatively closer to the results of the DLHBS model. Thus it is evident that a model in which the ions are treated as point ions is a poor approximation, and that the second-order (band-structure, $E_{\rm BS}$) effects are small compared to the first-order (Hartree, E_H) effects. Nevertheless, as will be discussed below, it is necessary to include the full 3D electron response properly in order to enable quantitative surface structure predictions to be made.

We turn now to a discussion of the results summarized in Tables II and III. Comparison of the results obtained via the PITB and DLH models shows that the inclusion of the dipole-layer and Hartree energies reduces overall the magnitude of relaxation. This reduction results from the interaction of the ions with the inhomogeneous surface electron density, which tends to fix the position of the first layer with respect to the bulk. In one case, Al(111), the inclusion of the Hartree term results in an outward displacement of the first layer and an expansion of the first interlayer spacing. In all other cases the Hartree force on the (unrelaxed) first layer is toward the bulk and thus does not oppose the Madelung force until the first layer is displaced inward. In this context we emphasize the cooperative nature of the multilayer relaxation, i.e., comparing results (Tables II–IV) obtained with increasing numbers, n_s, of layers participating in the relaxation, and it is observed that the near-surface spacings change in response to the movement of added deeper layers. Comparison of the results obtained through the use of the electrostatic type of models (PITB and DLH) with those obtained via models which include electron screening (DLHBS0 and DLHBS) demonstrates that the multilayer relaxation phenomena predicted by the simple electrostatic models does indeed occur when electron response is included. This observation resolves questions raised by several authors relating to multilayer relaxation.[15,18]

While certain qualitative features are revealed by the electrostatic model, from the comparison of the results obtained via the various models with values extracted from experimental data we conclude that *quantitative* structural predictions require a minimization of the complete total-energy expression [Eq. (8)] which retains the full 3D nature of the system, i.e., the DLHBS model. In particular, employment of the one-dimensional 1(D) electron response, DLHBS0, model does not yield adequate results.

Further support for our conclusions regarding the importance of multilayer relaxation at metal surfaces is provided in Table V by the relaxation energies calculated using the DLHBS model for single (in parentheses) and multilayer relaxation. The results demonstrate that the magnitude of the energy gained by relaxation is increased dramatically upon allowing for multilayer relaxation.

In summary, we have derived an expression for the total energy of a semi-infinite simple metal which depends explicitly on the ionic positions. Using an efficient relaxation algorithm and the different models described in Sec. IV A, we have systematically studied the energetics underlying metal surface relaxation. From these studies we conclude that quantitative surface structural predictions require the use of the full total-energy expression, which maintains the 3D nature of the system and accounts properly for the inhomogeneous surface electron density and the response of the electronic system to the ionic positions (screening). Furthermore, the vital role of multilayer relaxation in achieving structural predictions in good agreement with experiment is clearly demonstrated by our results.

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APPENDIX

In this appendix we derive expressions for $w_{ns}^{\lambda}(G,q_z)$ and $W_{ms}(G,q_z)$. The potential $w_n^{\lambda}(R,z)$ can be expressed in the form

$$w_n^{\lambda}(R,z)=\int d^2R'\int dz' p_n^{\lambda}(R',z')V_C(|\vec{R}-\vec{R}'|,z-z') , \tag{A1}$$

where $ep_n^{\lambda}(R,z)$ is some charge density (a local-model pseudopotential can always be expressed in this form). From the definition of the symmetrized potential,

$$w_{ns}^{\lambda}(G,q_z)=\int d^2R\int dz\, p_n^{\lambda}(R,z)\left[\lim_{L\to\infty}\int_0^L dz'\cos(q_zz')\int d^2R' e^{i\vec{G}\cdot\vec{R}}V_C(|\vec{R}-\vec{R}'|,z'-z)\right] . \tag{A2}$$

We substitute

$$V_c(R,z)=\frac{1}{(2\pi)^3}\int dz\, e^{-ik_zz}\int d^2R\, e^{-i\vec{K}\cdot\vec{R}}\left[-\frac{4\pi e^2}{K^2+k_z^2}\right]$$

into Eq. (A2) to obtain

$$w_{ns}^{\lambda}(G,q_z)=\int d^2R\, e^{i\vec{G}\cdot\vec{R}}\int dz\, p_n^{\lambda}(R,z)[\lim_{L\to\infty} I(L,z;G,q_z)] , \tag{A3}$$

where

$$I(L,z;G,q_z)=\frac{1}{2\pi}\int dk_z\frac{-4\pi e^2}{2G}\left[\frac{1}{k_z-iG}-\frac{1}{k_z+iG}\right]\times\left[\frac{1}{k_z+q_z}(e^{-ik_z(L-z)}e^{-iq_zL}-e^{ik_zz})+\frac{1}{k_z-q_z}(e^{ik_z(L-z)}e^{iq_zL}-e^{ik_zz})\right] . \tag{A4}$$

The integral over k_z in Eq. (A4) is done by contour integration to give

$$I(L,z;G,q_z)=-\frac{4\pi e^2}{G^2+q_z^2}[2\cos(q_zz)-e^{-Gz}]+\frac{4\pi e^2}{G^2+q_z^2}\left[\frac{q_z}{G}\sin(q_zL)-\cos(q_zL)\right]e^{-G(L-z)} . \tag{A5}$$

The second term in Eq. (A5) clearly vanishes in the limit $L\to\infty$ for all $G\neq 0$; with $G=0$ this term is independent of z (and of R) and the density $p_n^{\lambda}(R,z)$ integrated over all space is zero. Thus there is no contribution to w_{ns}^{λ} from this second term of Eq. (A5), and Eq. (A3) becomes

$$w_{ns}^{\lambda}(G,q_z)=-\frac{4\pi e^2}{G^2+q_z^2}\int dz\int d^2R\, e^{i\vec{G}\cdot\vec{R}}p_n^{\lambda}(R,z)[2\cos(q_zz)-e^{-Gz}] . \tag{A6}$$

The density $p_n^{\lambda}(R,z)$ is given by

$$p_n^{\lambda}(R,z)=p(R,z-z_n^{\lambda})-(N_A\Omega_0)^{-1}[\Theta(z-z_0-(n-1)d)-\Theta(z-z_0-nd)] , \tag{A7}$$

where $p(R,z)$ is the density which gives rise to the ionic pseudopotential V_p, so that

$$V_p(G,q_z)=[-4\pi e^2/(G^2+q_z^2)]p(G,q_z) .$$

The 3D Fourier transform of the pseudopotential used in our calculations, Eq. (5), is

$$V_p(G,q_z)=-\frac{4\pi Ze^2}{G^2+q_z^2}[(1-u_c)\cos[(G^2+q_z^2)^{1/2}r_c]+u_c\frac{\sin[(G^2+q_z^2)^{1/2}r_c]}{(G^2+q_z^2)^{1/2}r_c} . \tag{A8}$$

Substituting Eq. (A7) into Eq. (A6) yields finally the expression for $w_{ns}^{\lambda}(G,q_z)$:

$$w_{ns}^{\lambda}(G,q_z)=V_p(G,q_z)2\cos(q_zz_n^{\lambda})+(1-\delta_{\vec{G},\vec{0}})\frac{4\pi Ze^2}{G^2+q_z^2}e^{-Gz_n^{\lambda}}+\delta_{\vec{G},\vec{0}}\frac{4\pi Ze^2}{q_z^2}2\cos\{q_z[z_0+(n-\tfrac{1}{2})d]\}\frac{\sin(q_zd/2)}{q_zd/2} . \tag{A9}$$

From the definition of $W_{ms}(G,q_z)$ and Eq. (A9) we have

$$W_{ms}(G,q_z)=\lim_{N\to\infty}\left[\left[V_p(G,q_z)+\delta_{\vec{G},\vec{0}}\frac{4\pi Ze^2}{q_z^2}\frac{\sin(q_zd/2)}{q_zd/2}\right]2\sum_{l=1}^{N}\cos\{q_z[z_0+(2ln_R+2m-3)d/2]\}+(1-\delta_{\vec{G},\vec{0}})\frac{4\pi Ze^2}{G^2+q_z^2}2\sum_{l=1}^{N}\exp\{-G[z_0+(ln_R+m-3/2)d]\}\right] . \tag{A10}$$

The sums over l in Eq. (A10) can be done. We use the identity

$$\lim_{N\to\infty}\frac{\sin(Nq_zn_Rd)}{\sin(q_zn_Rd/2)}=\sum_{g_z}\frac{2\pi}{n_Rd}\delta(q_z-g_z)\cos(g_zn_Rd/2)\ , \tag{A11}$$

where $g_z=m(2\pi/n_Rd)$, $m=0,\pm 1,\pm 2,\ldots$, giving finally the expression for $W_{ms}(G,q_z)$:

$$\begin{aligned}W_{ms}(G,q_z)={}&\left[V_p(G,q_z)+\delta_{\vec{G},\vec{0}}\frac{4\pi Ze^2}{q_z^2}\frac{\sin(q_zd/2)}{q_zd/2}\right]\\&\times\Bigg[\cos\{q_z[z_0+(2m-n_R-1)d/2]\}\frac{2\pi}{n_Rd}\sum_{g_z}\delta(q_z-g_z)\cos(g_zn_Rd/2)\\&-\frac{\sin\{q_z[z_0+(2m-n_R-1)d/2\}}{\sin(q_zn_Rd/2)}\Bigg]+(1-\delta_{\vec{G},\vec{0}})\frac{4\pi Ze^2}{G^2+q_z^2}\frac{\exp\{-G[z_0+(2m-1)d/2]\}}{1-e^{-Gn_Rd}}\ .\end{aligned} \tag{A12}$$

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