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Interatomic interactions in solids: An effective-medium approach

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The description of the total energy of a solid in terms of the effective-medium theory has been studied. With use of the density-functional theory, an exact symmetric formula is presented for describing the total energy in terms of the embedding energies of individual atoms. Different approximate formulas are derived and compared to the conventional pair-potential representation, to the model of Gordon and Kim, and to the semiempirical embedded-atom scheme of Daw and Baskes. The theory is applied to estimate the pair potential in the rare gases He, Ne, and Ar, and the cohesive properties of Al metal. A fair agreement with the experimental results is obtained.

I. INTRODUCTION

The study of static and dynamic properties of lattice defects using molecular dynamics is based on the pair-potential representation of the structural part of the total energy of the system.[1] In metals this is usually written as

$$E_{\rm tot}=\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} V_p(\mathbf{R}_i-\mathbf{R}_j)+E_{\rm vol}\ , \tag{1.1}$$

where V_p is the pair potential, $\mathbf{R}_i$ a position of an atomic nucleus, and N is the total number of atoms. $E_{\rm vol}$ is an energy term which depends only on the volume (or density) of the system but not on the structure. A pair-potential expression of the form of Eq. (1.1) is formally obtained by describing the metal ions by pseudopotentials and applying second-order perturbation theory to calculate the total energy.[2,3] Several different schemes have been proposed to determine the pseudopotential and the corresponding pair potential. In alkali and other nontransition metals, the results obtained, for example, for the photon spectra are in fair agreement with the experimental results.[4] However, the pair-potential picture becomes questionable when applied to lattice defects which cause large perturbations to the nearly homogeneous valence electron density of the perfect metal. Also, the treatment of impurities in the pseudopotential scheme is not straightforward.

Recently, another method has been proposed for calculating the interionic interactions.[5,6] In this so-called "embedded-atom" method, one tries to write the total energy in the form

$$E_{\rm tot}=\sum_{i=1}^{N} F[n_i(\mathbf{R}_i)]+\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\Phi(\mathbf{R}_i-\mathbf{R}_j)\ , \tag{1.2}$$

where F is a function of the electron density n_i at the site of the atom i and Φ is the residual part of the pair ion interaction which can not be included in the first term of Eq. (1.2). The density n_i is the electron density at site $\mathbf{R}_i$ when the atom from that site is removed, i.e., it is electron density provided by the surrounding atoms. The idea is to approximate the total electron density as a superposition of atomic densities n_a in which case n_i is

$$n_i(\mathbf{R}_i)=\sum_{\substack{j=1\\ j\neq i}}^{N} n_a(\mathbf{R}_i-\mathbf{R}_j)\ . \tag{1.3}$$

Equations (1.2) and (1.3) are essentially as easy to use in the computer simulations as the standard pair potential, Eq. (1.1).

The function $F(n)$ is generally nonlinear and then the first term implicitly takes into account the volume-dependent terms of Eq. (1.1). Also, the expression (1.2) includes multi-ion interactions.[7] It is expected that the embedded-atom scheme can then better describe defects like vacancies and surfaces where the density variations are large.

The idea behind Eq. (1.2) comes from the so-called "effective-medium" or "pseudoatom" theory first presented for calculating the energetics of single impurities in metals.[8,9] Daw and Baskes[5] have successfully applied the embedded-atom method for many transition-metal systems by taking an empirical approach; the functions F and Φ are fitted to reproduce some experimental data.

The purpose of the present paper is to look more formally at the possibilities of deriving interionic interactions of the form of Eq. (1.2) using the effective-medium theory. First the total energy of the solid (in any ionic arrangement) is written in a symmetric way in terms of the electron densities provided by the surrounding atoms. This can be done formally exactly using the density-functional theory. Then approximate formulas are derived by using the same approaches which have been earlier applied for single impurities. It is shown that the first-order approximation, in the limit of a weak disturbance from a homogeneous lattice, reduces to the conventional pair-potential picture with the same pair potential as obtained from the perturbation theory. In the case of rare gases, on the other hand, the result is closely related to the Gordon-Kim[10] model for molecular binding.

In Sec. II we present a formal derivation of the total energy in terms of density functionals. In Sec. III approximations are made for obtaining a usable equation of the form of Eq. (1.2). In Sec. IV the results are compared to the conventional pair-potential picture, to the scheme of Gordon and Kim,[10] and to the semiempirical formalism of Daw and Baskes.[5] Approximate (*ab initio*) results for rare gases and Al metal are given in Sec. V. Section VI includes discussion and conclusions.

II. FORMAL THEORY

According to the density-functional theory[11,12] the total energy of system of electrons in an external potential can be expressed as a functional of the total electron density. This functional has the variational property that the exact ground-state electron density minimizes it.[13] In a solid, the external potential is provided by the atomic nuclei which are fixed at sites $\mathbf{R}_i$ (adiabatic Born-Oppenheimer approximation is assumed). The total energy of the metal consisting of N atoms is

$$E_{\text{tot}}^N = E_R^N[n] \ , \tag{2.1}$$

where n is the total ground-state electron density, and the subscript R indicates that the functional depends on the sites $\mathbf{R}_i$ and charges Z_i of the nuclei (also the electrostatic nucleus-nucleus repulsion is included). If one atom is removed from the metal the energy change, the so-called embedding energy, is

$$\Delta E_i = E_{\text{tot}}^N - E_{\text{tot}}^{N-1} - E_{\text{atom}} \ , \tag{2.2}$$

where E_{atom} is the total energy of a free atom in vacuum. The subscript i indicates that the energy depends upon which atom is removed. The embedding energy can be written as[8]

$$\Delta E_i = \Delta E_i[n_i] \ , \tag{2.3}$$

where n_i is the *self-consistent* ground-state electron density in the system *after* the atom i has been removed (but other atom sites are kept fixed). Equation (2.3) is a trivial generalization of the density-functional theorem. The density n_i uniquely defines the external potential of the $N-1$ nuclei. Then, since the site of the removed atom $\mathbf{R}_i$ is known, also the external potential of the original system with N atoms is known and both E_{tot}^{N-1} and E_{tot}^N can be formally expressed as functionals of the same density n_i. This is the key idea of the effective-medium theory when applied to calculate energies of impurities in metals. It simply means that the binding energy of the impurity can be calculated directly from the *unperturbed* electron density of the host metal.[8,9]

Using Eqs. (2.2) and (2.3), we write the total energy of the metal now in terms of the embedding energies. By removing one atom we can immediately write

$$E_{\text{tot}} = E_{\text{tot}}^{N-1}[n_i] + \Delta E_i[n_i] + E_{\text{atom}} \ . \tag{2.4}$$

We can successively remove atoms one by one and get finally

$$E_{\text{tot}} = N E_{\text{atom}} + \sum_{i=1}^{N-1} \Delta E_i[n_{1,2,3,\ldots i}] \ , \tag{2.5}$$

where N is the number of atoms in the system and $n_{1,2,3,\ldots i}$ is the self-consistent electron density of the system where atoms at the sites $1,2,3,\ldots i$ have been removed. Each term of this sum depends upon which atom is removed and which atoms had been taken out before. By taking an average of all possible orders of removing the atoms, Eq. (2.6) can be made symmetric:

$$\begin{aligned} E_{\text{tot}} &= N E_{\text{atom}} + \frac{1}{N}\sum_{i=1}^{N-1} \Delta E_i[n_i] + \frac{1}{N(N-1)} {\sum_{i,j}}' \Delta E_j[n_{ij}] \\ &\quad + \frac{1}{N(N-1)(N-2)} {\sum_{i,j,k}}' \Delta E_k[n_{ijk}] + \cdots \\ &= N E_{\text{atom}} + S_1 + S_2 + S_3 + \cdots \ . \end{aligned} \tag{2.6}$$

The prime in the sums above indicates that terms which have two or more indices the same are omitted. Each sum in Eq. (2.6) contributes about the same order of magnitude to the total energy. To find a convergent series we first define the sums

$$\tilde{S}_2 = \frac{1}{N(N-1)} {\sum_{i,j}}' (\Delta E_j[n_{ij}] - \Delta E_j[n_j]) \ , \tag{2.7}$$

$$\tilde{S}_3 = \frac{1}{N(N-1)(N-2)} {\sum_{i,j,k}}' (\Delta E_k[n_{ijk}] - \Delta E_k[n_{ik}] - \Delta E_k[n_{jk}] + \Delta E_k[n_k]) \ . \tag{2.8}$$

In these sums only those terms in which each of the removed atoms are close to each other are non-negligible. If the atoms are far apart they do not interact ($\Delta E_j[n_{ij}] \approx \Delta E_j[n_j]$ if $|\mathbf{R}_i - \mathbf{R}_j|$ large). The sums $\tilde{S}$ are related to the sums S in Eq. (2.6) by

$$S_n = \tilde{S}_n + \begin{Bmatrix} n-1 \\ n-2 \end{Bmatrix} \tilde{S}_{n-1} + \cdots + S_1 \ . \tag{2.9}$$

Equation (2.6) can now be rewritten as

$$\begin{aligned} E_{\text{tot}} &= N E_{\text{atom}} + \sum_i \Delta E_i[n_i] + \tfrac{1}{2} {\sum_{i,j}}' (\Delta E_j[n_{ij}] - \Delta E_j[n_j]) \\ &\quad + \tfrac{1}{6} {\sum_{i,j,k}}' (\Delta E_k[n_{ijk}] - \Delta E_k[n_{ik}] \\ &\qquad - \Delta E_k[n_{jk}] + \Delta E_k[n_k]) + \cdots \end{aligned} \tag{2.10}$$

Now in each sum (except in the first) each term is negligible if any pair of the sites are far from each other. It is then expected that the expansion converges fast even if each sum has seemingly more terms than the previous one. (For example, later it will be shown that in calculating electrostatic interactions between atoms, only the first two sums in this expansion are nonzero.)

In this functional form Eq. (2.10) is exact. In a large perfect crystal, each atom is in a similar surrounding. The cohesive energy can then be expressed as

$$E_{\text{coh}} = -\Delta E_i[n_i] - \tfrac{1}{2} \sum_j (\Delta E_j[n_{ij}] - \Delta E_j[n_j]) + \cdots \ , \tag{2.11}$$

and since, by definition, $\Delta E_i[n_i]$ is the embedding energy of an atom in a preexisting vacancy, the vacancy formation energy (for an unrelaxed vacancy) is

$$E_{\mathrm{vac}}=\tfrac{1}{2}\sum_{j}(\Delta E_j[n_{ij}]-\Delta E_j[n_j])+\cdots \; . \tag{2.12}$$

The exact symmetric expression, Eq. (2.10), is now a starting point in trying to find applicable approximate formulas.

III. APPROXIMATIVE EXPRESSIONS

A. Electron density

The electron density which determines the embedding energy in the functional $\Delta E_i[n_{1,2,3,\ldots i}]$ is the self-consistent ground-state electron density of the system where atoms from sites $1,2,3,\ldots i$ are removed. It is obvious that any expression based on the embedding energy functions can not be useful if the self-consistent electron density has to be calculated for each atomic configuration. (It would then be easier to calculate directly the total energy of the whole system self-consistently and the effective-medium theory would not be needed at all.) For making a practical scheme, the electron density has to be approximated by a superposition of densities associated with each atom. These densities $n_a(\mathbf{r}-\mathbf{R}_i)$ do not necessarily have to be the densities of free atoms but can be densities of some kind of pseudoatoms which better describe the screening charge in the metal. (In the linear screening of pseudopotentials n_a would be exactly the screening charge of the pseudopotential.)

In the following we will always make the approximation that the density can be expressed as

$$n_{1,2,3,\ldots i}(\mathbf{r})=\sum_{j=i+1}^{N} n_a(\mathbf{r}-\mathbf{R}_j)\;, \tag{3.1}$$

and specify later, whenever necessary, what exactly is meant by the pseudoatom density n_a.

B. Local approximation for the embedding functional

As an illustrative example we will now assume that the embedding energy is a *function* of the local electron density. This is the simplest form of the embedding energy functionals. The function can be calculated, for example, by embedding the atom in a homogeneous electron gas, in which case it can be viewed as the first term in a systematic expansion of the embedding energy in terms of density gradients or perturbation corrections.[8] In the local approximation

$$\Delta E_i[n_i]=\Delta E^{\mathrm{hom}}[n_i(\mathbf{R}_i)]\;, \tag{3.2}$$

where $\Delta E^{\mathrm{hom}}(n)$ is the embedding energy of the atom in a homogeneous electron gas of density n. To simplify the notations we have dropped the subscript i from the function ΔE^{hom} assuming that there is only one kind of atoms in the system. Using Eq. (3.1) for the density we can write

$$n_{ij}(\mathbf{R}_j)=n_j(\mathbf{R}_j)-n_a(\mathbf{R}_j-\mathbf{R}_i) \tag{3.3}$$

and the function $\Delta E^{\mathrm{hom}}(n_{ij})$ needed in Eq. (2.10) can be expanded as

$$\Delta E^{\mathrm{hom}}(n_{ij})=\Delta E^{\mathrm{hom}}(n_j) -n_a(\mathbf{R}_i-\mathbf{R}_j)\frac{\partial \Delta E^{\mathrm{hom}}(n_j)}{\partial n_j}+\cdots \; . \tag{3.4}$$

Expanding also $\Delta E^{\mathrm{hom}}(n_{ijk})$ in the same way and substituting in Eq. (2.10) we find (by neglecting a small second-order term and all higher-order terms, see Appendix A)

$$E_{\mathrm{tot}}\approx NE_{\mathrm{atom}}+\sum_i\left[\Delta E^{\mathrm{hom}}(n_i)-\tfrac{1}{2}n_i\frac{\partial\Delta E^{\mathrm{hom}}(n_i)}{\partial n_i}+\tfrac{1}{6}n_i^2\frac{\partial^2\Delta E^{\mathrm{hom}}(n_i)}{\partial n_i^2}\right]. \tag{3.5}$$

By defining a function

$$F^{\mathrm{hom}}(n)=E_{\mathrm{atom}}+\Delta E^{\mathrm{hom}}(n)-\tfrac{1}{2}n\frac{\partial\Delta E^{\mathrm{hom}}(n)}{\partial n}+\tfrac{1}{6}n^2\frac{\partial^2\Delta E^{\mathrm{hom}}(n)}{\partial n^2}\;, \tag{3.6}$$

the total energy of the metal can be written as

$$E_{\mathrm{tot}}=\sum_{i=1}^{N}F^{\mathrm{hom}}(n_i(\mathbf{R}_i))\;. \tag{3.7}$$

This is the desired form of Eq. (1.2). In this simplest local approximation there is no additional pair-potential sum. The relationship (3.6) between the function F^{hom} and the embedding energy function ΔE^{hom} can also be obtained directly by requiring that the total energy is written in the form of Eq. (3.7) as shown in Appendix A. A purely local expression of the form of Eq. (3.7) cannot be a good approximation for solids since it results in unreasonable results for elastic constants as shown by Daw and Baskes.[5]

C. Corrections from the perturbation theory

One systematic way to improve the local approximation in the effective-medium theory is to use the perturbation theory.[8,9] The first-order correction to the homogeneous electron-gas term of Eq. (3.2) is

$$\Delta E^{(1)}(\mathbf{R}_i)=\int d^3\mathbf{r}\,\Delta\rho(\mathbf{r}-\mathbf{R}_i)\,\delta v^{\mathrm{ext}}(\mathbf{r})\;, \tag{3.8}$$

where $\Delta\rho_i(\mathbf{r})$ is the atom which induces charge density in the homogeneous electron gas $[\Delta\rho(\mathbf{r})=\Delta n(\mathbf{r})-Z\delta(\mathbf{r})$, where Δn is the reduced density] and $\delta v^{\mathrm{ext}}(\mathbf{r})$ is the difference in the external potentials between the homogeneous electron gas and the real metal. Equation (3.8) can be written in a more useful form by using for the homogeneous electron gas density an average density

$$\bar{n}_i(\mathbf{R}_i)=-\frac{1}{\alpha}\int d^3r\, n_i(\mathbf{r})\int d^3r'\frac{\Delta\rho(\mathbf{r}'-\mathbf{R}_i)}{|\mathbf{r}-\mathbf{r}'|}\;, \tag{3.9}$$

where α is defined as

$$\alpha=-\int d^3r\int d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\;, \tag{3.10}$$

and is assumed to be nonzero [which is not necessarily true for all $\Delta\rho$ (Refs. 8 and 9)]. Using Eqs. (3.9) and (3.10) it is straightforward to show that the first-order correction reduces to the electrostatic interaction between the induced charge density of the embedded atom, $\Delta\rho$, and the total charge density of the system in which the atom is embedded. Equation (3.8) then becomes

$$\Delta E^{(1)}(\mathbf{R}_i)=\int d^3r\,\Delta\rho(\mathbf{r}-\mathbf{R}_i)\phi(\mathbf{r}) , \tag{3.11}$$

where ϕ is the total electrostatic potential of the system (without the potential of the atom to be embedded). To be consistent with the approximation (3.1) the pseudoatom density n_a should be taken to be the electron density corresponding to the induced charge $\Delta\rho$ (i.e., $\Delta\rho$ minus the nuclear charge). With this approximation the correction $\Delta E^{(1)}$ can be written as

$$\Delta E^{(1)}(\mathbf{R}_i)=\sum_{j\,(\neq i)}\int d^3r\int d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} . \tag{3.12}$$

Substituting this for Eq. (2.10) it turns out that only the two first sums of the expression are nonzero. Including also the local part of the embedding energy from Sec. III C, the total energy of the metal will be

$$E_{\text{tot}}=\sum_i F^{\text{hom}}[\bar{n}(\mathbf{R}_i)] + \frac{1}{2}\sum_i\sum_{j\,(\neq i)}\int d^3r\int d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} . \tag{3.13}$$

This expression is again of the form of Eq. (1.2), the pair potential being now the electrostatic interaction between the pseudoatoms. The fact that the average density $\bar{n}$ now appears in the function F^{hom} does not make the application of the Eq. (3.13) more difficult since the averaging can be made to the pseudoatom density before the summation of the total density [i.e., the pseudoatom density in Eq. (3.1) is replaced by an averaged pseudoatom density $\bar{n}_a$]. However, there is a self-consistency requirement: the induced density $\Delta\rho$ should be calculated by embedding the atom in a homogeneous electron gas of density $\bar{n}$ which depends on $\Delta\rho$ through Eqs. (3.1) and (3.9). This condition cannot be strictly fulfilled if the superposition approximation for the total electron density is required. The most consistent way is to calculate $\Delta\rho$ in a density $\bar{n}_0$ which is an average over all atom sites [as defined in Appendix C, Eq. (C3)]. The induced charge density is spherically symmetric. At small distances from the nucleus it is governed by the core electrons and is very close to that of a free atom. At large distances $\Delta\rho(r)$ has Friedel oscillations, whereas the free-atom density goes to zero exponentially. If the short-range atomic-like behavior is dominating in the electrostatic sum of Eq. (3.13), then the results should not be sensitive on which density $\Delta\rho$ is determined. However, if the long-range Friedel oscillations turn out to be important, then the self-consistency becomes essential, and, also, the approximation of the superposition of the pseudoatom densities becomes questionable.

In the perturbation theory also higher-order corrections can be systematically added in calculating the embedding-energy function in an inhomogeneous electron gas. Since we want to keep the approximation of Eq. (3.1), there is not any obvious systematic way to improve the total energy functional, Eq. (2.10), using higher-order perturbation theory.

D. Corrections using the mixed perturbation scheme

For taking advantage of the local nature of the screening in metals and for avoiding the problem arising from the long-range Friedel oscillations, Nørskov[14] has proposed a "mixed perturbation scheme." The key idea is that in the close vicinity of the embedded atom (region a_i), the potential is governed by the atom and can be approximated to be the same both in the homogeneous electron gas and in the real metal. Further out, on the other hand, the potential can be approximated to be that of the host, i.e., unaffected by the embedded atom. The lowest-order correction to ΔE^{hom} in this approach can be written as[6,14]

$$\delta\Delta E_i=\int_{a_i} d^3r\,\Delta\rho(\mathbf{r}-\mathbf{R}_i)\delta\phi^{-a_i}(\mathbf{r}) + \int_{a_i} d^3r\,\Delta\rho(\mathbf{r}-\mathbf{R}_i)\delta v^{a}_{\text{ext}}(\mathbf{r}) + \delta\int_{-\infty}^{\varepsilon_F} d\varepsilon\,\varepsilon\Delta n(\varepsilon) , \tag{3.14}$$

where $\delta\phi^{-a_i}(\mathbf{r})$ is the part of the electrostatic potential of the metal which is caused by the charges outside the region a_i, and $\delta v^{a}_{\text{ext}}(\mathbf{r})$ is the change in the external potential caused by the positive charges inside the region a_i. The last integral comes from the change in the one-electron energy eigenvalues when the atom is moved from the homogeneous electron gas to the real metal. The first two integrals are extended over a sphere a_i centered at $\mathbf{R}_i$. In practice, the sphere a_i is always so small that inside it there is no other nuclei than that of the embedded atom. Then $\delta v^{a}_{\text{ext}}$ is caused by the positive background charge of the homogeneous electron gas. By making again the approximation (3.1) of superposition of pseudoatom densities, Eq. (3.14) can be written as (see Appendix B for details)

$$\delta\Delta E_i=\sum_{j\,(\neq i)}\int d^3r\int d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} - \sum_{j\,(\neq i)}\int_{-a_i} d^3r\int d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} + \delta\int_{-\infty}^{\varepsilon_F} d\varepsilon\,\varepsilon\Delta n(\varepsilon) , \tag{3.15}$$

where the notation $-a_i$ under the integral means that the sphere a_i is omitted in the integration.

The change in the one-electron eigenvalues is difficult to estimate. Nørskov *et al.*[6] have studied approximate ways to derive this term and thus go beyond the result of Eq. (3.13). Here we only want to mention that if the potential outside the sphere a_i is assumed to be purely electrostatic and apply simple perturbation theory to estimate the change in the eigenvalues, the last term in Eq. (3.15) cancels exactly the second term. The result of the normal perturbation theory of Sec. III C is then recovered. Note that in this limit the result is independent of the choice of the radius of the sphere a_i.

IV. RELATION TO OTHER METHODS

A. Pair potential

The present result of the effective-medium theory, Eq. (3.13), which includes the perturbation correction to the local energy function, can be related to the conventional pair-potential picture derived from the pseudopotentials. This can be done by extracting from the first term of Eq. (3.13), the pair interaction part and the structure-independent part. The straightforward derivation is done in Appendix C and it gives

$$E_{\mathrm{tot}} \approx \sum_i [E_{\mathrm{atom}} + \Delta E^{\mathrm{hom}}(\bar{n}_0) - \alpha \bar{n}_0] + \tfrac{1}{2} \sum_i \sum_{j\,(\neq i)} \int d^3r \int d^3r' \frac{[\Delta\rho(\mathbf{r}-\mathbf{R}_i) - n_a(\mathbf{r}-\mathbf{R}_i)]\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} , \tag{4.1}$$

where $\bar{n}_0$ is an average of the (averaged) densities in Eq. (3.9) and $\Delta\rho$ and n_a are the charge density and electron density of the pseudoatom, respectively. The first sum is now structure independent but depends on the volume of the system through $\bar{n}_0$. The second sum is the pair interaction: it is the sum of the electrostatic interactions between a screened atom (screened pseudopotential) and a bare pseudopotential expressed in the form

$$V_{\mathrm{pseudo}} = \int d^3r' \frac{\Delta\rho(\mathbf{r}-\mathbf{r}') - n_a(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}|} . \tag{4.2}$$

Note that here n_a is the electron density corresponding to the charge density $\Delta\rho$ so that the difference of these is caused by the atomic core (nucleus) or a positive pseudocharge corresponding to the pseudopotential.

Equation (4.1) has exactly the same form of that obtained from the pseudopotential theory using local pseudopotentials. The volume-dependent term is the embedding energy of an atom in a homogeneous electron gas without a compensating positive background charge [subtracting this out gives the third term in Eq. (4.1)]. The electrostatic interaction between the atom and compensating positive charges enters now in the second sum as interaction between the atom and bare pseudopotentials (which have replaced the positive background). The volume-dependent term [the first sum in Eq. (4.1)] can be cast to the form familiar from the perturbation theory by noticing that ΔE^{hom} is the sum of embedding energies of the bare pseudopotential and free electrons minus the binding energy of the atom (E_{atom}). The average electron density $\bar{n}_0$ as defined in Appendix C is not exactly the overall average of the valence electron density which appears in the formulas of the conventional pseudopotential theory. However, if the potential is weak, the difference between these two densities is small and in this limit of weak pseudopotentials the effective-medium result agrees with the pseudopotential result.

Rasolt and co-workers[15,16] have developed a method for deriving pair interactions in metals which is related in the effective-medium theory in the sense that the results of atoms embedded in an electron gas was used. In their method the key quantity is the induced electron density of an atom embedded in a jellium vacancy. This has two obvious advantages. First, the electron density inside a jellium vacancy describes better than the homogeneous jellium the electron density in the vacancy of the actual metal. The second advantage is that the density of the electron gas is fixed to the average valence electron density which, e.g., guarantees that the Friedel oscillations have correct wavelength. In the theory of Dagens *et al.*[16] and Rasolt *et al.*[15] the induced electron density was used to derive a pseudopotential which then was used in a normal way to calculate the pair-ion interaction. In the effective-medium theory one could also use the jellium vacancy model as a reference system instead of a homogeneous electron gas. One would then first calculate the embedding energy of an atom in a jellium vacancy and approximate the functional $\Delta E_i[n_i]$ by

$$\Delta E_i[n_i] = \Delta E^{\mathrm{vac}}(\bar{n}_i^{v}) + \sum_{j\,(\neq i)} \int d^3r \int d^3r' \frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} , \tag{4.3}$$

where the effective electron density $\bar{n}_i^{v}$ is now defined requiring

$$\int d^3r \int d^3r' \frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\bar{n}_i^{v}\Theta(|\mathbf{r}-\mathbf{R}_i| - R_{\mathrm{WS}})}{|\mathbf{r}-\mathbf{r}'|} = \sum_{j\,(\neq i)} \int d^3r \int d^3r' \frac{\Delta\rho(r-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} . \tag{4.4}$$

The Wigner-Seitz radius is determined here from the average density of the metal. Another possibility to satisfy Eq. (4.4) would be to fix the density $\bar{n}_i^{v}$ to be the average valence electron density and vary R_{WS}. In any case, the use of the systematic expansion (2.10) would no longer be straightforward since the evaluation of functionals $\Delta E_j[n_{ij}]$ would be more difficult. Also, the electron-gas calculations would have two parameters, the density and the Wigner-Seitz radius which determines the size of the vacancy. Approximation (4.3) would nevertheless lead to a formula which would have the same form as (3.13), but where the function F would be related to the embedding energy in a jellium vacancy [not necessarily in the same way as in F^{hom} to ΔE^{hom} in Eq. (3.6)].

B. Gordon-Kim model

Gordon and Kim[10] have proposed a non-self-consistent method for calculating binding energies of molecules. In the simplest form this theory makes an assumption that the total electron density of a molecule is the superposition of atomic electron densities. Density-functional approximations are then used to estimate the energy change when atoms are brought together to form a molecule. The total energy consists of kinetic, electrostatic, and exchange-correlation parts. The electrostatic contribution is exactly the same as in Eq. (3.13) when the charge density $\Delta\rho$ is taken to be the charge density of a free atom. The simplest approximation for the kinetic and exchange-correlation parts is a local approximation:

$$\Delta T+\Delta E_{\text{xc}}=\int d^3r n(\mathbf{r})f(n(\mathbf{r}))-N\int d^3r\, n_a(\mathbf{r})f(n_a(\mathbf{r}))\ , \tag{4.5}$$

where $n(\mathbf{r})$ is the total electron density of the molecule of N atoms (supposed to be similar to simplify notations) and $f(n)$ is the energy per electron of a homogeneous electron gas of density n. By substituting the superposition approximation (3.1) to $n(\mathbf{r})$, Eq. (4.5) can be written as

$$\Delta T+\Delta E_{\text{xc}}=\sum_i\int d^3r\, n_a(\mathbf{r}-\mathbf{R}_i)\left[f\left[\sum_j n_a(\mathbf{r}-\mathbf{R}_j)\right]-f[n_a(\mathbf{r}-\mathbf{R}_i)]\right]\ . \tag{4.6}$$

If we now define an effective density $\bar{n}_i^{\text{GK}}$ [different from that used in the normal effective medium theory, Eq. (3.9)] as a solution of the equation

$$\int d^3r\, n_a(\mathbf{r}-\mathbf{R}_i)\left[f\left[n_a(\mathbf{r}-\mathbf{R}_i)-\sum_{j\,(\neq i)}n_a(\mathbf{r}-\mathbf{R}_j)\right]-f[n_a(\mathbf{r}-\mathbf{R}_i)-\bar{n}_i^{\text{GK}}]\right]=0\ , \tag{4.7}$$

we can write the total energy as

$$E_{\text{tot}}=\sum_i F^{\text{GK}}(\bar{n}_i^{\text{GK}})+\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\int d^3r\int d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{4.8}$$

where

$$F^{\text{GK}}(\bar{n})=E_{\text{atom}}+\int d^3r\, n_a(\mathbf{r})\{f[n_a(\mathbf{r})+n]-f[n_a(\mathbf{r})]\}\ . \tag{4.9}$$

Equation (4.8) now has the same form as Eq. (3.13), but the function F is slightly different. Moreover, the average density appearing in Eq. (4.8) cannot, in general, be expressed as a simple superposition of (averaged) atomic densities without doing additional approximations. The non-self-consistent (NSC) approach could also be used to estimate the embedding energy of an atom in a homogeneous electron gas. Since the atom electron density is kept frozen there will be no Coulomb contribution to the embedding energy and it will be, using the same local approximation as in Eq. (4.6),

$$\Delta E_{\text{NSC}}^{\text{hom}}(\bar{n})=\int d^3r\{[n_a(\mathbf{r})+n]f[n_a(\mathbf{r})+n]-\bar{n}f(\bar{n})-n_a(\mathbf{r})f[n_a(\mathbf{r})]\}\ . \tag{4.10}$$

The relation between $\Delta E_{\text{NSC}}^{\text{hom}}$ and F^{GK} is not exactly the same as in Eq. (3.6) but gives additional terms which nevertheless are smaller than the three first terms in Eq. (3.6). The use of the local density approximation for the exchange-correlation energy functional in Eq. (4.6) is commonly accepted and widely used in the density-functional calculations. For the kinetic energy, however, the local approximation (Thomas-Fermi) is not accurate. Harris[17] has made an extension to the Gordon-Kim model, by calculating the kinetic-energy change from single-particle energy eigenvalues. This approach clearly improves the local model, but seems not to be very useful here where we want to express the energy with help of the electron density alone. Recently Plumer and Stott[18] have made an extensive study on approximations of the kinetic-energy functional. The resulting approximations for embedding energies of atoms in a *inhomogeneous* electron gas could be better used in looking for approximations of the form of Eq. (1.2) for the total energy.

C. Semiempirical method of Daw and Baskes

Using the ideas of the pseudoatom method of Stott and Zaremba[8] and Daw and Baskes[5] postulated that the total energy is written as

$$E_{\text{tot}}=\sum_i F(n_i)+\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\Phi(\mathbf{R}_i-\mathbf{R}_j)\ , \tag{4.11}$$

where n_i is the density defined in Eq. (3.1) and taking n_a to be the free atom density. The pair potential Φ was assumed to be a purely repulsive short-range potential describing the core-core repulsion. The functions F and Φ were fitted to reproduce experimental lattice constant, elastic constants, vacancy formation and sublimation energies, and the energy difference between fcc and bcc phases. Equation (4.11) was found to give good results to surface geometries of solid Pd and Ni,[5] and properties of several transition-metal liquids.[7] The comparison of Eq. (4.11) to Eq. (3.13) shows that even if they have the same form, the individual terms are very different. The pair potential in (3.13) is attractive in typical interatomic distances in metals, whereas in Eq. (4.11) it is weakly repulsive. However, there is an ambiguity in determining the functions F and Φ: any part of the function F which is proportional to the density n can be equally well included in the pair-potential sum.[5,7] This means that one can always add to the pair potential $\Phi(r)$ a term $\gamma n_a(r)$, where

γ is any constant by subtracting from the function $F(n)$ the linear term γn. The functions F and Φ from a semiempirical scheme can then not be separately compared to those determined from an *ab initio* theory.

In the semiempirical model one uses directly the density n_i without any averaging of the type of Eq. (3.9). If one can approximate $\bar{n}_a \approx c n_a$, where c is a constant, then also in Eq. (3.13) $\bar{n}_a$ can be replaced by n_a by redefining the function F. This approximation is reasonable if only the short-range behavior of n_a is important [meaning also that one could use the free-atom densities in Eq. (3.13)]. The form of the total energy assumed by Daw and Baskes[5] can thus be obtained in an approximate way also from the present theory. One should also mention that in the transition metals the semiempirical formula also includes the interactions between the localized d electrons, which are strongly underestimated in the approximate formula (3.13).

V. RESULTS

In rare gases the function $\Delta E^{\text{hom}}(\bar{n})$ is proportional to the density $\bar{n}$ and the total energy of the form of Eq. (3.13) can be expressed as sum of pair interactions. In Fig. 1 the calculated pair potentials for He, Ne, and Ar are compared to the experimental scattering potentials.[19] In the calculations the free-atom densities were used for $\Delta\rho(r)$. This is a good approximation in the case of a rare gas which is a closed-shell atom and relaxes only slightly when embedded in an low-density electron gas. The effective-medium theory cannot reproduce the attractive part of the potential which is mainly due to the van der Waals interaction. In the repulsive region the calculated potentials are in fair agreement with the experimental results.

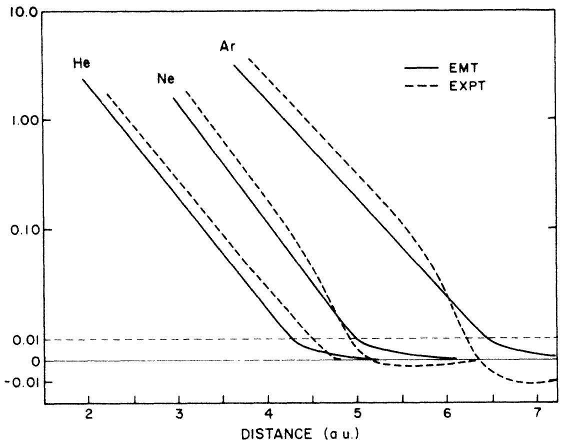

FIG. 1. Interatomic potentials for He, Ne, and Ar. The solid lines are the results of the present calculation and the dashed lines the experimental results (Ref. 19). Note the change of the vertical scale from linear to logarithmic at 10 meV.

For Al metal we have estimated the cohesive energy, equilibrium lattice constant, bulk modulus, vacancy formation energy, and surface energy, using for $\Delta\rho$ both the free-atom density and (in an approximate way) the induced densities in homogeneous electron gas. The results are shown in Table I. The free-atom density gives too large a lattice constant and too small a cohesive energy. The reason is that the function $F(n)$ becomes too repulsive due to the fact that the core electrons are overemphasized in determining $\bar{n}$. When the atom is embedded in an electron gas the screening makes the atom more compact (only the Friedel oscillations reach further out). This means that if $\Delta\rho$ is the induced density in an electron gas, the average density $\bar{n}_i$ in Eq. (3.13) will be smaller and the lattice constant will be reduced from the too large value obtained using the free-atom densities. The function $\Delta\rho$, calculated in a self-consistent way so that it is the induced density of the atom when embedded in the electron gas of density $\bar{n}_i$, is very tedious to obtain due to the long-range Friedel oscillations. As a first approximation we have completely neglected these oscillations and approximate that $\Delta\rho(r)$ is zero beyond a radius R_m which is determined as the first radius which satisfies

$$\int_{r<R_m} d^3r\, \Delta\rho(r) = 0 \ . \tag{5.1}$$

The radius R_m depends on the electron density in which $\Delta\rho$ is calculated, and for Al it varies from 4.5 to 3.9 when $\bar{n}$ goes from 0.001 to 0.03. Since this radius is smaller than the interatomic distance in Al, the electrostatic interactions in Eq. (3.13) reduce to $\alpha_{\text{at}}(\bar{n})\bar{n}$, where α_{at} is defined in Eq. (B3) (the integrals go over a sphere of radius R_m). The total energy then becomes

$$E_{\text{tot}} = \sum_i [F(\bar{n}_i) - \tfrac{1}{2}\alpha_{\text{at}}(\bar{n}_i)\bar{n}_i] \tag{5.2}$$

and depends in this approximation only on the density.

TABLE I. Calculated properties of aluminum metal. In the non-self-consistent model Eq. (3.13), and in the semi-self-consistent model Eq. (5.2), were used, respectively. In both cases the electron densities of free atoms were used. The experimental surface energy is estimated from the surface tension of the liquid phase.

	Non-self-consistent	Semi-self-consistent	Expt.
Lattice constant (a.u.)	9.8	7.3	7.6
Cohesion energy (eV)	2.2	3.3	3.3
Bulk modulus (Mbar)	0.1	0.3	0.7
Vacancy formation energy (eV)	0.05	0.2	0.7
Surface energy (111) (erg/cm^2)	50	260	700
Surface energy (100) (erg/cm^2)	30	170	700

Since there is no pair potential part, Eq. (5.2) cannot reproduce the correct elastic constants or lattice structure (any structure would have the same energy). However, it is known that the contribution from the pair-potential sum to the cohesive energy, for example, in Al is very small[3] and that the energy difference between different lattice structures, e.g., bcc and fcc is small in simple metals. In Fig. 2 the total energy of Eq. (5.1) is shown as a function of the density $\bar{n}$ for aluminum. The cohesive properties of Al metal are estimated using the expression (5.2) and again the free-atom electron densities for determining the density $\bar{n}$. The interpolation formulas for all the numerical data for Al are given in Appendix D and the results are shown in Table I. The agreement with the experimental results is better than using the free-atom densities also as the averaging function. This demonstrates the importance of the screening of the atomic densities in metal. Still better agreement with the experiments could perhaps be obtained by the full self-consistent application of the formula (3.13), but the method would no longer be practical.

VI. DISCUSSION AND CONCLUSIONS

Using the effective-medium approach we have shown that the total energy of a metal can be written in the form of Eq. (1.2), where the function F can be calculated from the embedding energy of an atom in a homogeneous electron gas, and the pair-potential contribution becomes the electrostatic interaction between screened atoms. The resulting equation (3.13) reduces to the conventional pair-potential result in the limit of a weak pseudopotential. In the case where the total electron density is well described as a superposition of *free-atom* densities, the result of the effective-medium theory is closely related to the Gordon-Kim model of molecular binding.

The application of the formula (3.13) has some unwanted difficulties. The charge density $\Delta\rho$ is the induced density of an atom embedded in a homogeneous electron gas of density $\bar{n}_0$, and thus has long-range Friedel oscillations. Since the density $\bar{n}_0$ is generally lower than the average valence electron density of the metal, these oscillations have a longer wavelength than the Friedel oscillations in the real metal. The existence of these oscillations makes the summations in Eqs. (3.1) and (3.13) slowly converging. Another problem is the self-consistency requirement, that $\bar{n}_0$ should be consistent with $\Delta\rho$ through Eqs. (3.1), (3.9), and (C.1). Fortunately, the main part of the electrostatic interaction comes from small distances where the induced electron density is nearly that of a free atom and fairly independent on $\bar{n}_0$.

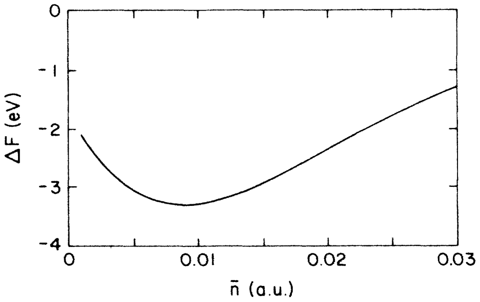

FIG. 2. The variation of the approximate total energy of Eq. (5.2) as a function of the average electron density $\bar{n}$ at a lattice site in aluminum. The quantity plotted is $\Delta F + E_{\text{tot}}/N - E_{\text{atom}}$.

Even if Eq. (3.13) is a result of a systematic calculation it contains only the first terms of the exact expansion (2.10). Moreover, it has the additional approximation (3.1) of superposition of pseudoatom densities. In the case of closed-shell atoms, rare gases, free-atom densities can be used to replace the induced densities in Eq. (3.13). In the case of metals, however, the screening is more important and cannot be totally neglected. Estimations of the properties of Al gives reasonable results for the cohesive energy and equilibrium lattice constant but underestimates the bulk modulus, vacancy formation energy, and surface energy.

In conclusion, we have derived an approximate formula for interatomic interactions in solids. In the limit of weak pseudopotentials it reduces to the conventional pair-potential formula for simple metals and in the limit of extremely rigid atoms (e.g., rare gas) it is closely related to the Gordon-Kim model for molecular binding. Because the formula describes these two extreme limits correctly, it gives support for replacing pair potentials for more general interatomic interactions of the form of Eq. (1.2) in computer simulations. It seems however, that *ab initio* calculations for the functions in Eq. (1.2) do not give as accurate results as one would want in applications of the method. A semiempirical approach might then be more fruitful in practical applications to molecular dynamics, and the present theory would merely serve as a guideline for parametrizing the functions needed.

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APPENDIX A

Assuming superposition of atomic densities, Eq. (3.1), and taking $n_a(\mathbf{R}_i-\mathbf{R}_j)$ to be small if $\mathbf{R}_i \neq \mathbf{R}_j$, we can write Eq. (3.4) to the second order as

$$\Delta E^{\text{hom}}(n_{ij})=\Delta E^{\text{hom}}(n_j)-n_a(\mathbf{R}_i-\mathbf{R}_j)\frac{\partial \Delta E(n_j)}{\partial n_j}+\tfrac{1}{2}[n_a(\mathbf{R}_i-\mathbf{R}_j)]^2\frac{\partial^2 \Delta E(n_j)}{\partial n_j^2} \tag{A1}$$

and

$$\Delta E^{\text{hom}}(n_{ijk})=\Delta E^{\text{hom}}(n_k)-[n_a(\mathbf{R}_i-\mathbf{R}_k)+n_a(\mathbf{R}_j-\mathbf{R}_k)]\frac{\partial \Delta E^{\text{hom}}(n_k)}{\partial n_k}+\tfrac{1}{2}[n_a(\mathbf{R}_i-\mathbf{R}_k)+n_a(\mathbf{R}_j-\mathbf{R}_k)]^2\times\frac{\partial^2 \Delta E^{\text{hom}}(n_k)}{\partial n_k^2}\,. \tag{A2}$$

Substituting these in Eq. (2.10) keeping all terms shown, we get

$$E_{\text{tot}}=NE_{\text{atom}}+\sum_i \Delta E^{\text{hom}}(n_i)$$
$$-\tfrac{1}{2}\sum_i \left[\sum_{j\,(\neq i)} n_a(\mathbf{R}_i-\mathbf{R}_j)\right]\frac{\partial^2\Delta E(N_i)}{\partial n_i}$$
$$+\tfrac{1}{6}\sum_i \left[\sum_{j\,(\neq i)} n_a(\mathbf{R}_i-\mathbf{R}_j)\right]^2\frac{\partial^2\Delta E(n_i)}{\partial^2 n_i}$$
$$+\tfrac{1}{12}\sum_i \left[\sum_{j\,(\neq i)} n(\mathbf{R}_i-\mathbf{R}_j)^2\right]\frac{\partial^2\Delta E(n_i)}{\partial n_i^2}\ . \tag{A3}$$

Since in a solid each atom has of the order of 10 nearest neighbors, it is obvious that the last term in Eq. (A3) is much smaller than the other second order term. If this last term is neglected we get Eq. (3.5) by using the definition of Eq. (3.1) for n_i.

Now we demonstrate that Eq. (3.6) follows directly if we require that the total energy is written in the form of Eq. (3.7). We assume a perfect lattice and derive the vacancy formation energy for an unrelaxed lattice:

$$E_{\text{vac}}=\sum_{i\,(\neq j)}[F(n_{ji})-F(n_i)]$$
$$=\sum_{i\,(\neq j)}\left\{-n_a(\mathbf{R}_j-\mathbf{R}_i)\frac{\partial F(n_i)}{\partial n_i}+\tfrac{1}{2}[n_a(\mathbf{R}_j-\mathbf{R}_i)]^2\frac{\partial^2 F(n_i)}{\partial n_i^2}+\cdots\right\}$$
$$\approx n_i\frac{\partial F(n_i)}{\partial n_i}\ . \tag{A4}$$

The second-order term can be neglected since it is proportional to the sum of squares of individual atomic densities which is much smaller than n_i^2. The embedding energy is the negative of the sum of the vacancy formation and cohesion energies and in the local approximation this means that

$$\Delta E^{\text{hom}}(n_i)\approx F(n_i)-E_{\text{atom}}-n_i\frac{\partial F(n_i)}{\partial n_i}\ , \tag{A5}$$

for which the expansion (3.6) is a solution.

APPENDIX B

Since the electron density is described as in Eq. (3.1) the electrostatic potential $\delta\phi^{-a_i}(\mathbf{r})$ can be written as

$$\delta\phi^{-a_i}(\mathbf{r})=\sum_{j\,(\neq i)}\int_{-a_i}d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{B1}$$

We assume that there is no other positive charges inside a_i then the nucleus of the atom in question. Then δV_{ext}^a is caused solely by the homogeneous background charge of the jellium. In the mixed perturbation theory the effective density is defined as

$$\bar{n}_i=-\frac{1}{\alpha_{\text{at}}}\sum_{j\,(\neq i)}\int_{a_i}d^3r\int_{a_j}d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{B2}$$

where

$$\alpha_{\text{at}}=-\int_{a_i}d^3r\int_{a_i}d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{B3}$$

The second term in Eq. (3.14) can now be written as

$$-\alpha_{\text{at}}\bar{n}_i=\sum_{j\,(\neq i)}\int_{a_i}d^3r\int_{a_i}d^3r'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_i)}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{B4}$$

Combining this to the first term of Eq. (3.14), where the substitution (B1) has been made, results in Eq. (3.15).

APPENDIX C

In a nearly homogeneous metal where the pseudopotential approach is good, the variation in the average densities $\bar{n}(\mathbf{R}_i)$ at different sites $\mathbf{R}_i$ is small. We define

$$\bar{n}_0=\frac{1}{N}\sum_{i=1}^{N}\bar{n}(\mathbf{R}_i) \tag{C1}$$

and write the first term in Eq. (3.13) as

$$\sum_i F^{\text{hom}}[\bar{n}(\mathbf{R}_i)]=\sum_i F^{\text{hom}}\left[\sum_{j(\neq i)} n_a(\mathbf{R}_i-\mathbf{R}_j)\right]$$
$$\approx\sum_i\left[F^{\text{hom}}(\bar{n}_0)+\left[\sum_{j\,(\neq 1)}\bar{n}_a(\mathbf{R}_i-\mathbf{R}_j)-\bar{n}_0\right]\frac{\partial F^{\text{hom}}(\bar{n}_0)}{\partial\bar{n}_0}\right]\ . \tag{C2}$$

Describing F^{hom} in terms of ΔE^{hom} and including only the first two terms in the expansion (3.6) we get

$$\sum_i F^{\text{hom}}(\bar{n}_0)=\sum_i\left[\Delta E^{\text{hom}}(\bar{n}_0)-\bar{n}_0\frac{\partial\Delta E^{\text{hom}}(\bar{n}_0)}{\partial\bar{n}_0}\right]$$
$$+\frac{1}{2}\frac{\partial\Delta E^{\text{hom}}(\bar{n}_0)}{\partial\bar{n}_0}\sum_i\sum_{j\,(\neq i)}\left[-\frac{1}{\alpha}\int d^3r\,n_a(\mathbf{R}_i-\mathbf{R}_j-\mathbf{r})\right]\int d^3r'\frac{\Delta\rho(r')}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{C3}$$

where $\bar{n}_a$ is described in terms of n_a using Eq. (3.9). Since α defined in Eq. (3.10) can be shown to be exactly[7,8]

$$\alpha = + \frac{\partial \Delta e^{\text{hom}}(\bar{n}_0)}{\partial \bar{n}_0} , \tag{C4}$$

Eq. (C3) immediately gives Eq. (4.1).

APPENDIX D

The embedding energy ΔE^{hom} was approximated by an analytic fit to the numerical data. This was chosen to be

$$\Delta E^{\text{hom}}(n) = -1.65 + 1250n - 490e^{-120n} , \tag{D1}$$

where n is in atomic units and ΔE in eV. The function $\alpha_{\text{at}}(n)$ was approximated by

$$\alpha_{\text{at}}(n) = -1002 - 68.24n^{2/3} . \tag{D2}$$

Both above expressions describe the numerical results for aluminum with 0.1 eV accuracy within the density range $n = 0.001, \ldots, 0.03$. The averaging of the atomic electron density using the function $\Delta\rho$ with a cutoff radius R_m defined in Sec. V results to a nearly constant enhancement to the local density. This is approximated by

$$\bar{n}_a(r) = \gamma(\bar{n}) n_a(\bar{n}) , \tag{D3}$$

where γ depends on the average density $\bar{n}$ as

$$\gamma(n) = 1.3696 + 0.0478n^{1/3} . \tag{D4}$$

The Gunnarsson-Lundqvist interpolation formula[20] for the exchange-correlation potential was used in the calculation of ΔE^{hom} and the electron densities of free atoms.

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