PHYSICAL REVIEW B **81**, 224113 (2010)

Pair potentials for simple metallic systems: Beyond linear response

J. A. Porter
Division of Natural Sciences, New College of Florida, Sarasota, Florida 34243, USA

N. W. Ashcroft and G. V. Chester
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA

(Received 25 March 2010; revised manuscript received 11 May 2010; published 23 June 2010)

The formalism of electron response theory is extended to second order in a perturbing pseudopotential, and the consequences for effective ionic pair potentials of simple metals under standard conditions are then examined. Inclusion of second-order response terms in the pair potentials leads to the potential minima for sodium, magnesium, aluminum, and metallic silicon being located quite close to the experimental nearest-neighbor distances in the respective crystalline solids. Second-order effects are found to become increasingly important with higher valence. As a test case, it is also found that, for an assumed metallic form of hydrogen, inclusion of second-order response terms is insufficient to reproduce the experimental intramolecular distance under standard conditions: higher-order response terms are necessary to obtain the correct (Heitler-London-type) result. For any element treatable by response methods, the results further show that neglect of even one of the second-order response terms may significantly impact the determination of the pair potential.

DOI: 10.1103/PhysRevB.81.224113 PACS number(s): 34.20.Cf

I. INTRODUCTION

In contrast to semiempirical approaches, it is possible to derive interionic potentials for "simple" metals (where valence and core electrons are well separated in energy) from fundamental considerations[1,2] as explicit functions of the average electron density. The approach is based on electron response theory, in which the electron density induced by the presence of ions is expanded (in $\vec{k}$ space) as a sum of terms, the first of which is linear in the electron-ion interaction, with all other terms being both nonlinear *and* successively higher order in the electron-ion interaction. The mth term in the expansion ($m=1$ being the linear term) is governed by the mth-order *response function* $\chi^{(m)}(m\geq 1)$.[2] It can be shown that the linear term yields purely density-dependent expressions ("volume terms") as well as pair potentials that explicitly depend not only on ionic coordinates but also on the average electron density $\rho_e=N_e/V$, where N_e is the number of electrons and V is the system volume (both taken as macroscopic). Nonlinear terms yield additional contributions not only to the volume terms and the pair potentials but also to triplet (three-body) and higher-order (four-body, five-body, etc.) potentials. So far as is known, the convergence of these multi-ion interaction expansions (for arbitrary pseudopotentials and densities) has not been rigorously established.

In this paper, we present the first part of a study that will examine the pair and triplet potentials obtained analytically by extending the response theory formalism to include contributions from second-order (nonlinear) response. This paper focuses on pair potentials obtained at atmospheric pressure; since our primary interest lies in position-dependent potentials, the explicit functional forms of the volume terms (which have no direct effect on ionic structure at fixed V) are not specifically displayed. In addition to determining the effects of ionic potentials arising from nonlinear-response terms, we have also been motivated by the following consideration: while there has been considerable previous work on second-order response effects,[3–7] in most cases leading to explicit expressions for the second-order contributions to the total potential (i.e., both pair and triplet potentials), there is minimal agreement on the precise *forms* of the resulting potentials (particularly those of the pair potentials). In addition, we have found the functional forms of the pair (and triplet) potentials presented to date to be insufficiently explicit (and in some cases unduly complicated). The current exposition is aimed at providing greater elucidation of these matters. Finally, because our theory is valid over a wide range of densities, it may be used to model not only commonly regarded simple metals such as sodium, magnesium, and aluminum at atmospheric pressure but also high-pressure phases of these and other simple metals (e.g., lithium and sodium, both of which have seen increased theoretical and experimental interest in recent years[8–14]), liquid silicon (which is metallic[15]), and even metallic (wideband, unpaired) forms of hydrogen, to which response methods have previously been applied.[7] With slight modifications, the formalism that follows may also be extended to wideband (but small-band-gap) semiconductors, such as (solid) silicon and germanium, and even states induced to be metallic by pressure. An eventual goal of this research is to gain insight into the success of the semiempirical potentials (e.g., the Stillinger-Weber and Tersoff potentials[15,16]) used in modeling both solid and liquid phases of silicon.

The outline of the present paper is as follows: in Sec. II, we briefly recapitulate the basic theoretical development leading to volume terms, pair potentials, and triplet potentials, all accurate to second order in the electron-ion pseudopotential (here taken to be local, for simplicity, but the methods can be straightforwardly extended to nonlocal equivalents). Important details concerning the response functions used in this development are presented in the Appendix. In Sec. III, we use the theory to calculate pair potentials for metallic phases of sodium, magnesium, aluminum, silicon, and hydrogen, each at the density corresponding to atmospheric pressure for that element. The extent to which the potentials may account for the experimental nearest-neighbor distances in crystalline structures of Na, Mg, Al, and Si (valence 1, 2, 3 and 4, respectively) is discussed in some detail. In the case of hydrogen, we compare the pair potential with that of Nagao *et al.*[7] at near-atmospheric pressure, and we use this comparison as a springboard to show that each individual contribution to the total pair potential is important and that neglect of any contribution may lead to significant inaccuracies. In Sec. IV, we summarize our findings and outline possible directions for future extensions (to include high-density systems as well as the derivation of the triplet potential and its application to metallic and semiconducting systems).

II. PSEUDOPOTENTIAL THEORY FOR WIDEBAND SYSTEMS

A. Fundamentals: The Hamiltonian

We begin by considering a metal as an electrically neutral, two-component canonical assembly of N_I nuclei (each of mass M and charge $+Z_a e$) and $Z_a N_I$ electrons (each of mass m and charge $-e$), where Z_a is the atomic number. As noted, the entire system is confined to a macroscopic volume V. The Hamiltonian for this system consists of sums of kinetic-energy terms (nuclear and electronic) and (Coulombic) interaction terms (nucleus-nucleus, electron-electron, and nucleus-electron),

$$H = \sum_i \frac{\hat{P}_i^2}{2M} + \sum_j \frac{\hat{p}_j^2}{2m} + \frac{1}{2}\sum_{i\neq i'} \frac{(Z_a e)^2}{|\vec{R}_i - \vec{R}_{i'}|} + \frac{1}{2}\sum_{j\neq j'} \frac{e^2}{|\vec{r}_j - \vec{r}_{j'}|} - \sum_{i,j} \frac{Z_a e^2}{|\vec{R}_i - \vec{r}_j|}, \tag{1}$$

where the $\{\vec{R}_i\}$ and $\{\vec{r}_j\}$ represent nuclear and electronic coordinates, respectively, and the $\{\hat{P}_i\}$ and $\{\hat{p}_j\}$ represent the corresponding momenta.

Under standard conditions, a certain fraction of the electrons (the eventual core electrons) will condense about the nuclei to form N_I ions (each of charge $+Ze$, where Z is the conventional valence). The remaining N_e $(=ZN_I)$ electrons are then taken to be the valence electrons, which, in simple metals (the only type considered in this paper), are assumed well separated in energy from the core electrons, the cores being nonoverlapping. With this redistribution, the resulting Hamiltonian for a system of ions and valence electrons is given (to within the condensation energy per ion) by

$$\begin{aligned} H &= \sum_i \frac{\hat{P}_i^2}{2M} + \sum_j \frac{\hat{p}_j^2}{2m} + \frac{1}{2}\sum_{i\neq i'} v_{II}(\vec{R}_i,\vec{R}_{i'}) + \frac{1}{2}\sum_{j\neq j'} v_{ee}(|\vec{r}_j - \vec{r}_{j'}|) + \sum_{i,j} v_{eI}(\vec{R}_i,\vec{r}_j) \\ &\equiv K_I + K_e + V_{II} + V_{ee} + V_{eI}, \end{aligned} \tag{2}$$

where K_I is the total kinetic energy of the ions, K_e the total kinetic energy of the electrons, V_{II} the total ion-ion potential energy, V_{ee} the total electron-electron potential energy, and V_{eI} the total electron-ion potential energy. The $\{\vec{R}_i\}$ and $\{\vec{r}_j\}$ now represent ionic and valence electronic coordinates, respectively, and the $\{\hat{P}_i\}$ and $\{\hat{p}_j\}$ again represent the corresponding momenta. The function v_{II} represents the interaction between ion i and ion i' $(i\neq i')$, v_{ee} the Coulombic interaction between electron j and electron j' $(j\neq j')$, and v_{eI} the interaction between ion i and electron j. At reasonable separations, when the cores have minimal overlap (and by assumption low polarizability), the functional forms of both v_{II} and v_{eI} may be well approximated as Coulombic (by Gauss' law); however, when the cores overlap substantially and/or when a valence electron approaches the core, Pauli exclusion must be taken into account. As a result, the exact functional forms of both v_{II} and v_{eI} will be nonlocal; even so, it is often valid to approximate each of these terms as local, as we now discuss.

In those cases where the ion cores (of assumed valence Z) have minimal overlap, we may write v_{II} as

$$v_{II}(|\vec{R}_i - \vec{R}_{i'}|) = \frac{(Ze)^2}{|\vec{R}_i - \vec{R}_{i'}|}, \tag{3}$$

though it is important to keep in mind that this approximation will fail at some sufficiently high density. Similarly, we can also replace v_{eI} by

$$v_{eI}(|\vec{R}_i - \vec{r}_j|) = -\frac{Ze^2}{|\vec{R}_i - \vec{r}_j|} \tag{4}$$

but only for the case where, on average, the valence electron can be considered to be *well outside* the ionic core. More generally, the electron-ion interaction is represented by a (typically) much weaker *pseudopotential*,[2,17,18] which will, as noted, be nonlocal; however, since the focus is only on how the electrons respond to the presence of the ions, an initial and simple choice for the pseudopotential is a local empty-core model,[17,18]

$$v_{eI}(r) = \begin{cases} 0, & r < R_c \\ -\dfrac{Ze^2}{r} & r \geq R_c. \end{cases} \tag{5}$$

Here, R_c denotes an effective *core radius*, which is comparable to the experimental ionic radius in many cases.[17,18] Throughout the remainder of this paper, we will only be concerned with the $\vec{k}$-space representation of Eq. (5), namely,

$$v_{eI}(k) = \frac{-4\pi Ze^2}{k^2}\cos(kR_c), \tag{6}$$

which could be replaced by a more complex form, if desired.

The Hamiltonian given by Eq. (2) can be rewritten in terms of Fourier transforms as[1,2]

$$\begin{aligned} H &= H_{OCP} + H_{eg} + H_{eI} + E_0 \equiv (K_I + U_M) + H_{eg} + H_{eI} + E_0 \\ &= \left(K_I + \frac{1}{2V} \sum_{\vec{k}\neq 0} Z^2 v_c(k) [\hat{\rho}_I^{(1)}(\vec{k}) \hat{\rho}_I^{(1)}(-\vec{k}) - N_I] \right) \\ &\quad + \left(K_e + \frac{1}{2V} \sum_{\vec{k}\neq 0} v_c(k) [\hat{\rho}_e^{(1)}(\vec{k}) \hat{\rho}_e^{(1)}(-\vec{k}) - N_e] \right) + \frac{1}{V} \sum_{\vec{k}\neq 0} v_{eI}(k) \hat{\rho}_I^{(1)}(\vec{k}) \hat{\rho}_e^{(1)}(-\vec{k}) \\ &\quad + \frac{1}{V} \lim_{\vec{k}\to 0} ([Z v_c(k) + v_{eI}(k)] \hat{\rho}_I^{(1)}(\vec{k}) \hat{\rho}_e^{(1)}(-\vec{k})), \end{aligned} \tag{7}$$

where H_{OCP} and H_{eg} are, respectively, the Hamiltonians for the one-component plasma and the interacting electron gas, H_{eI} is the electron-ion interaction Hamiltonian, U_M is the structural (Madelung) energy of the ions, and E_0 is the Hartree energy,[1,2,19] which does not depend on ionic structure. The function $v_c(k)$ is the Fourier transform of the Coulomb potential,

$$v_c(k) = \frac{4\pi e^2}{k^2} (k \neq 0), \tag{8}$$

and the functions $\hat{\rho}_I^{(1)}(\vec{k})$ and $\hat{\rho}_e^{(1)}(\vec{k})$ are the Fourier transforms of the ionic and electronic one-particle density operators,[1,2]

$$\hat{\rho}_I^{(1)}(\vec{r}) = \sum_i \delta(\vec{r} - \vec{R}_i) \tag{9}$$

and

$$\hat{\rho}_e^{(1)}(\vec{r}) = \sum_j \delta(\vec{r} - \vec{r}_j). \tag{10}$$

The absence of $\vec{k}=0$ terms in Eq. (7) results from the requirement of charge neutrality in the thermodynamic limit.[1,2] Taken together, Eqs. (6)–(10) complete the description of the initiating Hamiltonian to be used in this paper.

B. Reduction of the two-component system to an effective one-component system

A primary aim in what follows is the development of potentials useful for describing both microscopic and macroscopic aspects of metallic (and semiconducting) systems. An appropriate starting point is the Helmholtz free energy of the system,

$$F = -k_B T \ln Q \equiv -(\ln Q)/\beta, \tag{11}$$

where k_B is Boltzmann's constant, T is the system temperature, and Q is the canonical partition function,

$$Q = Tr[e^{-\beta H}], \tag{12}$$

the trace being taken over all states of the combined (canonical and neutral) two-component system described by Eq. (7). Because of the significant disparity in ionic and electronic time scales, we invoke the adiabatic (Born-Oppenheimer) approximation, which allows us to take separate traces over ionic and electronic coordinates, the electronic trace being taken for a temporarily fixed ionic configuration. With this approximation, we can rewrite Eq. (12) as

$$Q \approx Tr_I Tr_{e(I)}[e^{-\beta H}]. \tag{13}$$

We assume here that the system is in, or close to, its electronic ground state, which is reasonable under ordinary conditions.[20] Since, as stated, our primary focus is on the determination of effective ionic *potentials*, we shall henceforth omit ionic kinetic energies while recognizing that these can be important for structural applications in light-element systems. This approximation is least valid for the case of hydrogen (see Sec. III).

Upon substitution of our expression for H from Eq. (7) (with $K_I=0$) into Eq. (13), the canonical partition function can be rewritten as

$$Q = Tr_I(e^{-\beta(U_M+E_0)} Tr_{e(I)}[e^{-\beta(H_{eg}+H_{eI})}]), \tag{14}$$

where all individual terms are now thermodynamically well defined. We next define the Helmholtz free energy F' of an interacting but inhomogeneous electron gas (characterized by the Hamiltonian H_{eg} in the presence of an external potential H_{eI}) through the relation

$$Tr_{e(I)}[e^{-\beta(H_{eg}+H_{eI})}] \equiv e^{-\beta F'}. \tag{15}$$

Associating a coupling constant λ $(0 \leq \lambda \leq 1)$ with H_{eI}, we can use the ground-state energy formula,[1,2,21]

$$F' = F_{eg} + \int_0^1 d\lambda \langle H_{eI} \rangle_\lambda, \tag{16}$$

to determine F'. Here, F_{eg} is the Helmholtz free energy of the interacting, *uniform* electron gas when $H_{eI}=0$, and the brackets indicate an average calculated over an ensemble characterized by the Hamiltonian $H_{eg}+\lambda H_{eI}$. Substituting our expression for H_{eI} into Eq. (16), we obtain

$$F' = F_{eg} + \frac{1}{V} \sum_{\vec{k}\neq 0} v_{eI}(k) \hat{\rho}_I^{(1)}(\vec{k}) \int_0^1 d\lambda \langle \hat{\rho}_e^{(1)}(-\vec{k}) \rangle_\lambda, \tag{17}$$

where the term in brackets is the Fourier transform of the one-particle electron density induced by the perturbing potential, at strength λ. The assumption here is that no phase transition occurs as λ traverses its domain.

If the electron-ion interaction is taken to be a perturbation on the interacting electron gas, the induced density is, to second order in the perturbation,[1,2]

$$\langle \hat{\rho}_e^{(1)}(-\vec{k})\rangle_\lambda = \lambda V'(\vec{k})\hat{\rho}_I^{(1)}(\vec{k})\chi^{(1)}\left(\frac{k}{2k_F}\right) + \frac{1}{V}\sum_{\vec{q}\neq 0,\vec{k}} \lambda V'(\vec{q})\hat{\rho}_I^{(1)}(\vec{q})\lambda V'(-\vec{k}-\vec{q})\hat{\rho}_I^{(1)}(-\vec{k}-\vec{q}) \times \chi^{(2)}\left(\frac{\vec{k}}{2k_F},\frac{\vec{q}}{2k_F}\right), \tag{18}$$

valid for $\vec{k}\neq 0$. Here, $V'(\vec{k})$ is the Fourier transform of the *total* electron-ion interaction,

$$V'(\vec{k}) = \left(-\frac{4\pi Z e^2}{k^2}\right)\cos(kR_C)\hat{\rho}_I^{(1)}(\vec{k}) \equiv v_{eI}(k)\hat{\rho}_I^{(1)}(\vec{k}), \tag{19}$$

the functions $\chi^{(1)}$ and $\chi^{(2)}$ are the first- and second-order response functions for the homogeneous interacting electron gas (see the Appendix for their explicit functional forms), and k_F is the magnitude of the Fermi wave vector, defined as usual through

$$\rho_e \equiv \frac{N_e}{V}\left(=\frac{ZN_I}{V}\right) = \frac{k_F^3}{3\pi^2}. \tag{20}$$

Substituting Eq. (18) into Eq. (17) and performing the λ integrations, we obtain

$$F' = F_{eg} + \frac{1}{2V}\sum_{\vec{k}\neq 0} |v_{eI}(k)|^2 \hat{\rho}_I^{(1)}(\vec{k})\hat{\rho}_I^{(1)}(-\vec{k})\chi^{(1)}(k/2k_F) + \frac{1}{3V^2}\sum_{\vec{k}\neq 0}\sum_{\vec{q}\neq 0,-\vec{k}} v_{eI}(k)v_{eI}(q)v_{eI}(|\vec{k}+\vec{q}|) \times \hat{\rho}_I^{(1)}(\vec{k})\hat{\rho}_I^{(1)}(\vec{q})\hat{\rho}_I^{(1)}(-\vec{k}-\vec{q})\chi^{(2)}\left(\frac{\vec{k}}{2k_F},\frac{\vec{q}}{2k_F}\right) \equiv F_{eg} + U^{(1)} + U^{(2)}, \tag{21}$$

which serves to define the functions $U^{(1)}$ and $U^{(2)}$. We can now rewrite Eq. (14) in the form

$$Q = Tr_I(\exp[-\beta(U_M + E_0 + F_{eg} + U^{(1)} + U^{(2)})]) \equiv Tr_I(\exp[-\beta U_{eff}]), \tag{22}$$

where

$$U_{eff} \equiv U_M + E_0 + F_{eg} + U^{(1)} + U^{(2)} \equiv U_{eff}(\{\vec{R}_i\};\rho_e), \tag{23}$$

which clearly represents an effective ion-ion interaction depending on the ionic coordinates $\{\vec{R}_i\}$ and the average electron density ρ_e. It has long been stipulated[22] that one can write such a function in the general form

$$U(\{\vec{R}_i\};\rho_e) = U(\rho_e) + \frac{1}{2}\sum_i\sum_{j\neq i}\phi^{(2)}(\vec{R}_i,\vec{R}_j;\rho_e) + \frac{1}{6}\sum_i\sum_{j\neq i}\sum_{l\neq i,j}\phi^{(3)}(\vec{R}_i,\vec{R}_j,\vec{R}_l;\rho_e) + \cdots, \tag{24}$$

where the first term consists of those contributions to U_{eff} that depend solely on the average electron density, the second on those contributions that depend on the average electron density and all *pairs* of ionic coordinates $(i\neq j)$, the third on those contributions that depend on the average electron density and all *triplets* of ionic coordinates $(i\neq j\neq l)$, and so forth.

It is now straightforward to show explicitly that Eq. (23) can be written exactly in the form suggested by Eq. (24), with

$$\phi^{(2)}(\vec{R}_i,\vec{R}_j;\rho_e) = \frac{1}{V}\sum_{\vec{k}}\left[Z^2 v_c(k) + |v_{eI}(k)|^2\chi^{(1)}\left(\frac{k}{2k_F}\right)\right] \times e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} + \frac{1}{V^2}\sum_{\vec{k},\vec{q}} 2\Gamma^{(2)}(\vec{k},\vec{q})e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} + \frac{1}{V}\sum_{\vec{k}}\left[-\frac{N_I}{V}\right]2\Gamma^{(2)}(\vec{k},0)e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} \equiv \phi_{11}^{(2)}(\vec{R}_i,\vec{R}_j;\rho_e) + \phi_{21}^{(2)}(\vec{R}_i,\vec{R}_j;\rho_e) + \phi_{22}^{(2)}(\vec{R}_i,\vec{R}_j;\rho_e) \tag{25}$$

and

$$\phi^{(3)}(\vec{R}_i,\vec{R}_j,\vec{R}_l;\rho_e) = \frac{1}{V^2}\sum_{\vec{k},\vec{q}} 2\Gamma^{(2)}(\vec{k},\vec{q})e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_l)}e^{i\vec{q}\cdot(\vec{R}_j-\vec{R}_l)} \equiv \phi_{21}^{(3)}(\vec{R}_i,\vec{R}_j,\vec{R}_l;\rho_e). \tag{26}$$

In Eqs. (25) and (26), the function $\Gamma^{(2)}$ is the second-order electronic response function but weighted by three factors of the electron-ion pseudopotential, namely,

$$\Gamma^{(2)}(\vec{k},\vec{q}) = v_{eI}(k)v_{eI}(q)v_{eI}(|\vec{k}+\vec{q}|)\chi^{(2)}\left(\frac{\vec{k}}{2k_F},\frac{\vec{q}}{2k_F}\right). \tag{27}$$

It should be noted that the pseudopotential is usually variable in sign. Since the induced electron density [Eq. (18)] is given only to second order in the electron-ion interaction, Eq. (23) contains no four-body, five-body, etc., terms; moreover, as noted, the explicit functional forms for the volume terms arising from Eq. (23) will not be displayed here.

Each superscript in parentheses serves to indicate the type of n-body $(n\geq 2)$ potential. Each accompanying subscript is written with two numbers, the meaning of which is as follows: the first refers to the order of the interacting response function used in constructing the potential (e.g., 1 for $\chi^{(1)}$) and the second simply denotes a label. For example, $\phi_{22}^{(2)}$ in Eq. (25) is a two-body potential constructed using the inter-

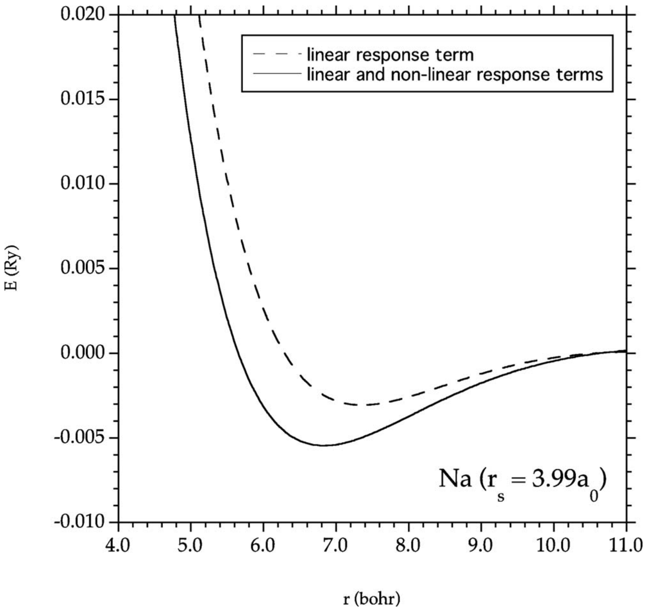

FIG. 1. Plot of the pair potential for sodium ($Z=1$; $R_c=1.75a_o$) at conditions corresponding to 1 atm ($k_Fa_0=0.487$; $r_s=3.99a_0$). The dashed line indicates the pair potential (i.e., $\phi_{11}^{(2)}$) obtained from linear-response alone, the solid line the pair potential (i.e., $\phi_{11}^{(2)}+\phi_{21}^{(2)}+\phi_{22}^{(2)}$) from both linear and second-order response. Energies are given in Rydbergs (1 Ry=13.6 eV), and distances in Bohr radii ($a_0=0.529$ Å).

acting second-order response function $\chi^{(2)}$ and is the second such two-body potential thus determined. The potentials in Eqs. (25) and (26) can be rewritten in forms more suitable for numerical integration by converting the various sums over wave vectors into integrals and then making the necessary substitutions. For the pair potential, this procedure is straightforward; the analogous procedure for simplifying the triplet potential is far less trivial (and will be the subject of a future paper). Standard numerical integration techniques[23] are then used to generate the potentials.

III. PAIR POTENTIALS FOR SIMPLE METALS AT NORMAL DENSITIES

In this section, we present pair potentials for sodium, magnesium, aluminum, and metallic silicon at densities corresponding to atmospheric pressure, as well as an unpaired *model* form of hydrogen assumed, through choice of structure, to be metallic at one atmosphere. Energies are expressed in Rydbergs (1 Ry=13.6 eV) and distances in units of the Bohr radius a_0 (=0.529 Å [1 bohr]). In the following figures, the dashed line indicates the pair potential obtained by including only the linear-response term (i.e., $\phi_{11}^{(2)}$), and the solid line indicates the pair potential obtained by including both linear and second-order (nonlinear) response terms (i.e., $\phi_{11}^{(2)}+\phi_{21}^{(2)}+\phi_{22}^{(2)}$).

In Fig. 1, we show the pair potential for monovalent sodium (Na) [$Z=1$; $R_c=1.75$ bohr (Ref. 24)] at a density corresponding to $k_Fa_0=0.481(r_s=3.99a_0)$.[24] It is apparent that inclusion of nonlinear terms noticeably shifts both the position and energy of the minimum in the figure. When the nonlinear contributions are included, the calculated position of the minimum just slightly underestimates the experimental nearest-neighbor distance in bcc Na under standard conditions [i.e., 6.92 bohr (Ref. 25)].

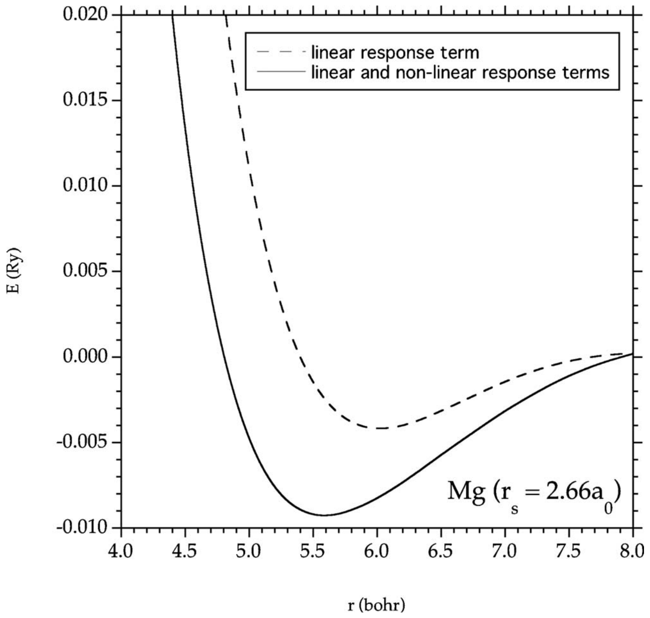

FIG. 2. Same as in Fig. 1 but for magnesium: ($Z=2$; $R_c=1.31a_0$) and ($k_Fa_0=0.722$; $r_s=2.66a_0$).

Next, in Fig. 2, we show the pair potential for divalent magnesium (Mg) [$Z=2$; $R_c=1.31$ bohr (Ref. 24)] at a density corresponding to $k_Fa_0=0.722(r_s=2.66a_0)$.[24] The shifts in both the position and the energy of the minimum are seen to be significantly larger in magnesium, as compared with sodium: this increase can readily be attributed to each of the nonlinear-response terms in the pair potential being proportional to either the second or third power of the valence [in Eqs. (25) and (27), $v_{eI}(k)$ is proportional to Z]. Since the experimental value of the nearest-neighbor distance in hcp Mg is about 6.0 bohr,[25] there is a small disagreement between our result for the position of the first minimum and the experimental nearest-neighbor distance, which may be attributable to:

(a) *Effects that more distant atoms may have on the interaction between a specified pair of atoms.* The work of Nagao *et al.*[7] suggests that arranging atoms in a crystalline formation may lead to a nearest-neighbor distance in the crystal that differs from the position of the minimum in the two-body potential, an effect resulting from interpair interactions.

(b) *Intrinsic three-body effects.* Since the effect of a *realistic* three-body potential (one derived from fundamental considerations, as opposed to a semiempirical potential[15,16]) on a crystalline arrangement has not (to our knowledge) been studied, it is conceivable that realistic three-body potentials may be significant in modeling crystalline structures in metals (and, possibly, semiconductors).

These issues will be addressed in a future work. Observe that the position of the minimum in the magnesium pair potential differs from the nearest-neighbor distance in hcp Mg by about 7% (the values are 5.6 and 6.0 bohr, respectively)

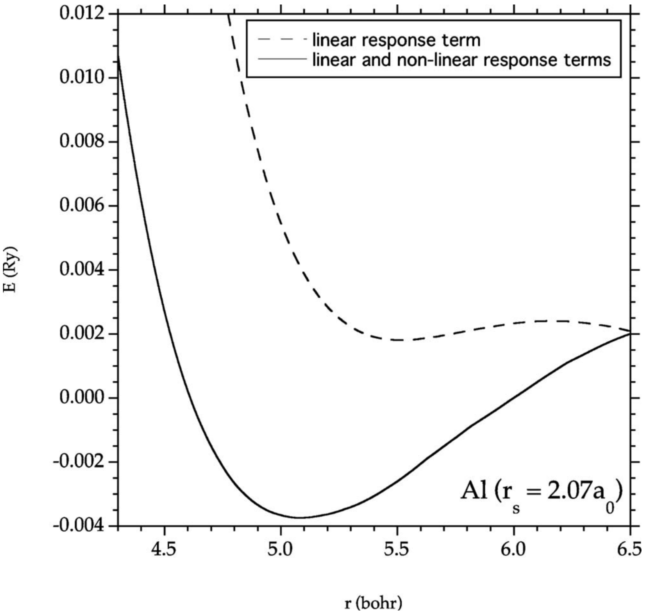

FIG. 3. Same as in Fig. 1 but for aluminum: ($Z=3$; $R_c=1.11a_0$) and ($k_Fa_0=0.928$; $r_s=2.07a_0$).

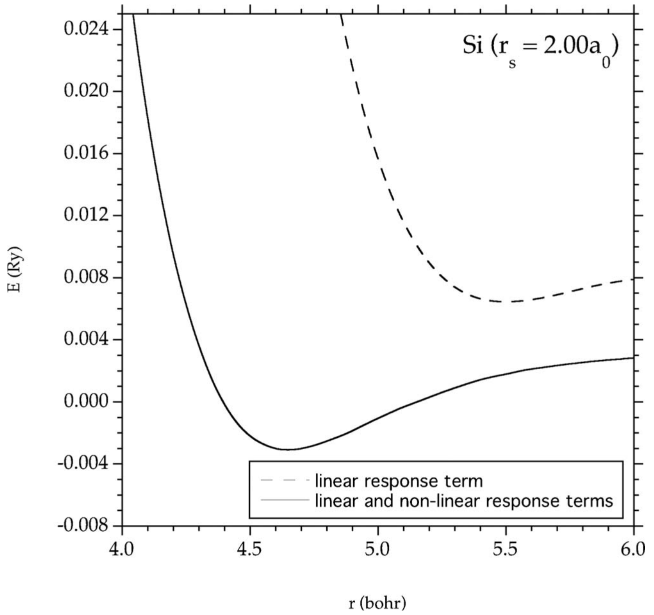

FIG. 4. Same as in Fig. 1 but for silicon: ($Z=4$; $R_c=1.20a_0$) and ($k_Fa_0=0.960$; $r_s=2.00a_0$).

and that the difference in energy between these two positions is only about 1 mRy; therefore, just a small effect from either of the above possibilities would be needed to obtain good agreement with experiment. Although points (a) and (b) certainly apply to sodium as well, it appears, from a comparison of Figs. 1 and 2, that neither interpair interactions nor three-body effects are nearly as significant in sodium under normal conditions.

In Fig. 3, we present the pair potential for trivalent aluminum (Al) [$Z=3$; $R_c=1.11$ bohr (Ref. 24)] at a density corresponding to $k_Fa_0=0.928(r_s=2.07a_0)$.[24] Once again, there is a noticeable shift in both the position and energy of the minimum, resulting from inclusion of nonlinear effects. Note that the energy of the minimum has a positive value when only the linear-response term is considered, which Pettifor and Hafner[24,26] considered an apparent result of using an empty-core pseudopotential; however, upon inclusion of nonlinear-response terms, this unusual feature disappears—the binding energy of the pair potential becomes negative at the position of the minimum (as one might find in studies of *semiempirical* potentials). Moreover, the potential is noticeably less "flat" when nonlinear-response contributions are included (i.e., the difference between the first minimum and next local maximum is much larger): the dashed curve seems to suggest that, at the level of linear response, aluminum might be unstable with respect to binding at the position of the first minimum; by comparison, the solid (linear-plus-nonlinear-response) curve is more in keeping with general expectations of stability. As for the difference between the position of the minimum of the solid curve and the experimental nearest-neighbor distance in fcc Al (~5.4 bohr),[25] we refer the reader to points (a) and (b) under the discussion of the results for magnesium.

In Fig. 4, we present the pair potential for a presumed metallic state of tetravalent silicon (Si) [$Z=4$; $R_c=1.20$ bohr (Refs. 24, 27, and 28)] at a density corresponding to $k_Fa_0=0.96(r_s=2.00a_0)$.[26] (Note that silicon is known to be metallic when r_s is reduced by a mere 3%.[29]) Our chosen value for R_c does not follow the trend established by the preceding plots—moving across the periodic table from Na to Mg to Al, the core radius decreased from 1.75 to 1.31 to 1.11 bohr, namely, a decrease of 0.44 bohr followed by a decrease of 0.2 bohr. An additional decrease of about 0.1 bohr, leading to a value of $R_c \sim 1.0$ bohr for Si, might have been anticipated. Studies on pseudopotentials do predict values between 0.96 and 1.02 bohr for the core radius of silicon;[29] however, the comprehensive work by Yin and Cohen[27] suggests that the actual core radius is closer to 1.2 bohr, a value also obtained when the total energy is minimized with respect to the parameter r_s.[28] This latter procedure yields values for the core radii of Na, Mg, and Al in almost perfect agreement with those obtained from pseudopotential studies. Given that the two methods for determining the core radius agree for all simple metals under consideration except silicon, we have opted for the value ($R_c=1.20$ bohr) obtained from minimizing the total energy since this also agrees with the Yin-Cohen study.

Comparing Figs. 1–4, the difference between the linear and linear-plus-nonlinear-response curves clearly increases with valence (as may be expected) and is most significant for the case of silicon. When the effects of nonlinear response are included in silicon, the position of the first minimum noticeably shifts from 5.5 to 4.65 bohr [this latter value then comparing quite favorably with the experimental nearest-neighbor distance of 4.45 bohr in diamond-structure Si (Ref. 25)]. As was the case in Al, the value of the energy at the position of the first minimum also decreases significantly for Si, from +6 to −3 mRy; the addition of nonlinear-response terms again results in the pair potential becoming negative at the position of the first minimum. Since nonlinear-response contributions to the pair potential yield a negative energy at the position of the first minimum (which, in turn, is quite close to the nearest-neighbor distance in silicon under normal conditions, as noted), it is reasonable to speculate about whether additional potentials are necessary for a complete description of the interactions between the ions in metallic (or even semiconducting) silicon. Widely used semiempirical potentials assume that angular-dependent (often three-body) potentials are essential for stabilizing solid, liquid, and amorphous silicon structures;[15,16] however, the pair potentials in Fig. 4 suggest that explicitly *density-dependent* pair potentials (at the level of second-order response) may be sufficient, at least for stabilizing *metallic*-Si systems.

Since the electronic structure of solid-Si exhibits wide bands and small (but nonzero) band gaps, we also believe that the results presented here may be a reasonable approximation for *semiconducting* silicon at the same density and pressure. The primary modification required for our theory to accurately model semiconducting-Si is the introduction of a band gap in the electronic energies, such as the Callaway model[30] for the dielectric function. Although the Callaway model[30] does not strictly apply at very small q ($<0.1k_F$), we believe that, since we integrate over all q in the derivation of the potentials and since very small q should correspond to very large r (well beyond the range of interest), we should not expect a significant change in using the Callaway model instead of the Penn model[31] for the range of r values in which we are interested.

The last element considered is monovalent hydrogen ($Z=1$; $R_c=0$ bohr) but in an assumed metallic form; its inclusion here is therefore mainly for formal reasons (see below), relating to the role of higher-order response in a relatively simple system. At atmospheric pressure, the corresponding density is $k_Fa_0=0.613(r_s=3.13a_0)$.[32] Since hydrogen has no core states ($R_c=0$), the "perturbing" electron-ion interaction is the *full* Coulomb potential. This is certainly *not* a small perturbation on the system, so it would seem that the above formalism may be incapable *a priori* of modeling hydrogen; however, the formalism has been modified beyond the original perturbation development (derived for a *noninteracting* electron gas),[1,2,18] *specifically* to account for valence electron interactions (see the Appendix). The actual electron-proton interaction reflects a modified potential that accounts for exchange and correlation effects and is thus weaker than in the simple case of noninteracting electrons.

This modified interaction will clearly not be as weak as in the previous cases considered (Na, Mg, Al, and Si), so the inclusion of second-order response terms (and *no* higher-order response terms) may be insufficient for a complete description of the pair potential between two protons under the stated density conditions. Nevertheless, we still obtain a minimum in the interaction between two hydrogen ions at a location that is quite close to the experimental bond length in the hydrogen molecule [i.e., 1.4 bohr (Ref. 32)], a value also obtained from the Heitler-London method.[33] The main difference between the Heitler-London approach and the approach here is that we are expanding the actual induced electron density as a sum of terms [see Eq. (18)] that do not converge quickly for the case of hydrogen and that incorporate electronic exchange and correlation effects (primarily spin-dependent effects) only in an effective way (see the Appendix). Therefore, when describing hydrogen at *normal* densities, our approach is a formal exercise and not as suitable as the Heitler-London method and its variants; however, the results indicate that, at higher densities, where hydrogen is expected to dissociate and metallize, an approach such as the one being developed here is clearly needed.

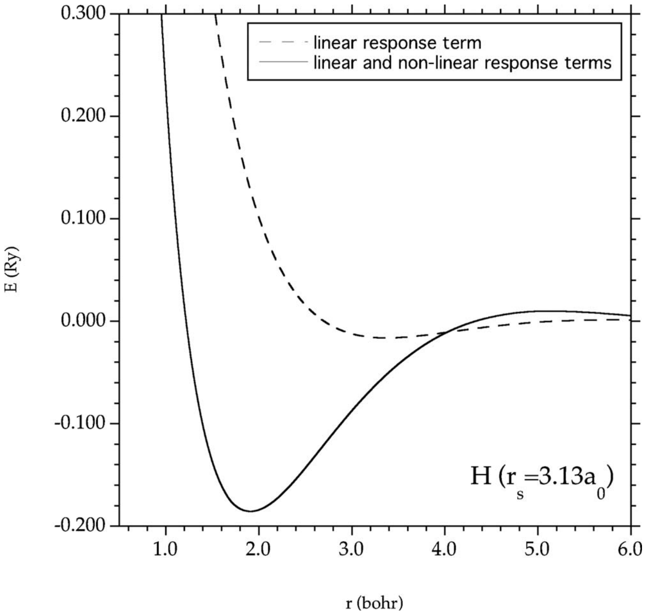

FIG. 5. Same as in Fig. 1 but for hydrogen ($Z=1$; $R_c=0$) and ($k_Fa_0=0.613$; $r_s=3.13a_0$).

In Fig. 5, we present the pair potential for hydrogen under the quite restrictive conditions stated above. Even though both the density and valence are smaller in hydrogen than in the last three elements considered, the inclusion of nonlinear-response terms in the pair potential again clearly results in significant changes from the linear-response results. The potential minimum (which appears, as noted, to correspond to the nearest-neighbor distance in the other simple metals under consideration) has shifted inwards from 3.3 to 1.85 bohr, approaching the experimental bond length of 1.4 bohr in the hydrogen molecule (part of a narrow-band system); however, as noted above, the theoretical approach takes the electron-ion potential to be weak. Even after the inclusion of exchange and correlation effects, the electron-ion potential in hydrogen will remain strong because of the lack of a core space (see below). To model the hydrogen pair potential more accurately, it is necessary to go beyond second-order response (to at least third order), as Louis and Ashcroft observed.[34]

It is also apparent that the energy at the position of the first potential minimum undergoes a much larger change than for any of the other four elements, from −16 to −186 mRy; in physical terms, this significant decrease can readily be attributed to the increased electron-ion interaction strength resulting from the lack of an ion core. In terms of well depth, Fig. 5 actually compares favorably with Fig. 43-2 of Pauling and Wilson[33] (obtained with the Heitler-London method), as their hydrogen potential shows a well depth of approximately 200–250 mRy in magnitude. Although the positions of the minima in each figure differ by 0.45 bohr, inclusion of at least third-order response contributions to the pair potential for hydrogen may significantly reduce this disparity.

Inclusion of both first- and second-order response contributions in the pair potential leads to a prediction for the position of the first potential minimum in hydrogen at normal density (~1.85 bohr, recently confirmed by the work of Gravel and Ashcroft[35]) which is noticeably less than that predicted in a previous, related paper by Nagao *et al.*[7,36] for a density corresponding to $k_F a_0 = 0.64 (r_s = 3.0 a_0)$. The approximation used by Nagao *et al.* actually omits consideration of the pair potential term we have identified as $\phi_{22}^{(2)}$ and considers only those terms we have identified as $\phi_{11}^{(2)}$ and $\phi_{21}^{(2)}$. Figures 6(a) and 6(b) show the pair potential curves for hydrogen at $k_F a_0 = 0.64 (r_s = 3.0 a_0)$: the solid curve is calculated from Eqs. (25) and (27) at this density, with $Z=1$ and $R_c=0$; the dot-dashed curve is calculated under the same conditions but without the $\phi_{22}^{(2)}$ term. A comparison of the dot-dashed pair potential in Figs. 6(a) and 6(b) with the $r_s = 3.0 a_0$ $\phi_{pp}^{(3)}$ pair potential in Fig. 1b of Ref. 7 shows that these two curves are apparently identical, as we would expect.

Evidence that the $\phi_{22}^{(2)}$ term should be included in the pair potentials of other simple metals is presented in Fig. 7, where the pair potential for aluminum shown in Fig. 3 (the solid curve, accurate to second order in the electron-ion pseudopotential) is compared with a pair potential identical in all respects except that the term $\phi_{22}^{(2)}$ is omitted (the dot-dashed curve). The lack of a $\phi_{22}^{(2)}$ term results in a potential minimum that is not only significantly deeper than the full aluminum potential but is also located at a position nearly 1 bohr closer to the origin. This finding leads to the conclusion that care is required in the determination of nonlinear terms: the omission of even one nonlinear-response pair potential term can lead to inaccurate effective potential-energy curves.

IV. CONCLUSION

Electron response theory has been used to derive effective ion-ion interactions for simple wideband systems; in particular, pair potentials have been determined for sodium, magnesium, aluminum, metallic silicon, and an assumed metallic form of hydrogen, all under standard conditions. The positions of the potential minima actually correspond quite closely (within ~8%, in fact) to the experimental nearest-neighbor distances under normal conditions in all elements under consideration, with the exception of hydrogen. To obtain still better agreement, interpair and/or three-body effects will need to be included. Hydrogen is clearly a special case: higher-order (at least third-order) response terms in the pair potential will also need to be incorporated in order to reproduce the Heitler-London result since we have approximated the electron density and have included spin-dependent effects only in an approximate way. A clear extension of this work will be the generalization of the development outlined in Sec. II and the Appendix to include contributions to both pair and triplet potentials from third-order response (and thus the explicit calculation and evaluation of both the noninteracting and interacting forms of the third-order response function).

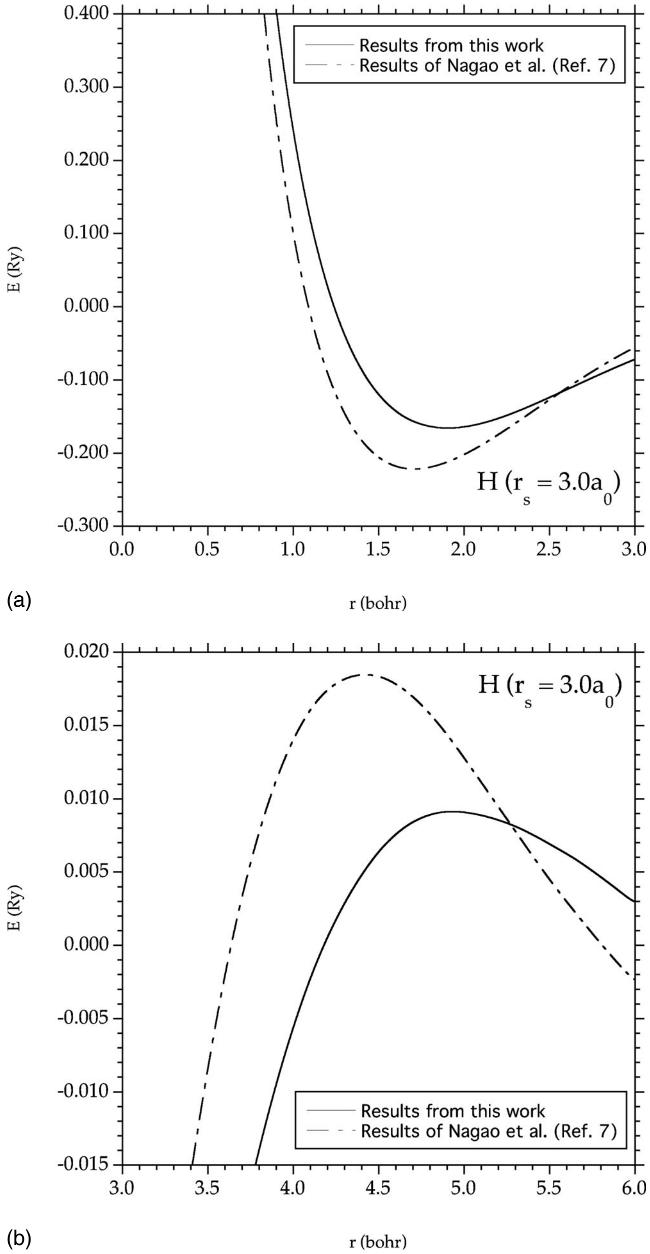

FIG. 6. (a) Plot of the pair potential for hydrogen ($Z=1$; $R_c=0$) at slightly elevated pressure ($k_F a_0 = 0.64$; $r_s = 3.00 a_0$), from 0 to $3a_0$. The solid curve represents our results $(=\phi_{11}^{(2)} + \phi_{21}^{(2)} + \phi_{22}^{(2)})$, the dot-dashed curve that of Ref. 7 $(=\phi_{11}^{(2)} + \phi_{21}^{(2)})$. (b) Same as in Fig. 6(a) but over the range from $3a_0$ to $6a_0$ and enlarged by a factor of 20.

Density-functional approaches can obviously provide a very detailed accounting of ionic energetics and, in principle, can go further than the methods detailed above; however, the latter provide considerable intuitive insight into the physical origin of the microscopic interactions which ultimately do lead to the structures actually taken up by simple systems under prescribed thermodynamic conditions. Though the physical forms of the potentials presented are intuitively reasonable, as are the positions of the minima with respect to known arrangements, near-neighbor separations alone cannot, of course, be taken as a guide to the actual preferred crystal structures at a given density. To determine these, it will be necessary (as the foregoing emphasizes) to include

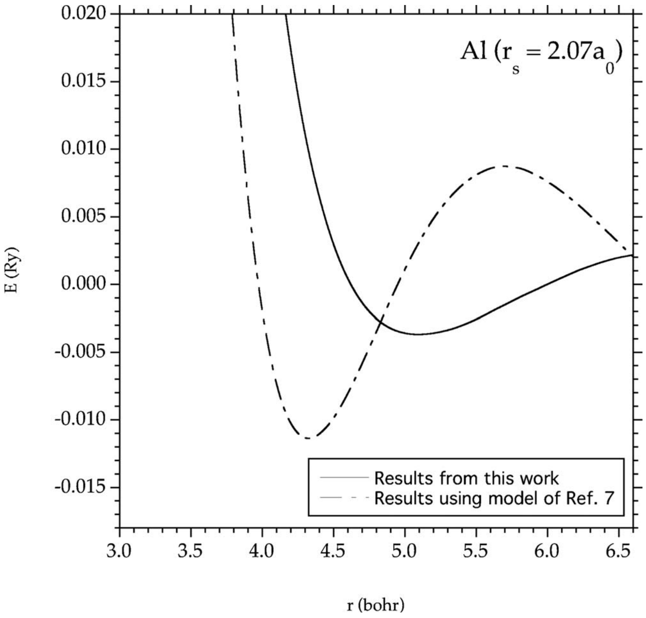

FIG. 7. Comparison of the pair potential for aluminum ($=\phi_{11}^{(2)}+\phi_{21}^{(2)}+\phi_{22}^{(2)}$; the solid curve in Fig. 3) with that obtained using the formalism in Ref. 7 ($=\phi_{11}^{(2)}+\phi_{21}^{(2)}$; the dot-dashed curve). The parameters are the same as in Fig. 3.

higher-order interactions; these matters will be addressed, in part, in a successor to the present paper. Also along these lines, future extensions relating to the effects of density on pair potentials are clearly of interest; these would likely focus on the monovalent elements (which have received much experimental and theoretical interest in recent years). In addition, the effects of three-body potentials on high-density systems need to be studied: as ions move closer together, three-body effects simply cannot be ignored and may well prove crucial to a complete understanding of the structure of high-density solids for the simple systems of interest.

The pair and triplet potentials we are developing may be suitable for simulations of metallic fluids at both normal and elevated densities. With the current theoretical and experimental interest in high-density fluids, in particular, we suggest that a reasonable and fairly accurate alternative to full *ab initio* simulations of metallic fluids is of some importance. Even for solids, the approach here will be of interest in elucidating the remarkable developments in structure at higher densities, which range, in the light elements, from the simplest of all structures (simple cubic in calcium[37]) to perhaps the most complex (some 512 atoms per unit cell in sodium[38]). In addition to serving as a convenient way to verify the general forms of our potentials (at normal densities), simulations using these potentials may reveal interesting new physics at higher densities that simulations using semiempirical potentials, generally fit to *pre-existing* data, would be unable to provide.

ACKNOWLEDGMENTS

We would like to thank the National Science Foundation (NSF) for their funding of this research (Grants DMR-0302347, DMR-0601461, and DMR-0907425), as well as the Cornell Center for Materials Research Computing Facility (CCMRCF), Colby College Information Technology Services (ITS), Bates College Information and Library Services (ILS), and the Office of Information Technology at New College of Florida for providing the necessary computing resources while this paper was being prepared.

APPENDIX: FIRST- AND SECOND-ORDER RESPONSE FUNCTIONS

The first-order ($n=1$) response function is given by[18]

$$\chi^{(1)}(y)=\frac{\chi_0^{(1)}(y)}{1-\{v_c(y)+\mu_1(y)\}\chi_0^{(1)}(y)}\equiv\frac{\chi_0^{(1)}(y)}{\varepsilon(y)}, \tag{A1}$$

where $y\equiv k/2k_F$, v_c is the Fourier transform of the Coulomb potential [Eq. (8) in Sec. II], $\chi_0^{(1)}$ is the first-order response function for a *noninteracting* electron gas[5,20] (originally derived by Lindhard[39]),

$$\chi_0^{(1)}(y)=-\frac{mk_F}{\hbar^2\pi^2}\left[\frac{1}{2}+\left(\frac{1-y^2}{4y}\right)\ln\left|\frac{1+y}{1-y}\right|\right], \tag{A2}$$

and μ_1 is the first functional derivative of the exchange-correlation potential (μ_{xc}) with respect to the induced electron density ρ_{ind}.[18] The exchange-correlation potential μ_{xc} can be written as[18,40]

$$\mu_{xc}[\vec{k};\rho_{ind}(\vec{k})]=\mu_1(k)\rho_{ind}(\vec{k})+\frac{1}{2V}\sum_{\vec{q}\neq 0,-\vec{k}}\rho_{ind}(\vec{q})\rho_{ind}(\vec{k}-\vec{q})\times\mu_2(\vec{k},\vec{q})+\cdots. \tag{A3}$$

The function μ_1 has the analytical form[41]

$$\mu_1(k)=-v_c(k)G(k), \tag{A4}$$

where $G(k)$ is a local-field correction (incorporating exchange and correlation), for which various reasonable approximations have been proposed. Here, we have elected to use the expression proposed by Vashishta and Singwi,[42]

$$G(k)=A(1-e^{-B(k/2k_F)^2}), \tag{A5}$$

which satisfies the following *sum rules*,[1]

$$\lim_{k\to 0}G(k)=(\pi k_F a_0)\left(\frac{k}{2k_F}\right)^2\left(1-\frac{K_0}{K}\right) \tag{A6}$$

and

$$\lim_{k\to\infty}G(k)=1-g(0). \tag{A7}$$

The first sum rule is technically not a limit in the mathematical sense (that limit would be zero) but is instead the leading-order term in the Taylor-series expansion of $G(k)$ as $k\to 0$. In

Eq. (A6), K_0/K is the ratio of the isothermal compressibility of the noninteracting electron gas to that of the interacting electron gas. An approximate expression for this ratio (which we use here) was given by Ashcroft and Langreth,[19]

$$\frac{K_0}{K} \cong 1 - (\lambda')^2 - 0.158(\lambda')^4, \tag{A8}$$

where

$$(\lambda')^2 \equiv \left(\frac{k_{TF}}{2k_F}\right)^2 = \frac{1}{\pi k_F a_0} = \left(\frac{r_s/a_0}{\pi}\right)\left(\frac{4}{9\pi}\right)^{1/3}, \tag{A9}$$

where k_{TF} is the Thomas-Fermi wave number.

In Eq. (A7), $g(0)$ is the $r \rightarrow 0$ limit of the electronic pair-correlation function and can be approximated by the function[43]

$$g(0) = \frac{1}{8}\left(\frac{z'}{I_1(z')}\right)^2, \tag{A10}$$

where I_1 is a modified Bessel function of the first order with an argument given by

$$z' = 4\sqrt{(\lambda')^2}. \tag{A11}$$

To date, explicit functional forms for the other μ_n have only been developed within the local-density approximation,[44] using the expression for the exchange-correlation energy proposed by Vosko *et al.*[45] The resulting expression for μ_2 was used to obtain the plots shown in Sec. III.[18,46]

The analytical form for the second-order response function for the interacting electron gas is given by[18]

$$\chi^{(2)}(\vec{y},\vec{y}\,') = \frac{\chi_0^{(2)}(\vec{y},\vec{y}\,')}{\varepsilon(y)\varepsilon(y')\varepsilon(|\vec{y}+\vec{y}\,'|)} + \frac{\mu_2(\vec{y},\vec{y}\,')}{2}\,\frac{\chi_0^{(1)}(y)\chi_0^{(1)}(y')\chi_0^{(1)}(|\vec{y}+\vec{y}\,'|)}{\varepsilon(y)\varepsilon(y')\varepsilon(|\vec{y}+\vec{y}\,'|)}, \tag{A12}$$

where the functions μ_2 and ε are defined above, and $\chi_2^{(0)}$ is the second-order response function for a noninteracting electron gas,[5,47,48]

$$\begin{aligned}\chi_2^{(0)}(\vec{y},\vec{y}\,') = {} & \left(\frac{1}{8\pi^2 k_F}\right)\left(\frac{2m}{\hbar^2}\right)^2\left(\frac{1}{2yy'\sin^2\theta}\right) \\ & \times\left([y' + y\cos\theta]\ln\left|\frac{1+y}{1-y}\right| + [y + y'\cos\theta]\ln\left|\frac{1+y'}{1-y'}\right| - [|\vec{y}+\vec{y}\,'|\cos\theta]\ln\left|\frac{1+|\vec{y}+\vec{y}\,'|}{1-|\vec{y}+\vec{y}\,'|}\right|\right) \\ & + \left(\frac{1}{8\pi^2 k_F}\right)\left(\frac{2m}{\hbar^2}\right)^2\left(\frac{\sqrt{R'}}{2yy'\sin^2\theta}\right)\ln\left|\frac{1+yy'\cos\theta - |\vec{y}+\vec{y}\,'|^2 + yy'\sqrt{R'}}{1+yy'\cos\theta - |\vec{y}+\vec{y}\,'|^2 - yy'\sqrt{R'}}\right|, \quad (R' \geq 0),\end{aligned} \tag{A13}$$

where m is the electron mass and

$$|\vec{y}| = y \equiv \left|\frac{\vec{k}}{2k_F}\right|,$$

$$|\vec{y}\,'| = y' \equiv \left|\frac{\vec{k}'}{2k_F}\right|,$$

$$\cos\theta \equiv \frac{\vec{y}\cdot\vec{y}\,'}{|\vec{y}||\vec{y}\,'|}, \tag{A14}$$

and

$$R' \equiv |\vec{y}+\vec{y}\,'|^2 - 4k_F^2\sin^2\theta.$$

In deriving Eq. (A13), we assume that $R' \geq 0$. When $R' < 0$, the term depending on R' in Eq. (A13) (ignoring overall factors lacking R' dependence) has the form[49]

$$i\sqrt{-R'}\,\ln\left|\frac{1-iA\sqrt{-R'}}{1+iA\sqrt{-R'}}\right|. \tag{A15}$$

Here, the quantity A is a (known) function of y, y', and $\cos\theta$. Using standard references,[50] we find that Eq. (A15) may be rewritten as $2\sqrt{-R'}\arctan(A\sqrt{-R'})$ so that, for $R' < 0$, the term in Eq. (A13) that depends on R' can explicitly be written as

$$\left(\frac{1}{8\pi^2 k_F}\right)\left(\frac{2m}{\hbar^2}\right)^2\left(\frac{2\sqrt{-R'}}{2yy'\sin^2\theta}\right)\arctan\left(\frac{yy'\sqrt{-R'}}{1+yy'\cos\theta - |\vec{y}+\vec{y}\,'|^2}\right), \quad (R' < 0), \tag{A16}$$

Together with Eq. (A13), Eq. (A16) agrees with the form of the noninteracting second-order response function derived by Brovman *et al.*,[48] as well as by Milchev and Pickenhain.[5] The original expression for $\chi_2^{(0)}$ (originating with Lloyd and Sholl[47]) apparently differs from the other two expressions only in the *arctan* term (i.e., only when $R'<0$). These differences have minimal effect on the pair potential terms, as we have verified through direct calculation in the case of hydrogen (which exhibits the strongest dependence on $\chi^{(2)}$ of all the elements we consider).

The expression for the second-order response function obtained in Eqs. (A13) and (A16) is not valid when the angle θ between the vectors $\vec{y}$ and $\vec{y}\,'$ is equal to either 0 or π. Instead, it is found that

$$\chi_2^{(0)}(y,y',\cos\,\theta=\pm 1)=\left(\frac{1}{8\pi^2 k_F}\right)\left(\frac{2m}{\hbar^2}\right)^2\left[-\frac{F(y)}{y'(y+y')}-\frac{F(y')}{y(y+y')}+\frac{F(y+y')}{yy'}\right], \tag{A17}$$

where

$$F(x)\equiv\frac{1}{2}-\left(\frac{1-x^2}{4x}\right)\ln\left|\frac{1+x}{1-x}\right|, \tag{A18}$$

which is similar in form to, though not identical with, the Lindhard function.[39] This completes our discussion of the lowest-order response functions.

---

[1] N. W. Ashcroft and D. Stroud, *Solid State Physics* (Academic Press, New York, 1978), Vol. 33, p. 1; a extended summary of this article (with additional references and minor corrections) can be found in J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic Press, New York, 2006).

[2] J. A. Porter, Ph.D. thesis, Cornell University, 2001.

[3] M. Hasegawa, J. Phys. F: Met. Phys. **6**, 649 (1976).

[4] K. Ebina and M. Kaburagi, Surf. Sci. **242**, 124 (1991).

[5] A. Milchev and R. Pickenhain, Phys. Status Solidi B **79**, 549 (1977). This paper presents clear derivations of the first- and second-order noninteracting response functions using density matrices but the derivation given in its Appendix II contains several typographical errors in the mathematical formulas.

[6] S. Haldar and D. Sen, Phys. Status Solidi B **237**, 439 (2003).

[7] K. Nagao, S. A. Bonev, A. Bergara, and N. W. Ashcroft, Phys. Rev. Lett. **90**, 035501 (2003).

[8] M. Hanfland, K. Syassen, N. E. Christensen, and D. L. Novikov, Nature (London) **408**, 174 (2000).

[9] N. W. Ashcroft, Nature (London) **419**, 569 (2002).

[10] J. B. Neaton and N. W. Ashcroft, Nature (London) **400**, 141 (1999).

[11] E. Gregoryanz, O. Degtyareva, M. Somayazulu, R. J. Hemley, and H.-K. Mao, Phys. Rev. Lett. **94**, 185502 (2005).

[12] M. Hanfland, I. Loa, and K. Syassen, Phys. Rev. B **65**, 184109 (2002).

[13] J. B. Neaton and N. W. Ashcroft, Phys. Rev. Lett. **86**, 2830 (2001).

[14] M. Hanfland, I. Loa, K. Syassen, U. Schwarz, and K. Takemura, Solid State Commun. **112**, 123 (1999).

[15] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[16] S. Erkoc, Phys. Rep. **278**, 79 (1997) and references cited within. This article lists all known semiempirical interatomic/interionic potentials for Si as well as for other elements and compounds up to that date.

[17] N. W. Ashcroft, J. Phys. C **1**, 232 (1968); the empty-core pseudopotential was originally introduced for quite different reasons than those in which we are interested here. For a comprehensive discussion of pseudopotentials, see, *Solid State Physics* (Academic Press, New York, 1970), Vol. 24.

[18] A. A. Louis, Ph.D. thesis, Cornell University, 1998.

[19] The form for the Hartree energy was first given in terms of the empty-core pseudopotential in N. W. Ashcroft and D. C. Langreth, Phys. Rev. **159**, 500 (1967).

[20] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College/Harcourt Brace College, New York, 1976).

[21] N. Iwamoto, Phys. Rev. A **30**, 2597 (1984).

[22] M. H. Cohen, in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W.A. Benjamin, New York, 1963).

[23] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran 77: The Art of Scientific Computing*, 2nd ed. (Cambridge University Press, New York, 1996). When performing the numerical integrations, we split up both the $\vec{k}$ and $\vec{k}'$ integrals at the value $2k_F$ [i.e., at $y=k/(2k_F)=1$ and $y'=k'/(2k_F)=1$, respectively] in order to avoid mathematical complications resulting from logarithmic divergences. All multiple integrals were evaluated to a precision of 1 part in 100, which represented the best compromise between speed and accuracy. Our minimum integration cutoff value was $(50)(2k_F)$; in most cases, the cutoff was much larger: $(10^5)(2k_F)$.

[24] The electronic valences for all elements were obtained from Ref. 20. All other Na, Mg, and Al parameters used in this paper were obtained from D. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford University Press, New York, 1995).

[25] Experimental nearest-neighbor values were calculated using Ref. 20. See also J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[26] J. Hafner, *From Hamiltonians to Phase Diagrams* (Springer-Verlag, New York, 1987). This is the source for the k_F (r_s) value for Si at atmospheric pressure.

[27] M. T. Yin and M. L. Cohen, Phys. Rev. **26**, 5668 (1982).

[28] P. H. Nguyen, K. R. Hofmann, and G. Paasch, J. Appl. Phys. **92**, 5359 (2002); to obtain their R_c value for Si, see M. Hietschold, G. Paasch, and P. Ziesche, Phys. Status Solidi B **70**, 653 (1975); and N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967).

[29] W.-H. Shih and D. Stroud, Phys. Rev. B **31**, 3715 (1985); W. Jank and J. Hafner, *ibid.* **41**, 1497 (1990).

[30] J. Callaway, Phys. Rev. **116**, 1368 (1959).

[31] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[32] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[33] L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Me-*

chanics With Applications to Chemistry (McGraw-Hill, New York, 1935).

[34] A. A. Louis and N. W. Ashcroft, Phys. Rev. Lett. **81**, 4456 (1998); J. Non-Cryst. Solids **250-252**, 9 (1999).

[35] S. Gravel and N. W. Ashcroft, Phys. Rev. B **76**, 144103 (2007).

[36] In Ref. 7, it is stated that the potential minimum at the given density is approximately 1.5 bohr; upon closer examination of their published figures, we believe that the value should actually be about 1.6–1.65 bohr.

[37] T. Yabuuchi, Y. Nakamoto, K. Shimizu, and T. Kikegawa, J. Phys. Soc. Jpn. **74**, 2391 (2005).

[38] E. Gregoryanz, L. F. Lundegaard, M. I. McMahon, C. Guillaume, R. J. Nelmes, and M. Mezouar, Science **320**, 1054 (2008).

[39] J. Lindhard, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **28**, 8 (1954).

[40] We note that the factor of 1/2 in the second term on the right-hand side of the equation is inadvertently omitted in Ref. 18 (as printed) and we thank Bruno Rousseau (Laboratory of Atomic and Solid State Physics, Cornell University) for bringing this omission to our attention.

[41] K. S. Singwi and M. P. Tosi, *Solid State Physics* (Academic Press, New York, 1981), Vol. 36, p. 177.

[42] P. Vashishta and K. S. Singwi, Phys. Rev. B **6**, 875 (1972).

[43] S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982).

[44] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965); R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[45] S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980); S. H. Vosko and L. Wilk, Phys. Rev. B **22**, 3812 (1980).

[46] The derivation was considerably aided by unpublished notes given to one of the authors (JAP) by Dr. Aitor Bergara.

[47] P. Lloyd and C. A. Sholl, J. Phys. C **1**, 1620 (1968).

[48] E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. **61**, 737 (1971) [Sov. Phys. JETP **34**, 394 (1972)].

[49] A. Milchev and K. Unger, Phys. Status Solidi B **87**, 227 (1978).

[50] I. S. Gradshteyn and I. M. Rhyzik, *Table of Integrals, Series, and Products*, 5th ed. (Academic Press, Boston, 1994); M. R. Spiegel and J. Liu, *Mathematical Handbook of Formulas and Tables*, 2nd ed. (McGraw-Hill, New York, 1999).