PHYSICAL REVIEW B VOLUME 40, NUMBER 6 15 AUGUST 1989-II

First-principles method for calculating electronic properties of layered structures

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(Received 20 December 1988; revised manuscript received 5 May 1989)

We present a first-principles, computationally efficient method for calculating the electronic structure of layered systems consisting of simple metals. The method involves forming a one-dimensional, planar-averaged potential from a three-dimensional array of ionic pseudopotentials. As an example of its use, we have calculated the work function, electron density, and effective potential for ultrathin Na, K, and Li films. The calculations, which can be performed on a workstation, show good agreement with experimental results and three-dimensional, self-consistent-field pseudopotential calculations taking several hours of central-processing-unit time on a Cray Research, Inc. supercomputer.

I. INTRODUCTION

Currently there is considerable interest in the properties of layered structures such as ultrathin metallic films,[1-5] overlayers,[4-6] and superlattices.[7,8] In particular, semiconductor superlattices[8] have attracted considerable attention both because of their novel physical properties, and the possibility of tailoring their electronic properties for specific technological applications.[9]

A number of calculational techniques have been used in the study of layered structures. The simplest of these are the infinite- and finite-square-well (i.e., Sommerfeld) models, which a number of workers have used to investigate the electronic properties of metallic,[3,10] superconducting,[11] and semiconducting and semimetallic[12] systems. These non-self-consistent models largely ignore electron-electron interactions and offer only limited insight into the physical behavior of the systems modeled. More sophisticated calculations have been done by Schulte,[13] who applied the Hohenberg-Kohn-Sham density-functional formalism[14-16] with the jellium approximation to calculate self-consistently the dependence of the work function on film thickness in thin metallic films. This approach includes electron-electron interactions but ignores the discreteness of the crystal lattice.

Lang and Kohn partially included the effects of the crystal lattice in density-functional calculations of surface energies[17] and work functions[18] of bulk systems. Their "ion-lattice" model incorporated the empty-core pseudopotentials of Ashcroft and Langreth,[19] via perturbation theory, into integral expressions for the surface energy[17] and work function.[18] This model predicts work functions in better agreement with experimental values than does the jellium model; it also permits calculation of the dependence of the work function on surface orientation. However, it takes into account the effect of the lattice on the effective potential only, and not on the electron density, and thus cannot yield self-consistent densities or potentials which reflect the discreteness of the lattice.

The discrete lattice has been included in a fully self-consistent way in calculations by Feibelman,[4] and Feibelman and Hamann,[5] who used a self-consistent-field (SCF), linear combination of atomic orbitals (LCAO) approach to calculate electronic properties of metallic thin films and overlayers. Ciraci, Batra, and co-workers[1,2] have also done discrete-lattice SCF pseudopotential calculations[20,21] in investigations of quantum size effects in thin metallic films. The SCF calculations of Feibelman and Hamann and of Ciraci *et al.* are first-principles, fully three-dimensional approaches which give good results compared with experiment. However, they require very substantial computer time and memory; a typical calculation of the electronic density and eigenvalues may require several hours of supercomputer time and several megawords of memory.

In this paper, we present a computationally efficient, first-principles, self-consistent method of calculating the electronic properties of layered systems, i.e., systems in which significant variation in structure and/or composition occur in one dimension only. This method is described in Sec. II. In Sec. III the method is applied to the problem of calculating the work function and electron density of ultrathin alkali-metal films. The results are presented and compared with those obtained from fully three-dimensional SCF calculations. Concluding remarks are presented in Sec. IV.

II. METHOD

The method presented here provides a computationally efficient, first-principles approach for self-consistently calculating the electronic properties of layered systems.

It uses the density-functional approach to calculate the one-dimensional electron density and eigenvalue spectrum for such systems.[22] In contrast with many previous density-functional calculations, the discrete lattice is not replaced with a uniform jellium. Instead, the ions are represented by ion-core pseudopotentials distributed on the crystalline lattice(s) comprising the system. The three-dimensional potential formed by this array of ion-core pseudopotentials is converted into a one-dimensional ionic potential suitable for efficient one-dimensional calculations. This is done by performing a two-dimensional average of the ionic potential, over one surface unit cell in the plane of the layers, to form a planar-averaged ionic potential, $V_{\text{ion}}(z)$. That is,

$$V_{\text{ion}}(z) \equiv (1/A) \int\int_A V_{\text{ion}}(x,y,z)\,dx\,dy \ , \tag{1}$$

where z is the direction perpendicular to the layers, and A is the surface area of the unit cell. In this expression, $V_{\text{ion}}(x,y,z)$ is the sum of the contributions from the individual ion-core pseudopotentials located at all the lattice sites in the system; it is calculated by Fourier transform, as described below. Note that the unit cell is not restricted to that of a standard crystal structure, such as a bcc lattice, but may be a much larger cell (i.e., "supercell") which contains many atoms.

The planar-averaged ionic potential $V_{\text{ion}}(z)$ is one contribution to the potential V_{eff}, used in the effective one-electron Schrödinger equation of the density-functional method. A second contribution is the electrostatic term, V_{es}, which describes the electrostatic interactions of the conduction electrons among themselves. The third term is the exchange-correlation potential, V_{xc}, which accounts for the many-body interactions between the conduction electrons. Thus, the effective potential is

$$V_{\text{eff}}(z) = V_{\text{ion}}(z) + V_{\text{es}}(z) + V_{\text{xc}}(z) \ .$$

In the formalism presented here, $V_{\text{ion}}(z)$ is computed only once, at the beginning of the calculation, since the ions are not allowed to move. In contrast, $V_{\text{es}}(z)$ and $V_{\text{xc}}(z)$ are computed self-consistently, as follows. An initial trial electron density, $n(z)$, is chosen, and $V_{\text{es}}(z)$ and $V_{\text{xc}}(z)$ are computed. The resulting effective potential is then used in the one-dimensional effective Schrödinger equation,

$$[-(\hbar^2/2m)d^2/dz^2 + V_{\text{eff}}(z)]\phi_n(z) = E_n\phi_n(z) \ ,$$

which is solved self-consistently (using the Numerov method[23]) to obtain the eigenvalues and eigenfunctions of the system. Successive energy states, or levels in the potential well of $V_{\text{eff}}(z)$, are calculated until there are enough levels to accommodate all the electrons in the unit cell. A new density $n(z)$ is formed from the normalized sum of squares of the wave functions. The process is repeated until successive densities (or effective potentials) are deemed sufficiently self-consistent by some suitable criterion.

The planar-averaged ionic pseudopotential, $V_{\text{ion}}(z)$, is derived [see Eq. (1)] from the three-dimensional ionic potential $V_{\text{ion}}(x,y,z)$, which is given by

$$V_{\text{ion}}(x,y,z) = \sum_{\mathbf{R},\tau_j} V_{\text{pseudo}}(\mathbf{r}-\mathbf{R}-\tau_j) \ .$$

In this expression $V_{\text{pseudo}}(\mathbf{r})$ is the ionic pseudopotential of the ion at $\mathbf{r}$, and the sum is over all the lattice sites $\mathbf{R}$ in the system, and over all the basis vectors τ_j in the unit cell.

The pseudopotentials of Bachelet, Hamann, and Schlüter[24] were used in this work. These pseudopotentials are represented by a sum of local and nonlocal parts:

$$V_{\text{pseudo}}(\mathbf{r}) = V_{\text{local}}(\mathbf{r}) + V_{\text{nl}}(\mathbf{r}) \ .$$

The local and nonlocal contributions are given by

$$V_{\text{local}}(\mathbf{r}) = -(Z/r) \sum_{k=1}^{2} c_k \operatorname{erf}(\alpha_k^{1/2} r)$$

and

$$V_{\text{nl}}(\mathbf{r}) = \sum_{i=1}^{3} |Y_{00}\rangle (A_i + A_{i+3}r^2)\exp(-\alpha_i r^2)\langle Y_{00}| \ .$$

In the last expression, we have included only the nonlocal s contribution, which is a reasonable approximation for the alkali metals.

The three-dimensional ionic potential, $V_{\text{ion}}(x,y,z)$, is most easily constructed by Fourier transformation:

$$V_{\text{ion}}(x,y,z) = \sum_{\mathbf{G}} V_{\text{ion}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \ , \tag{2}$$

where

$$V_{\text{ion}}(\mathbf{G}) = \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} \left[\sum_{\mathbf{R},\tau_j} V_{\text{pseudo}}(\mathbf{r}-\mathbf{R}-\tau_j) \right] d^3r \ ,$$

or

$$\mathbf{V}_{\text{ion}}(\mathbf{G}) = \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} \times \left[\sum_{\mathbf{R},\tau_j} [V_{\text{local}}(\mathbf{r}-\mathbf{R}-\tau_j) + V_{\text{nl}}(\mathbf{r}-\mathbf{R}-\tau_j)] \right] d^3r \ .$$

Performing the integration, it follows that

$$V_{\text{ion}}(\mathbf{G}) = \sum_{\tau_j} e^{-i\mathbf{G}\cdot\tau_j} [V_{\text{local}}(\mathbf{G}) + V_{\text{nl}}(\mathbf{G})] \ , \tag{3}$$

where[24]

$$V_{\text{local}}(\mathbf{G}) = -\sum_{k=1}^{2} \left[\frac{4\pi Z_j c_k}{\Omega_c |G|^2} \right] e^{-|G|^2/4\alpha_k} \ , \tag{4}$$

and

$$V_{\text{nl}}(\mathbf{G}) = \sum_{i=1}^{3} \left[\frac{A_i}{\Omega_c} - \frac{|G|^2 A_{i+3}}{4\Omega_c \alpha_i^2} + \frac{3A_{i+3}}{2\Omega_c \alpha_i} \right] \left[\frac{\pi}{\alpha_i} \right]^{3/2} \times e^{-|G|^2/4\alpha_i} \ . \tag{5}$$

In these equations Ω is the crystal volume, Ω_c is the unit-cell volume, and Z_j, c_k, A_i, A_{i+3}, α_i, and α_k are parameters defined by Bachelet *et al.*[24] To calculate the value of $V_{\rm ion}(x,y,z)$, Eqs. (3)–(5) are inserted into Eq. (2), with enough terms being included in the summation in Eq. (2) to give convergence.

To convert the three-dimensional potential $V_{\rm ion}(x,y,z)$ into the one-dimensional potential $V_{\rm ion}(z)$, the integral in Eq. (1) is replaced by a double summation over the surface unit cell in the plane of the layers, i.e.,

$$V_{\rm ion}(z) \equiv (1/N_x N_y) \sum_{x_i}^{N_x} \sum_{y_i}^{N_y} V_{\rm ion}(x,y,z) ,$$

where N_x and N_y are the number of divisions of the x and y unit-cell lattice parameters. The number of divisions depends on the strength of the ionic pseudopotential, $V_{\rm pseudo}$; typically the points were spaced about 0.1 Å apart.

In a similar way, the electrostatic potential, $V_{\rm es}$, is obtained from the Fourier-transformed *one-dimensional* Poisson equation

$$V_{\rm es}(G) = 4\pi e n(G)/|G|^2 . \tag{6}$$

In this equation the G are the components of the reciprocal-lattice vectors normal to the layers, and $V_{\rm es}(G)$ and $n(G)$ are the Fourier transforms of $V_{\rm es}(z)$ and $n(z)$, respectively. Thus, to obtain $V_{\rm es}(z)$ one Fourier transforms $n(z)$, uses Eq. (6) to determine $V_{\rm es}(G)$, and then inverse Fourier transform to get $V_{\rm es}(z)$.

Note that the divergences that appear when $V_{\rm es}(z)$ and $V_{\rm ion}(z)$ are calculated separately are avoided, in the usual way, by discarding the zeroth-order Fourier components in the Fourier transforms of these quantities.

The exchange-correlation potential, $V_{\rm xc}$, is calculated from the (one-dimensional) electron density, using the Kohn-Sham local-density approximation.[15]

III. RESULTS

The planar-averaged pseudopotential, density-functional (PAPDF) method described above has been used to calculate the electron density and work functions of a variety of ultrathin (one to seven layer) K, Na, and Li films. The films were modeled by superlattices consisting of repeating film-vacuum structures, with the vacuum having a thickness of eight atomic layers in all cases. The correlation potential was calculated using the Wigner correlation formula.[16] Self-consistency of the potential to a minimum of six significant figures was obtained. For comparison, we have also carried out calculations (similar to those of Ciraci *et al.*[1,2]) using the fully three-dimensional SCF pseudopotential method,[20] employing the Hohenberg-Kohn local-density approximation,[15] with Wigner correlation,[16] applied in the momentum-space formalism.[21] (For simplicity, hereafter we refer to the method presented here as the "one-dimensional method," and the three-dimensional SCF pseudopotential approach as the "three-dimensional method.")

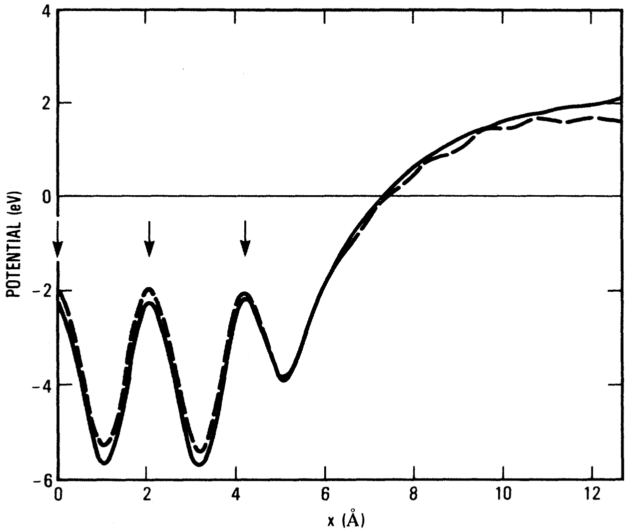

FIG. 1. The effective potential obtained for a five-layer Na(100) film by the one-dimensional method (solid line) and the three-dimensional SCF pseudopotential method (dashed line). The left edge of the plot corresponds to the center of the film, and the right edge indicates the center of the vacuum region separating two adjacent films. The arrows indicate the location of the three atomic layers in the half of the film shown. (Note that the zero level for the potential in this figure is arbitrary.)

Figure 1 shows the self-consistent potential obtained by the one- and three-dimensional methods for a five-layer Na film with (100) crystal surfaces. (The potential shown for the three-dimensional method is obtained by perform-

TABLE I. Work functions (in eV) for Li, Na, and K five-layer (100) films, computed by the one- and three-dimensional methods (1D and 3D), are compared with bulk theoretical and experimental values. The bulk theoretical values are from the "ion-lattice" and jellium density-functional calculations of Lang and Kohn (Ref. 18), the former being for (100) surfaces. The experimental results are taken from the selected work function values reported by Michaelson (Ref. 25), and are for polycrystalline samples.

	Five layer		Bulk		
Element	1D	3D	Ion-lattice	Jellium	Experimental
Li	3.15	2.83	a	3.3	2.9[b]
Na	2.81	2.56	2.75	3.06	2.75
K	2.45	2.24	2.40	2.74	2.30

[a] Lang and Kohn (Ref. 18) calculated two values of the work function of Li (2.40 eV and 3.30 eV) with the ion-lattice model, using two different empty-core pseudopotentials.

[b] Michaelson (Ref. 25) indicates that the value for the work function of Li is of unknown reliability.

ing a planar average of the potential after the completion of the self-consistency calculation.) It is seen that the one-dimensional method yields a potential that agrees well with that obtained with the three-dimensional SCF approach. The potentials generated by the two methods differ by no more than 0.5 eV. We note that, compared to the three-dimensional method, the one-dimensional method gives a somewhat smaller potential within the film, and a larger potential in the vacuum region.

Shown in Fig. 2 is the self-consistent electron density of the five-layer Na(100) film as obtained with the one-dimensional method. The well-known Friedel oscillations are evident in this plot. Furthermore, modulations in the electron density produced by the atomic layers are clearly seen.

The work functions obtained for five-layer K, Na, and Li films with (100) crystal surfaces are shown in Table I. They are compared with bulk polycrystalline experimental values,[25] and also with the bulk theoretical results of Lang and Kohn[18] (for both the jellium and "ion-lattice" models). Several observations can be made. First, the one- and three-dimensional results agree fairly well, differing by about 10%. Second, the values from the one-dimensional approach are in excellent agreement (within a few percent) with those produced by the (bulk) "ion-lattice" model. Third, for all but the one-layer film, the one-dimensional results are within 10% of the polycrystalline bulk results. Finally, we note that the one-dimensional method gives the correct qualitative variation in the work function among the three elements Li, Na, and K.

Table II shows the work function of Na (100) films with thickness of one, three, five, and seven layers, as computed by the one- and three-dimensional methods. The values agree fairly well, typically within 10%. We note that the variation in the work function of Na, determined by the one-dimensional method, as the thickness increases from one to seven layers, is qualitatively in close agreement with that found by Ciraci and Batra,[1] using a three-dimensional SCF approach, for one- to seven-layer Al films.

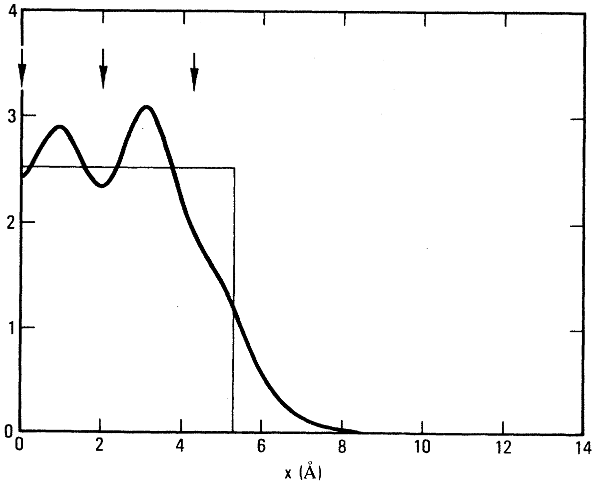

FIG. 2. The electron density for a five-layer Na(100) film, as calculated by the one-dimensional method. The box indicates the magnitude and width of the corresponding jellium which might have been used.

TABLE II. Comparison of work functions (in eV) of one- to seven-layer Na(100) films as computed by the one- and three-dimensional methods (1D and 3D).

Layers	1D	3D
1	3.09	2.83
3	2.77	2.52
5	2.81	2.56
7	2.89	2.42

The one-dimensional results for the work function are in general about 0.25 eV higher than those obtained with the three-dimensional approach (with the exception of Li, for which the difference is 0.32 eV). Part of this difference can be traced to the fact that the one-dimensional calculations did not include hybridization of the wave functions, while the three-dimensional calculations did. This is related to the way in which the pseudopotentials were utilized. The pseudopotentials in both the one- and three-dimensional calculations are the nonlocal, norm-conserving ionic pseudopotentials given by Bachelet, Hamann, and Schlüter.[24] The three-dimensional SCF calculations included the *s*, *p*, and *d* parts of these potentials to allow for hybridization. By contrast, the one-dimensional calculations used only the *s* part, since the Schrödinger equation was solved in real space, necessitating the use of a local potential. (The use of only the *s* potential is reasonable for the alkali metals considered.) Therefore the one-dimensional calculations do not permit hybridization of the wave functions. By doing additional three-dimensional SCF calculations using only the *s* potential, it was found that the hybridization of the wave functions accounted for approximately half of the difference in the work functions computed with the two methods. The use of *local* pseudopotentials which take into account wave-function hybridization may thus improve the results of the one-dimensional method.

IV. CONCLUSIONS

The planar-averaged pseudopotential, density-functional (PAPDF) method presented here is a major improvement over density-functional calculations that use jellium to represent the ion cores. The method is a first-principles, self-consistent approach that can be used in studies of the electronic properties of various types of layered systems. Although the method is not expected to give results as accurate as those obtained with fully three-dimensional SCF calculations (or other three-dimensional, first-principles methods), it yields results in good agreement with those calculations, but with a small fraction of the computational effort. It can be applied in first-principles investigations of the electronic properties of metallic superlattices, metal overlayers, film-vacuum interface structures, and other interesting systems. Finally, the computational efficiency of the one-dimensional method suggests that it can be applied to systems considerably larger than those that currently can be handled with three-dimensional methods.

ACKNOWLEDGMENTS

One of the authors (J.P.R.) wishes to thank Sandia National Laboratories (Livermore, California) for their hospitality during a recent visit sponsored by the U.S. Department of Energy (Division of Materials Science, Office of Basic Energy Sciences) during which part of this work was carried out. One of us (J.S.N.) gratefully acknowledges the support of the U.S. Department of Energy (Division of Materials Science, Office of Basic Energy Sciences). In addition we would like to thank Dr. C. Y. Fong for his helpful comments.

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