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Ab initio calculation of interatomic potentials and electronic properties of a simple metal—Al

M. Manninen
Nordita, Blegdamsvej 17, Copenhagen, Denmark

P. Jena
Department of Physics, Michigan Technological University, Houghton, Michigan 49931
*and Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284**

R. M Nieminen[†]
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

J. K. Lee
Department of Metallurgical Engineering, Michigan Technological University,
Houghton, Michigan 49931
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A simple scheme using a single-ion approach has been developed to calculate the pseudopotential and pair potential for aluminum. The electron density around an isolated Al nucleus in a homogeneous electron gas is calculated self-consistently using the density-functional method. The induced charge density is then used to produce an *ab initio* local pseudopotential and the interionic potential. Two different schemes for embedding the Al nucleus into the jellium have been considered. A model where the Al nucleus is in the jellium vacancy gives better pseudo- and pair potentials than the model where the Al nucleus is embedded into a completely homogeneous electron gas. Using the resulting potentials, the cohesion energy, equilibrium lattice constant, bulk modulus, vacancy formation energy, and the resistivity of the liquid phase were calculated. The sensitivity of the results to various approximations in the model, the volume dependence of the pair potential, and the effects of the ionic core are discussed.

I. INTRODUCTION

Computer simulation using molecular dynamics or Monte Carlo techniques is an attractive way to investigate disordered solids.[1,2] Structural study of lattice defects, alloys, and liquids can be facilitated by starting from an effective pairwise interaction between atoms rather than from the detailed calculation of the whole electronic structure. Computer simulation studies can provide an atomistic understanding of problems of importance to materials science, such as segregation of impurities at grain boundaries, grain boundary structure, diffusion at grain and interphase boundaries, hydrogen embrittlement, and radiation damage.

The key quantity in this approach is an assumed knowledge of the interionic potential. Thus several empirical[3–5] and theoretical[6–8] methods have been used to construct interionic potentials for metals. Consequently many different approaches[3–8] have been proposed. The most popular one,[3–5] adopted by researchers using computer simulation techniques, is the empirical determination of the pair-ion potential. Often a Morse or Lennard-Jones potential is chosen with parameters fitted to reproduce one or more of experimentally verifiable parameters, such as lattice parameter, elastic constants, vacancy formation and migration energies, and cohesive energy of the lattice. Such potentials are short-ranged, contain no Friedel oscillations, and are easy to use in computer simulation studies.

Another scheme[9] is to use empirically determined pseudopotentials as a starting point in the calculation of the interionic potential. The pseudopotentials may be, e.g., empty-core Ashcroft type[10] or Heine-Abarenkov type.[11] The parameters in the pseudopotential can be obtained by fitting certain electronic properties such as Fermi surface topology, electrical resistivity of liquid metal, or spectroscopic data to experiment. It is also possible to calculate pseudopotentials from first principles. These exhibit Friedel oscillations and may be either local, nonlocal, or energy dependent.

The difficulties commonly attributed to the above schemes are twofold. First, there is no guarantee that a pseudopotential or a pair potential fitted to reproduce one experimental parameter can predict another accurately. As a matter of fact, this is expected since interactions important in determining a certain experimental quantity may not be important for another, yet the empirically determined potentials contain this shortcoming. Second, the pseudopotentials used in the calculation of the interionic potential must be weak. However, it has been shown[12] that the electron density determined from a given pseudopotential in linear response theory can be very different from that determined by taking the pseudopotentials to all orders. This implies that an empirically determined pseudopotential cannot always be regarded as weak and thus their use in the computation of the interionic potential is not theoretically justified.

For simple metals, however, the interionic potential can be formally constructed from the first principles via the pseudopotential theory.[6] Rasolt and Taylor[7] have proposed a simple method for constructing the pseudopotential and interatomic potential for metals and alloys. In their approach the induced charge density of an isolated metallic ion in an electron gas is calculated by considering the full ionic potential and then a nonlocal pseudopotential is chosen which reproduces the original nonlinear charge density in linear response theory. In this way the nonlinear effects are partly included in the pseudopotential. Another advantage of this approach is that it is as simple for alloys as it is for pure metals. The pair potentials determined from these pseudopotentials have met with apparent success in calculating phonon spectra in several simple metals[13,14] and also other properties such as vacancy formation energies for alkali metals.[15]

In this paper we report detailed studies of the method of Rasolt and Taylor. For a test metal we have chosen Al, where the high valency of the ion makes the interionic potential sensitive to all approximations of the model. Our method of construction of the pseudopotential is somewhat different from that of Rasolt and Taylor. By taking a Fourier transform of the induced nonlinear charge density we are able to define a local pseudopotential which exactly reproduces the induced density in the linear theory. We have also studied the problems associated with an ion embedded in the electron gas. In addition to the model where the screening of the ion is calculated in a homogeneous electron gas, we also use a model where the ion is embedded in a jellium vacancy. It is shown that the latter model, which is physically more appealing, describes much better the cohesion in Al.

In Sec. II we outline the method of construction of the pair potential from the pseudopotential and give formulas for the total energy in the pseudopotential picture and also in the corresponding pair potential formulation, including all the structure-independent terms. In Sec. III two models for calculation of the induced charge density around the ion are described. The computational limitations and the numerical accuracy are discussed in Sec. IV. The resulting pair potentials and pseudopotentials are used to calculate the total energy of the metal, the equilibrium lattice constant, bulk modulus, vacancy formation energy, and the electrical resistivity of the liquid phase. These results are given in Sec. V where we also evaluate the validity and consequences of the often used approximations about the volume independence of the pseudopotential and pair potential. A discussion of the ion-core contributions to the pair potential is also given in this section. A summary of our results is given in Sec. VI.

II. TOTAL ENERGY IN THE PAIR POTENTIAL FORMULATION

In the pseudopotential formulation, where the interaction between the electrons and the ions in a metal is assumed to be weak, the total energy per atom can be given by the second-order perturbation theory[16,17] as

$$\epsilon_T = Z\epsilon_0(n_0) + \epsilon_M + \epsilon_{\mathrm{BS}} + \frac{1}{N}\sum_{i=0}^{N} \int d^3r\, n_0 W(\vec{r}-\vec{R}_i) \; . \qquad (1)$$

Here N is the total number of atoms, Z is the charge of the metal ion, and $\epsilon_0(n_0)$ is the energy per electron in a homogeneous electron gas of density $n_0 = NZ/V$, V being the volume of the metal. The Madelung energy ϵ_M can be formally written as (throughout this paper we use atomic units)

$$\epsilon_M=\frac{1}{2V}\sum_{\vec{k}\neq 0}\frac{4\pi Z^2}{k^2}[S(\vec{k})-1]\ , \tag{2}$$

where $S(\vec{k})$ is the structure factor defined as

$$S(\vec{k})=\frac{1}{N}\sum_{i,j}\exp[i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)]\ .$$

$W(\vec{r})$ in Eq. (1) is a short-range potential defined through the unscreened local pseudopotential $v(\vec{r})$ as

$$W(\vec{r})=\frac{Z}{r}+v(\vec{r})\ . \tag{3}$$

The so-called band-structure energy ϵ_{BS} in Eq. (1) can be expressed in terms of the structure factor $S(\vec{k})$, bare-ion pseudopotential form factor $v(\vec{k})$, and the dielectric response function $\epsilon(\vec{k})$,[16]

$$\epsilon_{BS}=\frac{1}{2V}\sum_{\vec{k}\neq 0}\frac{k^2}{4\pi}\,|v(\vec{k})|^2 S(\vec{k})\left[\frac{1}{\epsilon(\vec{k})}-1\right]\ . \tag{4}$$

In the pair potential formulation[6] ϵ_M and ϵ_{BS} are combined to form a structure-dependent term and a structure-independent but volume-dependent term. Adding and subtracting the $\vec{k}=0$ component in the sums and defining the pair potential as

$$\begin{aligned}\phi(\vec{r})&=\frac{1}{V}\sum_{\vec{k}}e^{-i\vec{k}\cdot\vec{r}}\left[\frac{4\pi Z^2}{k^2}+\frac{4\pi Z^2}{k^2}\left|\frac{v(\vec{k})k^2}{4\pi Z}\right|^2\left[\frac{1}{\epsilon(\vec{k})}-1\right]\right][S(\vec{k})-1]\\&=\frac{Z^2}{r}\left[1+\frac{2}{\pi}\int_0^\infty dk\,\frac{\sin(kr)}{k}\left|\frac{v(\vec{k})k^2}{4\pi Z}\right|^2\left[\frac{1}{\epsilon(\vec{k})}-1\right]\right]\ ,\end{aligned} \tag{5}$$

one obtains for the total energy

$$\begin{aligned}\epsilon_T=\tfrac{1}{2}\sum_{i\neq 0}\phi(\vec{R}_i)+Z\epsilon_0(n_0)-n_0\lim_{\vec{k}\to 0}\left[\frac{2\pi Z}{k^2\epsilon(\vec{k})}\right]\\+\frac{Z^2}{\pi}\int_0^\infty dk\left|\frac{v(\vec{k})k^2}{4\pi Z}\right|^2\left[\frac{1}{\epsilon(\vec{k})}-1\right]\ .\end{aligned} \tag{6}$$

Now all the structure dependence is included in this sum over pairwise interactions between atoms. It should be noted that in addition to the purely volume-dependent terms in Eq. (6), the total energy depends on volume also through $\phi(\vec{r})$, the volume dependence of which derives from the volume dependence of $\epsilon(\vec{k})$ and $v(\vec{k})$.

Finally, we note that for a perfect lattice the total energy in the pseudopotential formulation simplifies to[16]

$$\begin{aligned}\epsilon_T=Z\epsilon_0(n_0)+\frac{Z^2\alpha}{2R_{WS}}+n_0W(\vec{q}=0)\\+\tfrac{1}{2}n_0\sum_{\vec{G}\neq 0}\frac{\vec{G}^2}{4\pi Z}\,|v(\vec{G})|^2\left[\frac{1}{\epsilon(\vec{G})}-1\right]\ ,\end{aligned} \tag{7}$$

where α is the Madelung constant, R_{WS} is the Wigner-Seitz radius, and $\vec{G}$ is the reciprocal-lattice vector. For a perfect metal the pseudopotential formulation, Eq. (7), is more practical than the pair potential formulation, Eq. (6), since the sum over the reciprocal-lattice vectors converges more rapidly than the sum over the pair potentials in Eq. (6).

III. SINGLE-ION APPROACH TO THE CALCULATION OF PSEUDOPOTENTIAL

The approach of Rasolt and Taylor[7] is based on the idea that the electron density plays a central role in calculating the cohesive energy and other ground-state properties of a metal. Thus their theory emphasizes the need for the calculation of a pseudopotential that correctly reproduces the nonlinear electron density around a metal ion. To include the nonlinear effects they define an effective pseudopotential so that it gives in the linear theory the correct (nonlinear) electron density around the true pseudopotential, or the metal ion outside the core region. This pseudopotential is then used to calculate the pair potential.

The first step in this approach, which we follow, is to calculate the induced charge density around an ion. This is achieved by embedding a point charge into a homogeneous electron gas and calculating the screening cloud self-consistently using the Kohn-Sham method.[18] The point charge describes the charge on the nucleus of the metal atom (which has a value of $A=13$ for Al). The induced density around the ion is defined as

$$\delta n(\vec{r})=n(\vec{r})-\sum_i |\psi_i^{\text{ion}}|^2-n_0 \ . \tag{8}$$

Here $n(\vec{r})$ is the total electron number density and ψ_i^{ion} are the bound electron wave functions corresponding to the ion core. The charge neutrality requires that

$$\int d^3r\,\delta n(\vec{r})=Z \ . \tag{9}$$

Rasolt *et al.*[7,13] used local exchange only (no correlation) in their Kohn-Sham equations and the core states were frozen in the self-consistent procedure. We have used the Gunnarsson-Lundqvist form in the exchange-correlation potential[19] and included the core states in the self-consistent procedure. We also study two different models for embedding the nucleus into the electron gas describing the metal.

A. Atoms in jellium

In this model the nucleus is embedded into a homogeneous electron gas and thus the external positive charge density to which the electrons respond is

$$n_+^{(a)}(\vec{r})=A\delta(\vec{r})+n_0 \ , \tag{10}$$

where A is the atomic number of the metal atom nucleus. The corresponding electrostatic potential can be calculated by solving Poisson's equation,

$$\nabla^2 V_{\text{es}}(\vec{r})=-4\pi[n(\vec{r})-n_+(\vec{r})] \ . \tag{11}$$

The effective electron-ion potential including many-particle interactions can be approximated by the local-density formulation,

$$V_{\text{eff}}(\vec{r})=V_{\text{es}}(\vec{r})+V_{\text{xc}}[n(\vec{r})] \ , \tag{12}$$

where V_{xc} is the exchange-correlation potential in the local-density theory. The induced charge density can then be calculated by solving the Schrödinger-type equation,

$$[-\tfrac{1}{2}\nabla^2+V_{\text{eff}}(\vec{r})]\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r}) \ , \tag{13}$$

with

$$n(\vec{r})=\sum_i |\psi_i(\vec{r})|^2 \ , \tag{14}$$

and ϵ_i the eigenvalue of the state ψ_i. Equations (11)–(14) can be solved self-consistently.

In the case of aluminum, we carried out these calculations fully self-consistently by substituting $A=13$ in Eq. (10). In solving Eq. (13), all possible bound states had to be calculated. Thus the core-electron orbitals were allowed to relax in the presence of a homogeneous electron-gas background. In addition to $1s^2 2s^2 2p^6$ bound states, we also found a weak $3s^2$ bound state with a binding energy of $E=-0.248$ eV. Since the wave function for this energy state is rather long ranged, we have assumed it to belong to the scattering states while calculating the induced conduction-electron charge density in Eq. (8). Equation (9) then integrates to $Z=3$.

B. Atoms in a jellium vacancy

In the jellium model discussed above the positive charges of the ions are replaced by a neutralizing homogeneous background charge. When an ion is embedded into this jellium, there is a local increase in the amount of positive charge. To retain the correct amount of positive charge we have to remove the positive background charge in the Wigner-Seitz cell containing the ion. This model of placing the ion or nucleus into a jellium vacancy has been widely used in studying local electronic properties around metal atoms and impurities in simple metals.[20–23]

The induced density is calculated by taking the difference

$$\delta n(\vec{r})=n(\vec{r})-n_v(\vec{r})-\sum_i |\psi_i^{\text{ion}}|^2 \ , \tag{15}$$

where $n(\vec{r})$ and ψ_i^{ion} are, respectively, the electron density and the bound state wave functions calculated with the external positive background charge density

$$n_+^{(b)}(\vec{r})=A\delta(\vec{r})+n_0\Theta(r-R_{\text{WS}}) \ . \tag{16}$$

$n_v(\vec{r})$ is the electron density around a pure jellium vacancy, i.e., it corresponds to an external positive charge,

$$n_+^{(v)}(\vec{r})=n_0\Theta(r-R_{\text{WS}}) \ . \tag{17}$$

As in the previous case, the induced charge density in Eq. (15) integrates to $Z=3$ for Al [see Eq. (9)]. In this model no $3s$ bound states were found for Al. The repulsive potential introduced by the vacancy was enough to kick the shallow $3s$ bound states found in atom in jellium model to the continuum.

The induced charge densities of the two models would be identical to each other if the electrons would respond linearly to both the nucleus and the vacancy. However, this is not the case, as our results show in the next section.

Having obtained the induced electron density in either model the computation of the pseudopotentials and interionic potentials follow the same common procedure as outlined below. In linear response theory,

$$\delta n(\vec{q}) = \left[\frac{1}{\epsilon(\vec{q})} - 1 \right] \frac{q^2}{4\pi} v(\vec{q}) , \tag{18}$$

where $\delta n(\vec{q})$ is the Fourier transform of the induced charge density and $v(\vec{q})$, as before, is the bare-ion pseudopotential form factor. We calculate $\delta n(\vec{q})$ from the self-consistent induced densities where the electron-ion interaction is taken to all orders. Equation (18) then yields an effective local pseudopotential which, when used in the linear response theory, is guaranteed to yield the exact induced density. In this way, as noted by Rasolt and Taylor,[7] some of the nonlinear screening effects are included into the pair potential calculated from this pseudopotential.

Rasolt and Taylor have used parametrized local[24] or nonlocal[7,13] formulas for the pseudopotential, the parameters of which are fitted to give the correct induced density. Using a local potential, the direct Fourier transform uniquely gives the pseudopotential, and not much is gained by an analytical form of the pseudopotential since the complexity of the dielectric function nevertheless usually requires numerical computations. On the other hand, when a nonlocal pseudopotential is used additional parameters are needed to specify the form factor, i.e., one can construct different nonlocal pseudopotentials which give exactly the same induced density, but result in different pair potentials. To avoid this ambiguity we have evaluated only the local pseudopotentials.

IV. NUMERICAL PROCEDURE AND COMPUTATIONAL ACCURACY

Since the numerical accuracy of the computed interionic potentials depends rather sensitively on the computational procedure and input parameters, we devote this section to a detailed discussion of the limitations of this kind of calculations. By so doing, it is hoped that an appreciation of the various problems involved in the calculation of interionic potentials is developed, thereby producing a better feeling for the reliability of the various predictions.

The induced density $\delta n(\vec{r})$ was computed using a density functional computer code where the bound states are obtained via a modified Herman-Skillman subroutine.[25] We have used the same $\vec{r}$-space division as in Herman-Skillman and the boundary condition which requires the effective potential to be zero for $r \gtrsim 13.5a_0$ (a_0 being the Bohr radius). For the calculation of the scattering state contribution to $\delta n(\vec{r})$, we have retained as many as seven partial waves ($l_{\max} = 7$) and divided the region $0 \le k \le k_F$ into 30 intervals. The resulting charge density and potentials were self-consistent to an accuracy of better than 0.01%. The accuracy in the Friedel sum rule was better than 1%.

In using the induced density to calculate the pseudopotential in Eq. (14), it should be remarked that $\delta n(\vec{r})$ contain wiggles at small $\vec{r}$ values due to the orthogonalization of conduction states to core orbitals. These should be missing in the pseudodensity. We achieved this by smoothing $\delta n(\vec{r})$ in terms of a polynomial at small $\vec{r}$, namely,

$$\delta n(\vec{r}) = A - Br^2 , \quad r \le R_0 \tag{19}$$

where A, B, and R_0 were chosen so that $\delta n(\vec{r})$ and $(\partial/\partial r)[\delta n(\vec{r})]$ are continuous at R_0, and Eq. (9) be satisfied by the smoothed density. Thus no adjustable parameters were introduced in the smoothing procedure. The absence of a linear term in Eq. (19) is due to the assumption that the pseudopotential $v(\vec{r})$ is constant near the origin. This is the case for all pseudopotentials of the Ashcroft[10] or Heine-Abarenkov type.[11] Higher order polynomials could, perhaps, also be fitted to the $\delta n(\vec{r})$ in Eqs. (8) or (15) near the origin by requiring that the higher order derivatives be zero at R_0. However, this may cause unwarranted oscillations in $\delta n(\vec{r})$ and was not attempted.

The Fourier transform of the induced charge density can now be evaluated from

$$\delta n(\vec{q}) = \int d^3r\, e^{i\vec{q}\cdot\vec{r}} \delta n(\vec{r}) . \tag{20}$$

In our calculation, the maximum $\vec{r}$ value $R_{\max}$ used for integration of $\delta n(\vec{r})$ was $13.5a_0$. Since it is essential to integrate Eq. (20) to infinity, we have fitted our calculated $\delta n(\vec{r})$ to an asymptotic form beyond $R_{\max}$, i.e.,

$$\delta n(r > R_{\max}) = A \cos(2k_F r + \theta)/r^3 . \tag{21}$$

The constants A and θ were obtained from our calculated $\delta n(\vec{r})$ for $r \simeq 13a_0$. To check the numerical accuracy of the Fourier transform, we have recalculated $\delta n(\vec{r})$ from $\delta n(\vec{q})$. The maximum error at any $\vec{r}$ value between the original $\delta n(\vec{r})$ and that obtained from the Fourier transform of $\delta n(\vec{q})$ was

0.1%.

From Eqs. (5) and (18), we compute the interionic potential. It should be emphasized that the Friedel oscillations in the interionic potential are sensitive to the asymptotic region of $\delta n(\vec{r})$. For example, an error of 0.1% in $\delta n(\vec{r})$ may cause as much as 1% error in the interionic potential.

A final note in this section concerns the dependence of the interionic potential on the choice of the dielectric function $\epsilon(\vec{q})$. Unfortunately, the interionic potential is sensitive to the dielectric function,[26,27] especially near the first minimum.

To be consistent with the local-density approximation used in the Kohn-Sham method, it seems natural to choose a dielectric function which involves essentially the same approximation. If the energy or the chemical potential of the electron gas is $\mu(n_0)$, $\epsilon(\vec{q})$ can be constructed as[28]

$$\epsilon(\vec{q})=1+\frac{4\pi}{q^2}\pi(\vec{q}) , \tag{22}$$

where

$$\pi(\vec{q})=\frac{\pi_0(\vec{q})}{1-(4\pi/k_F^2)(1-L)\pi_0(\vec{q})} , \tag{23}$$

with

$$L=\frac{\pi_0(0)}{\pi(0)}=\frac{\partial\mu}{\partial r_s}\bigg/\frac{\partial\epsilon_F}{\partial r_s} , \tag{24}$$

and

$$\mu(r_s)=\epsilon_F(r_s)+\mu_{\text{xc}}(r_s) . \tag{25}$$

Here $\pi_0(\vec{q})$ is the usual Lindhard polarizability. The way in which the exchange and correlation is included in this dielectric function essentially corresponds to the local-density approximation in the density-functional theory used to calculate the original nonlinear induced density. The dielectric function by construction satisfies the compressibility theorem, the importance of which in the connection of the pair potential has been pointed out by Duesbery and Taylor.[27] To test the sensitivity of $\phi(\vec{r})$ on the $\epsilon(\vec{q})$ in our case, we artificially changed $\epsilon(\vec{q})$ by taking $1-L$ in Eq. (23) to be 5% smaller than the correct value [the maximum change in $\epsilon(\vec{q})$ was about 1%]. This changed the pair potential at first minimum by as much as 0.03 eV, to be compared to the maximum amplitude of the Friedel oscillations which is about 0.06 eV (see Fig. 3). This caused an error of about 0.1 eV in the cohesion energy and in the vacancy formation energy.

V. RESULTS

A. Electron charge density, pseudopotentials, and interionic potentials

In Fig. 1 we have plotted the induced charge density around an Al ion in a homogeneous electron gas of density $r_s=2.07$ (corresponding to bulk Al) in the atoms in jellium and atoms in jellium vacancy models. The broken curve corresponds to the jellium model while the solid curve represents vacancy model. Note that the wiggles at small r, as mentioned earlier, are due to the core orthogonalization. The induced charge densities in the two models are clearly different at all r values. There is a significant shift in the phase of the Friedel oscillations in addition to a small difference in the amplitude of the oscillations. In addition to the two models used here, there exist several other ways to estimate the induced electron density. The effect of the surrounding lattice can be mimicked by using the spherical solid model of Almbladh and von Barth[29] or the variational self-consistent method.[30] Calculations made for light impurities[22,31] indicate that all these methods result in different density profiles, especially in the region of Friedel oscillation.

The bare-ion pseudopotentials calculated from the induced densities using Eq. (18) are plotted in Fig. 2. Of the various popular local model potentials (Ashcroft, Heine-Abarenkov, Shaw, etc.) none gives a particularly good fit to the form factors in Fig. 2. The simple empty-core Ashcroft potential ($\sim\cos qr_c$) comes closest to the solid line in Fig. 2 with the core radius $r_c\approx1.42$ a.u. This value is somewhat larger than the one ($r_c=1.12$ a.u.) which is obtained by adjustment to explain Fermi surface data.[17] While the oscillations are in phase, the amplitudes corresponding to the two ways of embedding are very different from each other. Figure 3 shows the corresponding interatomic potentials. They differ drastically from each other, and also from the potential of Rasolt *et al.*,[13] where the first nearest-neighbor site was in the repulsive part of the potential. In our calculation the nearest atom site is around the first minimum of the potential.

B. Total energy, equilibrium lattice constant, and bulk modulus

The results for the different energy terms and for the total energy per electron, calculated using Eq.

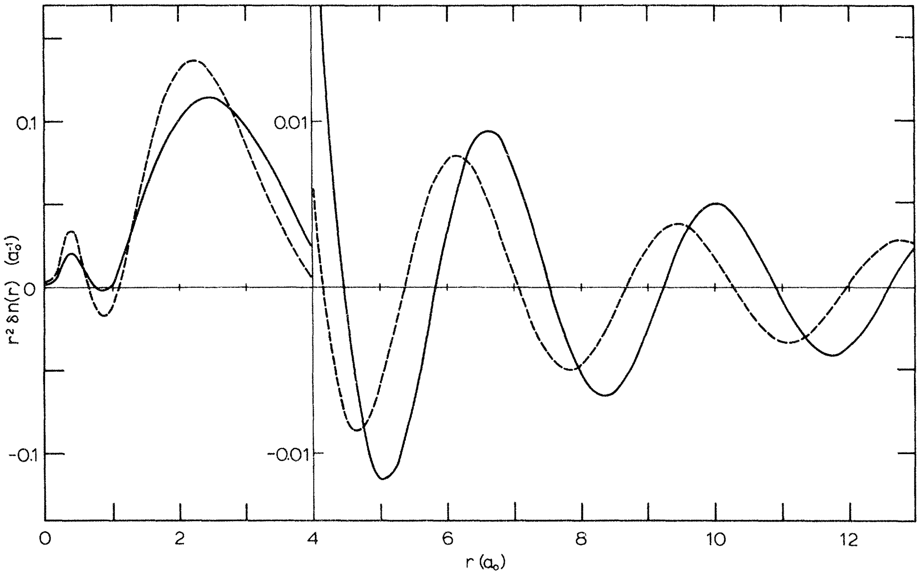

FIG. 1. Radial distribution of perturbed electron charge density in atomic units around an Al nucleus embedded in jellium with the density parameter $r_s = 2.07$ (corresponding to Al). The solid line is the atoms in jellium vacancy model whereas the broken line is the atoms in jellium model. The wiggles at small r are due to core-orthogonalization. Note that the electron densities at large r are shown on a magnified scale.

(7), are given in Table I. The experimental result for ϵ_T, given in Table I, is the sum of heat of sublimation and the ionization energy of Z electrons. In the pair-potential formulation, Eq. (6) gives naturally the same value for the total energy. The sum over the pair potentials turns out to be only a minor part (0.22 eV in the atoms in jellium model and 0.02 eV in the atoms in jellium vacancy

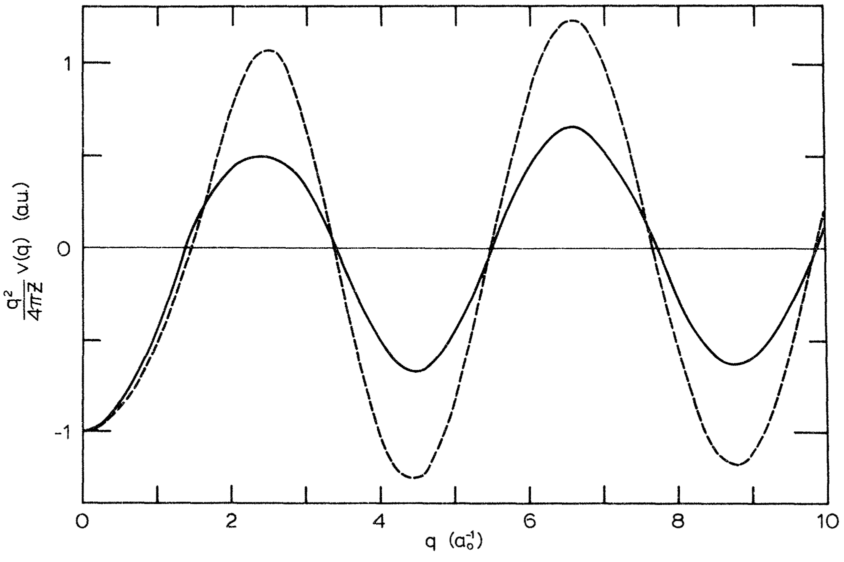

FIG. 2. The wave-vector dependence of the bare-ion pseudopotential of Al (in atomic units, 1 a.u. = 27.2 eV). The rest of the legend is same as in Fig. 1.

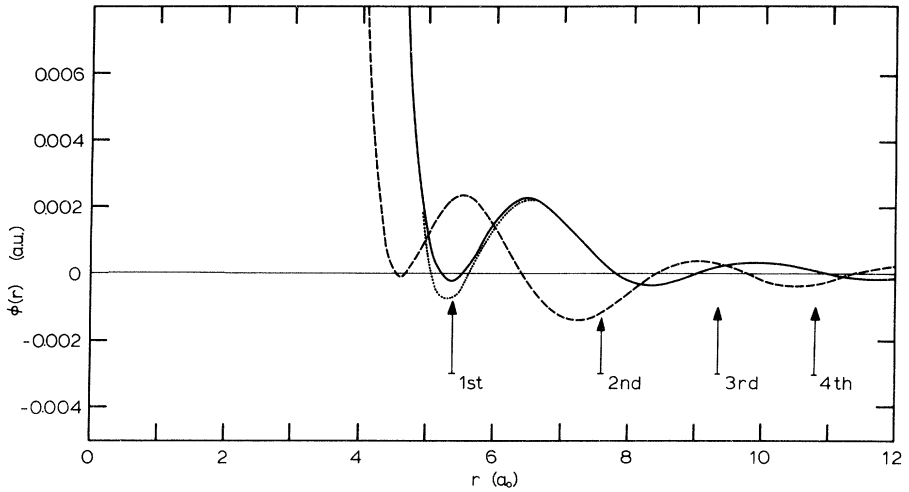

FIG. 3. Interionic potentials of Al. The arrows indicate the position of the near neighbors. The dotted line demonstrates the sensitivity of the pair potential on the dielectric function. (See Discussion at the end of Sec. IV.)

model) of the total energy. Thus the energy is almost totally determined by the structure-independent terms.

In calculating the equilibrium lattice constant and the bulk modulus the volume dependence of the pseudopotential and the pair potential has to be considered. In the present model they both depend on volume and one should, in principle, repeat the entire calculation for different electron gas densities. This would lead to a volume-dependent pair potential, which would be impractical in many computer simulation applications. To estimate the

TABLE I. Binding energy per electron, equilibrium lattice constant, and bulk modulus for Al. Numbers in parentheses are determined using the calculated equilibrium lattice constants.

Contributions to binding energy (eV)	"Atoms in jellium" model	"Atoms in jellium vacancy"	Experimental result
ϵ_M/Z	-24.5	-24.5	
$\epsilon(n_0)/Z$	-0.5	-0.5	
$n_0 W_R(q=0)/Z$	4.5	6.0	
ϵ_{BS}/Z	-1.4	-0.4	
ϵ_T/Z	-21.8	-19.4	-18.8
Equilibrium lattice constant (in units of 4.05 Å)	0.86^{a} 0.67^{b}	0.99^{a} 0.95^{b}	1.00
Bulk modulus (10^{10} dyn/cm^2)	-130 (300^{a}) -130 (8900^{b})	74 (87^{a}) 52 (390^{b})	76

[a] Pair potential volume independent.

[b] Pseudopotential volume independent.

errors made in assuming the pair potential to be volume independent we calculated the equilibrium lattice constant and bulk modulus in two different approximations: (i) Only the pseudopotential form factor was assumed to be volume independent, and (ii) the pseudopotential, the dielectric function, and the pair potential were *all* assumed to be volume independent. The assumption of the volume independence of the pseudopotential is physically justified, since the pseudopotential represents an effective potential due to an ion and thus depends only weakly on the surrounding electron gas. To obtain a volume independent pair potential from Eq. (5) one has to assume that the dielectric function is volume independent. The large differences in the equilibrium lattice constants and bulk moduli in Table I due to different approximations indicate the importance of the volume dependence of the pair potential. This point has recently been stressed by Taole and Glyde,[32] who evaluated the contribution to the longitudinal elastic constants C_{11} and C_{12} from the volume dependence of the screening. There is also a contribution to the bulk modulus from the volume forces; Taole and Glyde estimated this from the observed deviation from the Cauchy relation ($C_{12} \neq C_{44}$). In the present work, the pseudopotential of the atoms in jellium vacancy model gives results which are in much better agreement with the experimental values than those calculated in the atoms in jellium model. The total energy as a function of the lattice constant is plotted in Fig. 4 for the different models.

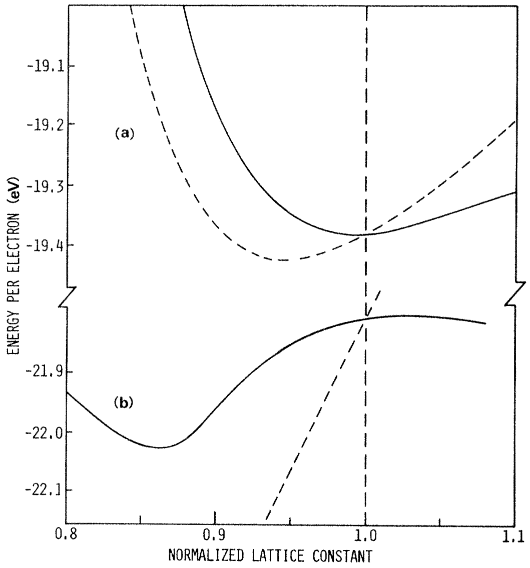

FIG. 4. Total energy per electron as a function of the lattice constant (in units of 4.05 Å) calculated in the atoms in jellium model (a) and in the atoms in jellium vacancy model (b). The solid lines are calculated by assuming both the pair potential and the pseudopotential to be volume independent, whereas in the dashed lines only the pseudopotential is assumed to be volume independent.

C. Vacancy formation energy

The vacancy formation energy is given by

$$E_v = E_v^V - p\Omega_0 \,, \tag{26}$$

where E_v^V is the constant-volume vacancy formation energy, Ω_0 is the atomic volume, and p the pressure of the metal. Within second-order perturbation theory, E_v^V depends only on the structure of the metal. Neglecting the relaxation of atoms around the vacancy, it can be written as

$$E_v^V = -\tfrac{1}{2} \sum_{i \neq 0} \phi(\vec{R}_i) - \tfrac{1}{6} \sum_{i \neq 0} R_i \frac{\partial \phi(R_i)}{\partial R} \,. \tag{27}$$

For an oscillating pair potential, this sum is not trivial to compute.[33] In some cases the asymptotic part can be summed exactly.[34]

The pressure of the metal can be calculated assuming either that the pseudopotential is volume independent or that both the pseudopotential and pair potential are volume independent. Both approximations were used and the results are given in Table II. Again the atoms in jellium vacancy model gives better agreement with the experimental result. The negative constant-volume vacancy formation energies would indicate that the perfect fcc lattice is not stable at the normal lattice constant.

It is known[12,35] that in the case of polyvalent metals the linear screening theory can not describe correctly the screening around a vacancy (the large difference between the two density profiles in Fig. 1 is also a manifestation of this) and thus it is not expected that a theory based on linear screening could give quantitatively correct vacancy formation energies. Although in the present approach part of the nonlinearity is (perhaps artificially) taken into account in determining the pseudopotential, the apparent good agreement with experiment of the atoms in jellium vacancy model should be taken with caution since the constant volume vacancy formation energy is negative. One should again note the large difference in results depending on

TABLE II. Vacancy formation energy E_v for the different models. E_v^V is the constant volume vacancy formation energy and $\Omega_0 p$ the pressure term in Eq. (22).

Model	E_v^V (eV)	$\Omega_0 p$ (eV)	E_v (eV)
"Atoms in jellium"	-0.6	-0.5[a]	-0.1[a]
		-5.0[b]	$+4.4$[b]
"Atoms in jellium vacancy"	-0.2	-0.2[a]	-0.0[a]
		-1.4[b]	$+1.2$[b]
Experimental result (Ref. 42)			$+0.7$

[a] Pair potential volume independent.

[b] Pseudopotential volume independent.

which quantities are assumed to be volume-independent.

D. Electrical resistivity of the liquid phase

Another sensitive test for the pseudopotential form factor is the electrical resistivity ρ_R in the liquid phase. It can be calculated from the Ziman formula[36]

$$\rho_R = \frac{3\pi}{\hbar e^2}\frac{1}{v_F^2\Omega_0}\int_0^1 d\left[\frac{q}{2k_F}\right] v_s^2(q) I(q) 4\left[\frac{q}{2k_F}\right]^3 , \tag{28}$$

where $v_F = \hbar k_F/m$ is the Fermi velocity. $I(q)$ is the liquid interference function and $v_s(q)$ is the *screened* pseudopotential form factor. The Ziman theory of transport properties for liquid metals is very successful when both the interference function and the pseudopotential form factors are accurately known. The interference function which contains the entire structural information can be found from neutron and/or x-ray scattering experiments. The validity of Eq. (28) relies on the assumed weakness of the pseudopotential and is based on the Born-approximation. Thus one requires that $I(q)v_s^2(q)/\epsilon_F^2 << 1$. We have plotted this quantity versus $0 \le k \le k_F$ in Fig. 5. The results clearly indicate that the Born approximation is valid.

Using Eq. (28), we have calculated the resistivity of liquid Al near the melting point. We have used for $I(q)$ the hard-sphere form of Ashcroft and Lekner[37] with the packing density $\eta = 0.46$ mainly because it is in excellent agreement with experiment[38] for q values of interest and because the experimental $I(q)$ for small q values is not accurately known. The results are given in Table III. Again the atoms in jellium vacancy model gives much

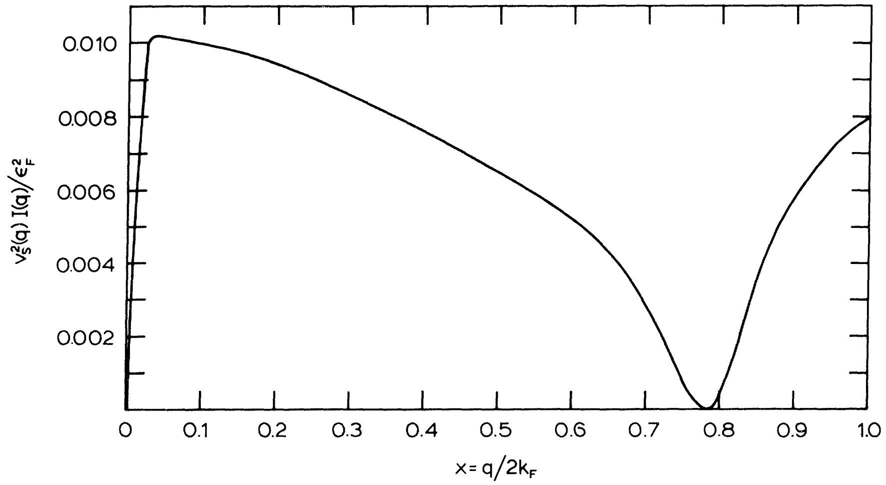

FIG. 5. Test for the validity of the Born approximation in the calculation of liquid metal resistivity. It is required that $V_s^2(q)I(q)/\epsilon_F^2 << 1$ for $0 \le q \le 2k_F$.

TABLE III. Electrical resistivity ρ_R ($\mu\Omega$ cm) of liquid Al at 667 °C.

Model	Theory	Expt.
"Atoms in jellium"	30.6	
"Atoms in jellium vacancy"	24.9	24.7

better agreement with experiment[39] than the atoms in jellium model.

We should remark that ρ_R in Eq. (28) is not only sensitive to the pseudopotential form factor and interference function, but also to the dielectric response function. Sharp and Smith[40] have discussed the dependence of ρ_R on various parameters. It should be noted that we took for the liquid structure factor the hard-sphere result, although to be completely consistent it should have been determined from the calculated pair potential, e.g., using Monte Carlo or integral-equation methods. However, the structure factor depends mainly on the repulsive part of the potential and the packing fraction $\eta = 0.46$ corresponds to a hard-sphere potential radius of 4.6 a.u. which is in good agreement with the radius of the strong repulsive part of the calculated pair potential of the atoms in jellium vacancy model (see Fig. 3).

E. The effects of the ion core on the pair potential

An interesting application of the present *ab initio* pair potential would be the calculation of the dynamical structure factor for the liquid phase using molecular dynamics techniques. Recent work by Ebbsjo *et al.*[41] indicates the existence of collective density excitations for wave vectors $k \leq 2$ a.u., a result somewhat sensitive to the choice of the pair potential.

The developments leading to the pair potential discussed above are based on two fundamental assumptions. *First,* it is assumed that the interionic separations considered are much in excess of ionic diameters. This assumption is usually satisfied for most simple metals under equilibrium conditions (although it may not hold under compression or for nonequilibrium processes such as interstitial migration), but is more questionable for metals with large (d-electron) ionic cores, e.g., noble metals. In cases where the short-range pair potential is needed, the direct screened Coulomb interaction considered above has to be augmented by the core-core exchange repulsion. The values of this contribution, often approximated by the so-called Born-Mayer form $\phi_{\text{BM}}(r) = Ae^{-Br}$ are difficult to evaluate, and the quoted values depend strongly on the representation chosen for the electron states. In the case of Al, Benedek[43] has obtained from a Hartree-Fock calculation with ionic wave functions $\phi_{\text{BM}}(r) \cong 4230e^{-r/0.223}$ a.u., which is insignificant in comparison with the Coulomb term for separations $r \gtrsim 4$ a.u. Certainly more theoretical efforts directed towards a reliable determination of the core-core exchange repulsion in general would be highly desirable.

The *second* assumption behind the standard pair potential formulation is that of a rigid ionic core. This view ignores the possibility of fluctuation or polarization effects, which typically manifest themselves as dispersion or van der Waals forces that are important in, e.g., condensed rare gases. Allowing the ionic cores to fluctuate in a metallic environment will (within perturbation theory) lead to three kinds of additional contribution to the total energy: (i) the direct Coulomb interaction between the static ions is screened by the fluctuating core electrons; (ii) the electron-ion potential leading to the band-structure energy is also screened; (iii) there is a van der Waals—type interaction between the fluctuating cores, screened by the conduction electrons. As far as the interionic potential is concerned, the effect of the contributions (i) and (ii) can be estimated by replacing

$$v(\vec{q}) \rightarrow \frac{v(\vec{q})}{\epsilon_c(\vec{q})}\ , \tag{29}$$

where $\epsilon_c(\vec{q})$ is the dielectric function of the polarizable ionic cores. In the important long-wavelength limit,

$$\epsilon_c(\vec{q} \rightarrow 0) = 1 + \frac{4\pi N}{V}\alpha(0)\ , \tag{30}$$

where $\alpha(0)$ is the static polarizability of the ion core. In the large $\vec{q}$ limit, $\epsilon_c(\vec{q})$ will approach unity proportional to q^{-4}.

The dynamically screened van der Waals contribution to the pair potential has recently been considered by Mon *et al.*,[44] who suggested it as the physical origin of the structural anomalies of some liquid simple metals (Ga, Sn). These anomalies show up as weak subsidiary maxima of the static structure factor observed by x-ray or neutron diffraction. The corresponding feature in the ion-ion interaction is a softening (the screened van der Waals term is always attractive) of the pair potential which in extreme cases can lead to additional minima at relatively short range. The effect is largest for highly polarizable ionic cores. Assuming the frequency-dependent polarizability of metal ion core to be of the Lorentz form

$$\alpha(\omega)=\frac{\alpha(0)}{1-(\omega/\omega_0)^2}\,, \tag{31}$$

where ω_0 is a characteristic frequency (ω_0 is typically $1-2$ a.u.), one obtains within the Drude model the following order-of-magnitude estimate (assuming fluctuating point dipoles) for the screened van der Waals contribution to the pair potential ϕ_{vdW}:

$$\phi_{\mathrm{vdW}}(r)\cong-\frac{3}{4}\frac{\alpha(0)^2}{(1+\omega_P/\omega_0)^3}\frac{\omega_0}{r^6}\,, \tag{32}$$

where ω_P is the plasma frequency.

For Al, the polarizability is presumably very small (for the free ion Al^{3+}, $\alpha(0)\cong0.36$ a.u.), and consequently the effects of both ionic background screening and screened van der Waals interaction are insignificant for normal metallic separations. However, even for the simple metals this is generally not the case.[43,44] This underscores the importance of obtaining reliable results for the static and frequency dependent polarizability of an atom embedded in a metal. Polarizability calculations[45] have recently been carried out successfully for free atoms using the density-functional theory; it would seem very worthwhole to extend such methods to the case of the atom in jellium vacancy considered in the present work. Then one would be in a position to obtain both the statically screened Coulomb and the dynamically screened van der Waals contributions on essentially equal footing, including the effect of the metallic environment beyond linear response.

VI. DISCUSSION AND CONCLUSION

In this paper we have outlined a method, similar in principle to that of Rasolt and Taylor,[7] to compute the interionic potential of a simple metal. The method consists of first calculating the induced electron density self-consistently around a metal nucleus embedded in a homogeneous electron gas. A pseudopotential is then constructed which, in linear response theory, reproduces the calculated self-consistent electron density exactly. The interionic potential can then be computed from the pseudopotential form factor and the dielectric function.

It is shown that the electron density, the pseudopotentials and the interionic potentials are sensitive to the models that represent the metal atom in a solid. Furthermore, as is well known, the interionic potential is also sensitive to the dielectric function. Using the computed potentials, we have investigated various electronic properties, such as binding energy of an electron in a metal, equilibrium lattice constant, bulk modulus, vacancy formation energy, and the electrical resistivity of the liquid phase. The atoms in jellium vacancy model gives rather good agreement with the experimental results, whereas the atoms in jellium model fails already in describing the cohesion of the perfect metal. An additional reason for preferring the atoms in jellium vacancy model is based upon the following physical picture: If we remove an atom from a metal, a vacancy is left behind. Thus the screening charge associated with one ion occupying a substitutional site is the electron density of a perfect metal minus that of a metal with a vacancy.

In computing the charge densities the effect of the discrete lattice has been ignored. In a simple metal like Al the lattice effects are generally regarded to be small. In any case, incorporating these effects using the spherical solid model or the variational self-consistent model would lead to slightly different charge densities compared to the atoms in jellium vacancy model. The effect of the lattice on the pair potentials and other calculated quantities has to be investigated before the validity of the present approach can be fully assessed. However, the present calculation clearly shows that in the jellium model one has to embed the ion into a jellium vacancy in order to get a reasonable description for the induced charge density.

The pseudopotential used in our calculation is local. Rasolt and Taylor and Dagens *et al.*[13] have used a parametrized nonlocal pseudopotential in an otherwise rather similar calculation. They have not carried out the direct Fourier transform of the charge density to get the correct local pseudopotential, and thus the importance of the nonlocality of the pseudopotential is not yet completely clear. The induced density can of course be fitted also by a nonlocal pseudopotential, but this involves additional parameters (the form of the nonlocality) which have to be calculated, e.g., by fitting some of the band-structure properties. In their embedding scheme Dagens *et al.*[13] used a method which parallels that of the atoms in the jellium model. However, they used linear screening theory in calculating the electron density n_V around the vacancy. This gives a slightly different induced electron density, since the linear screening theory is not able to describe correctly the electron density around a vacancy.[12] On the other hand, Dagens *et al.*[13] used a trapezoidal background charge density for a vacancy, which makes the use of linear screening more justified. In addition, the main emphasis of their study has been in alkali metals,[13–15] where the difference between our two models is also expected to be smaller than in Al. In alkali metals the linear screening describes a vacancy much better than in polyvalent metals like Al. The effect of the volume dependence of the pair potential on various electronic properties was estimated and found to be large. Thus caution should be taken in applying the pair potentials in problems which involve volume changes.

Another method of computing the interionic potential directly would be to study the interaction energy of two atoms separated by a distance r in a homogeneous electron gas using the Kohn-Sham formalism. This method requires the solution of a two-center problem and is numerically difficult. The same questions concerning the embedding atoms in the jellium would also arise in this approach.

One may question the need for going into the detailed calculations for computing the interionic potential particularly when such information can be obtained empirically by fitting to certain experimental data. The merit of the first-principles calculations is that they give physical insight to the form of the pair potential and reveal the sensitiveness of it to various approximations and parameters that enter into the calculations. Also the applicability of the potential to various problems can be evaluated. An accurate determination of an interatomic potential including all lattice and many-body effects is indeed difficult. Therefore, the correctness of an interatomic potential, empirical or otherwise, that reproduces a certain kind of experimental data should be assessed with caution.

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*Present address.

†Permanent address: Department of Physics, University of Jyväskylä, SF-40720, Jyväskylä, Finland.

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