Interatomic interactions in the effective-medium theory

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An expression is derived for the total energy of a system of interacting atoms based on an ansatz for the total electron density of the system as a superposition of atom densities taken from calculations for the atoms embedded in a homogeneous electron gas. This leads to an expression for the interaction energy in terms of the embedding energy of the atoms in a homogeneous electron gas, and corrections accounting, for instance, for the d-d hybridization in the transition metals. The density of the homogeneous electron gas is chosen as the average of the density from the surrounding atoms. Due to the variational property of the total-energy functional, the errors in the interaction energy are second order in the deviation of the ansatz density from the true ground-state value. The applicability of the approach is illustrated by calculations of the cohesive properties of some simple metals and all the $3d$ transition metals. The interaction energy can be expressed in a form simple enough to allow calculations for low-symmetry systems and is very well suited for simulations of time-dependent and finite-temperature problems. Preliminary results for the phonon-dispersion relations and the surface energies and relaxations for Al are used to illustrate the versatility of the approach. The division of the total energy into a density-dependent part, an electrostatic "pair-potential" part, and a hybridization part provides a very simple way of understanding a number of these phenomena.

I. INTRODUCTION

The calculation of the total energy for a system of interacting atoms is basically limited by the size or symmetry of the system. Increasing computing power and improvements in the numerical methods have given rise to an enormous increase in the number of first principles calculations available. Still one is limited to systems or unit cells up to about 50 atoms. If the aim is to describe extended defects this is still rather limited, and the present methods are far from fast enough to enable the study of the dynamics of more complex low-symmetry systems. Another limitation of many first-principles calculations is that the amount of physical insight that they provide by themselves is limited. In order to identify the important parameters in the problem and the concepts that allow understanding of different systems for which calculations have not been performed it is necessary to work with simpler models.[1-3]

In the present paper we suggest a different approach to the calculation of the total energy of a complicated system. We use the variational property of the total-energy functional $E[n]$ explicitly to construct a simplified energy function. The resulting expression for the total energy is not much more involved to evaluate than a pair potential. It is therefore well suited for large low-symmetry

systems or for molecular dynamics simulations of finite-temperature and time-dependent problems. Furthermore, the approach gives a very powerful physical picture of the bonding in a condensed, metallic system, which is readily transferrable from one situation to another.

The basic idea is very simple: The total energy of any given atom in a system is determined by the effect of the surrounding atoms. As a starting point we can include this by considering the atom embedded in a homogeneous electron gas set up by the electron density from the surrounding atoms. This means that the total binding energy of a system of N atoms is given, to a first approximation, by

$$\Delta E_{\text{tot}} = \sum_{i=1}^{N} E_{c,i}(\bar{n}_i),\tag{1.1}$$

where $E_{c,i}(\bar{n}_i)$ is a measure of the embedding energy of atom i in a homogeneous electron gas of density $\bar{n}_i$ given by the average of the density Δn_j from the neighboring atoms over the region occupied by atom i:

$$\bar{n}_i = \sum_{j \neq i} \langle \Delta n_j \rangle_i.\tag{1.2}$$

This point of view naturally leads to the concept of a universal energy function $E_{c,i}(n)$ describing (to a first approximation) the bonding of atom i in various situations.

The idea of a density-dependent energy was first introduced with the effective-medium[4,5] or the equivalent quasiatom[6] theory to calculate the binding energy of impurities and adsorbates interacting with metals.[7] A simple density-dependent binding energy can explain a large number of observations, and when corrections that describe the covalent interaction of the gas atom valence states with the d-electrons of transition metals and the interaction with the metal core electrons are included, semiquantitative or, in most cases, quantitative agreement with experimentally determined data has been obtained.[7]

The present paper is an extension of the effective-medium theory from being able to describe the embedding of a single atom in a host to the description of all the atoms in a condensed system. The derivation we shall present is fundamentally different from the one previously given for the single impurity case.[5] It does, however, include this situation in the appropriate limit.

Daw, Baskes, and Foiles[8] have previously proposed to use the effective-medium idea of a density-dependent total energy to treat a system of interacting atoms. By fitting the parameters of their model potential to experiment they have been able to describe a number of complex dynamical systems very successfully.[8] The present derivation of an energy function similar (but not identical) to the one they assume, can be regarded as some justification of their approach. We go one step further, though, in calculating all of the parameters within the local density approximation and use this to describe the bulk cohesive properties of some simple metals and all of the 3d-transition metals. We also show that the phonon spectra and the surface energies and relaxations for Al can be calculated in this way. Apart from illustrating the applicability of the approach, a transparent physical picture of metallic cohesion emerges.

The main emphasis of the paper will be placed on a detailed derivation of the total-energy function based on density functional theory. We therefore start in Sec. II with a discussion of the variational properties of the total energy from a point of view slightly different from that conventionally used, but very useful in what follows. In Sec. III we discuss the reference system used: An atom embedded in a homogeneous electron gas (the effective medium). The derivation of the effective-medium theory for a perfect solid then follows in Sec. IV. In Sec. V we discuss the special features to be considered when the atom shows a narrow resonance in the density of states when it is embedded in the homogeneous electron gas. The low-symmetry situations where the system is not on a perfect lattice are the subject of Sec. VI. Having all of the formalism at hand we then show the results of the applications to a number of high- and low-symmetry systems, and discuss the physical picture that follows in Sec. VII. Finally, in Sec. VIII we summarize.

II. DENSITY FUNCTIONAL THEORY AND THE VARIATIONAL PROPERTIES

In density functional theory the energy E_0 and the electron density n_0 in the ground state can be obtained by minimizing the Hohenberg-Kohn functional[9] of the density

$$E_{HK}[n] = T_{HK}[n] + F[n],   \tag{2.1}$$

where $T_{HK}[n]$ is the kinetic energy of a noninteracting electron gas with density n and $F[n]$ is the sum

$$F[n] = E_{es}[n] + E_{xc}[n],   \tag{2.2}$$

of the electrostatic energy

$$E_{es}[n] = \frac{1}{2} \int \int ' \frac{\rho \rho'}{|r-r'|} dr\, dr'   \tag{2.3}$$

(ρ is the sum of the electron density n and the nuclear charge; omission of the nuclear self-interaction is understood) and the exchange-correlation energy for which we use the local density approximation

$$E_{xc}[n] = \int f_{xc}(n(r))dr = \int n(r)\epsilon_{xc}(n(r))dr.   \tag{2.4}$$

In Eqs. (2.3) and (2.4) and in the following we only show the integration variables in cases where misunderstandings are possible. The kinetic energy term may be calculated as

$$T_{HK}[n] = \sum_{\alpha=1}^{N} \epsilon_\alpha[v[n]] - \int v[n]n.   \tag{2.5}$$

According to the Hohenberg-Kohn theorem the potential v and the one-electron energy parameters ϵ_α can, in principle, be obtained as functionals of n by solving the Kohn-Sham equations[10]

$$(-\tfrac{1}{2}\nabla^2 + v)\psi_\alpha = \epsilon_\alpha \psi_\alpha   \tag{2.6}$$

with the condition

$$\sum_{\alpha=1}^{N} |\psi_\alpha(r)|^2 = n(r).   \tag{2.7}$$

The potential v_0 corresponding to the ground state is related to the density (up to an additive constant) through the relation

$$v_0 = \frac{\delta F}{\delta n} = \phi + v_{xc},   \tag{2.8}$$

where ϕ is the Hartree potential

$$\phi = \int ' \frac{\rho_0'}{|r-r'|},   \tag{2.9}$$

and v_{xc} the exchange-correlation potential

$$v_{xc}(n_0(r)) = \frac{df_{xc}}{dn}(n_0(r)).   \tag{2.10}$$

Due to the variational property of $E_{HK}[n]$ we have

$$E_{HK}[n_0 + \delta n] = E_0 + O(\delta n^2).   \tag{2.11}$$

The potential appearing in expression (2.5) for the kinetic energy may be regarded as an independent variable:

$$T[n,v] = \sum_{\alpha=1}^{N} \epsilon_\alpha[v] - \int vn.   \tag{2.12}$$

For a variation around the ground-state configuration (n_0, v_0) we then have

$$\delta T[n,v]\,|_0 = \int n_0 \delta v - \int n_0 \delta v - \int v_0 \delta n$$

$$= -\int v_0 \delta n = \delta T_{HK}[n]\,|_0, \qquad (2.13)$$

so the generalized energy functional,

$$E[n,v] = T[n,v] + F[n], \qquad (2.14)$$

is stationary in the ground state with respect to independent variations of the density *and* the potential.

It may be noted that this variational property also holds for variations in the density not conserving the number of particles as long as we sum over the correct number of particles in the one-particle energy sum and fix the zero point of the potential as in Eq. (2.8).

Due to the variational property we immediately get

$$E[n_0 + \delta n, v_0 + \delta v] = E_0 + O(\delta n^2, \delta v^2, \delta n \, \delta v)$$

$$= E_0 + O^2(\delta n, \delta v), \qquad (2.15)$$

i.e., first-order errors in the density *and* the potential give rise only to second- and higher-order errors in the total energy.

A number of energy functionals with variational properties can be derived from Eq. (2.14). If the potential is considered as a functional of the density as given by Eqs. (2.6) and (2.7) we of course reobtain the Hohenberg-Kohn functional. Another possibility is to choose the potential as a density functional given by Eq. (2.8)

$$E'[n] = E[n, v[n]], \qquad (2.16)$$

with $v[n] = \int' \rho' / |\mathbf{r} - \mathbf{r}'| + v_{xc}(n)$. Yet another choice would be to regard the potential as the only independent variable and let the density be a potential functional defined by solving the Kohn-Sham equation (2.6) and use Eq. (2.7) to get the density. This is the approach that has been taken by Andersen[11] and others[12] when discussing the so-called *force theorem*. For a simple proof of the force theorem based directly on the functional (2.14), see Appendix A.

The kinetic energy functional (2.12) can be rewritten in a local form useful for our purposes in the following. The local density of states $n(\mathbf{r}, \epsilon)$ associated with solving Eq. (2.6) is given by

$$n(\mathbf{r}, \epsilon, [v]) = \sum_{\alpha} |\psi_{\alpha}(\mathbf{r})|^2 \delta(\epsilon - \epsilon_{\alpha}) \qquad (2.17)$$

and the kinetic energy can be written

$$T[n,v] = \int t(\mathbf{r}, [n,v]), \qquad (2.18)$$

where

$$t(\mathbf{r}, [n,v]) = e(\mathbf{r}, [v]) - n(\mathbf{r})v(\mathbf{r}), \qquad (2.19)$$

with

$$e(\mathbf{r}, [v]) = \int_{-\infty}^{\epsilon_F} d\epsilon \, \epsilon n(\mathbf{r}, \epsilon, [v]). \qquad (2.20)$$

III. AN ATOM EMBEDDED IN A HOMOGENEOUS ELECTRON GAS

The reference system that we shall return to repeatedly in the following is an atom embedded in a homogeneous electron gas. Using the density functional scheme the self-consistent density and potential can be obtained and the embedding energy $\Delta E^{hom}(\bar{n})$ can be calculated as a function of the density $\bar{n}$ of the homogeneous electron gas in which the atom in question is being embedded. If the resulting self-consistent density $n(\mathbf{r})$ is written

$$n(\mathbf{r}) = \bar{n} + \Delta n^{hom}(\mathbf{r}), \qquad (3.1)$$

where $\Delta n^{hom}(\mathbf{r})$ is the atom-induced change in the density, then the self-consistent potential is given by Eq. (2.8). That is,

$$v(\mathbf{r}) = v_{xc}(\bar{n}) + \Delta v^{hom}(\mathbf{r}), \qquad (3.2)$$

where the atom-induced change in the potential $\Delta v^{hom}(\mathbf{r})$ is

$$\Delta v^{hom} = \int' \frac{\Delta \rho^{hom\prime}}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\bar{n} + \Delta n^{hom}) - v_{xc}(\bar{n}). \qquad (3.3)$$

Associated with the embedding of an atom in a homogeneous electron gas we can define an embedding energy functional $\Delta \widetilde{E}_Z$ by

$$\Delta \widetilde{E}_Z(\bar{n}, [\Delta n]) = E_Z^{hom}[\bar{n} + \Delta n, \Delta v] - E^{hom}[\bar{n}, v = 0] - E^{atom}$$

$$= \int \Delta \tilde{t}(\bar{n}, [\Delta n, \Delta v]) + \frac{1}{2} \int \int \frac{\Delta \rho \Delta \rho'}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ \int [f_{xc}(\bar{n} + \Delta n) - f_{xc}(\bar{n})] - E^{atom}. \qquad (3.4)$$

In this expression E_Z^{hom} and E^{hom} denote the energy functionals analogous to (2.14) for a system with a positive jellium background density $\bar{n}$, with and without an added atom of nuclear charge Z. The "atom-induced" potential Δv is here taken to be given as a density functional by

$$\Delta v[\bar{n}, \Delta n] = \int' \frac{\Delta \rho'}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\bar{n} + \Delta n) - v_{xc}(\bar{n}) \qquad (3.5)$$

and the change in the local kinetic energy functional is

$$\Delta \tilde{t}(\mathbf{r}, \bar{n}, [\Delta n]) = \Delta \tilde{e}(\mathbf{r}, [\Delta v]) - \Delta v(\bar{n} + \Delta n), \qquad (3.6)$$

where

$$\Delta \tilde{e}(\mathbf{r}, [\Delta v]) = e(\mathbf{r}, [\Delta v]) - e(\mathbf{r}, [v = 0]). \qquad (3.7)$$

The embedding energy functional $\Delta \widetilde{E}_Z(\bar{n}, [\Delta n])$ is stationary around $\Delta n = \Delta n^{hom}$ and the embedding energy $\Delta E_Z^{hom}(\bar{n})$ is

$$\Delta E_Z^{hom}(\bar{n}) = \Delta \widetilde{E}_Z(\bar{n}, [\Delta n^{hom}]). \qquad (3.8)$$

The variational property can be expressed as

$$\Delta \widetilde{E}_Z(\bar{n}, [\Delta n]) = \Delta E_Z^{hom}(\bar{n}) + O((\Delta n - \Delta n^{hom})^2). \qquad (3.9)$$

The self-consistent induced density Δn^{hom} is of course an implicit function of the embedding density $\bar{n}$ as determined by the self-consistency requirement in the Kohn-Sham scheme.

The embedding energy function $\Delta E^{hom}(\bar{n})$ has been calculated for a number of atoms.[13] For a noble gas atom it increases nearly linearly with the electron gas density due to the kinetic energy repulsion while it develops a minimum for more chemically active atoms.

IV. EFFECTIVE MEDIUM THEORY
FOR A PERFECT SOLID

For a perfect, monatomic solid, space can in a natural way be divided into neutral Wigner-Seitz (WS) cells, and we shall in the following denote the WS cell associated with an atom i as a_i. In many situations, especially when dealing with closed-packed structures, it is reasonable to approximate the WS cells by so-called atomic spheres with radii chosen so that the volume (and charge) of a sphere equals the volume (and charge) of a WS cell. In this atomic-sphere approximation (ASA) the small region of space not contained in any sphere is simply neglected and at the same time the "double-counting" errors in the regions with overlapping atomic spheres are neglected.

In the present section we shall concentrate on perfect solids. The notation and most of the discussion can, however, be carried over to a situation with lower symmetry like, for instance, a surface. The modifications and further approximations necessary to deal with a low-symmetry system are discussed in Sec. VI.

To calculate the total energy of a solid in density functional theory we need the ground-state electronic density n_0 for which we shall make the following ansatz of overlapping densities:

$$n(\mathbf{r}) = \sum_i \Delta n_i(\mathbf{r}), \tag{4.1}$$

where the sum runs over all the atoms. A given density may of course be decomposed in the form Eq. (4.1) in many ways and we shall soon return to the question of how to choose the Δn_i's.

The potential $\tilde{v}(\mathbf{r})$ corresponding to the density Eq. (4.1) is given by the general formula Eq. (2.8). In the cell a_i we write this as

$$\tilde{v} = \Delta v_i + \sum_{j \neq i} \Delta \phi_j + v_{\mathrm{xc}} \left[\Delta n_i + \sum_{j \neq i} \Delta n_j \right]$$
$$- v_{\mathrm{xc}}(\Delta n_i + \bar{n}_i) + v_{\mathrm{xc}}(\bar{n}_i), \tag{4.2}$$

where Δv_i is related to Δn_i as in Eq. (3.3) with $\bar{n}$ replaced by $\bar{n}_i$, and where $\Delta \phi_j$ is the Hartree potential from the charge $\Delta \rho_j = \Delta n_j - Z_j \delta(\mathbf{r} - \mathbf{R}_j)$. We take the "background density" $\bar{n}_i$ to be defined as the average over the cell a_i of the sum of all the "density tails" sticking into this cell, i.e., we put

$$\bar{n}_i \equiv \left\langle \sum_{j \neq i} \Delta n_j \right\rangle_{a_i}. \tag{4.3}$$

In the same way we can define an average over the Hartree potential tails

$$\bar{\phi}_i \equiv \left\langle \sum_{j \neq i} \Delta \phi_j \right\rangle_{a_i}. \tag{4.4}$$

Now, if the sum of the density tails in cell a_i is nearly constant over the cell we can substitute this density tail sum by the average background density $\bar{n}_i$ in the potential Eq. (4.2). In this way the third and fourth terms on the right-hand side of Eq. (4.2) cancel each other. If furthermore the background density $\bar{n}_i$ does not vary too much from cell to cell (in a perfect solid this variation of course vanishes due to translational symmetry) the last term in the potential Eq. (4.2) can be regarded as a constant shift over all space and therefore neglected. Assuming in the same way only small variations in the Hartree potential tail sum we may use the average value $\bar{\phi}_i$ instead and again, if this value does not vary considerably from cell to cell, it may simply be dropped in the potential. In this way we have "frozen" the potential to be

$$v = \Delta v_i \quad \text{in } a_i. \tag{4.5}$$

It should be noted that due to the variational property of the energy functional Eq. (2.15) the approximations we make in the potential will only show up in the total energy in second and higher order. We may therefore write

$$E[n,v] = E_0 + O^2 \left[n - n_0, \ \bar{n}_i - \sum_{j \neq i} \Delta n_j \ (\text{in } a_i), \ \bar{n}_i - \bar{n}_j \ (i \neq j), \bar{\phi}_i - \sum_{j \neq i} \Delta \phi_j \ (\text{in } a_i), \ \bar{\phi}_i - \bar{\phi}_j \ (i \neq j) \right]. \tag{4.6}$$

The first term in the corrections involves a possible deviation between our ansatz Eq. (4.1) and the true ground-state density. The other terms come from the approximations in the potential just discussed.

With the ansatz Eq. (4.1) for the density and Eq. (4.5) for the potential, the total energy can be written [see Eq. (2.14)]

$$E[n,v] = \int t([n,v]) + \frac{1}{2} \sum_{i,j} \int \int' \frac{\Delta \rho_i \Delta \rho_j'}{|\mathbf{r} - \mathbf{r}'|} + \int f_{\mathrm{xc}}(n), \tag{4.7}$$

where

$$t(\mathbf{r}, [n,v]) = e(\mathbf{r}, [n,v]) - \Delta v_i(\mathbf{r}) n(\mathbf{r}) \tag{4.8}$$

for $\mathbf{r}$ in cell a_i.

Let us now turn to the question of how to choose the densities Δn_i. As discussed in the Introduction the effective-medium theory is based on the assumption that the self-consistency problem involving the screening is at least partly dealt with when embedding the atom in a homogeneous gas of the appropriate density. It is therefore natural to take the ansatz $\Delta n_i = \Delta n_i^{\mathrm{hom}}(\bar{n}_i)$. There is actually a self-consistency problem involved in this ansatz itself: The induced densities Δn_i are determined as functions of the background densities $\bar{n}_i$ that again are obtained by averaging the tails of the induced densities. In Sec. VII we shall discuss how to deal with this self-consistency problem in practice.

The tail of the induced density in the homogeneous gas exhibits Friedel oscillations and it is clearly unphysical to

superimpose these oscillations on the density in the neighboring cells. This constitutes, however, no serious problem for two reasons. Firstly, the variational property of $\Delta \widetilde{E}_i$ allows us to "smear out" the oscillations in the tail of Δn_i and still take $\Delta \widetilde{E}_i = \Delta E_i^{\text{hom}}(\bar{n}_i)$, and secondly, an important ingredient in the approach taken here is that the effect of an atom on the binding energy of a neighboring atom is treated in an averaged fashion and the oscillations are therefore of minor importance. To put the second point differently: It is important that the density being induced by embedding an atom in a vacant cell is well described by the induced density in a homogeneous gas

within the cell in question. The effect of the embedding on the neighboring atoms, however, is mainly described through the change in the averaged background density in these cells and this change is again mainly a consequence of charge conservation.

As discussed in the Introduction the aim of the effective-medium theory is to relate the binding energy ΔE to the embedding energy of an atom in a homogeneous electron gas and we therefore introduce the embedding energy functional $\Delta \widetilde{E}_i$, Eq. (3.4) (the subscript i indicates the type of atom), in the expression for the energy, Eq. (4.7). The binding energy can then be written

$$
\begin{aligned}
\Delta E[n,v] \equiv E[n,v] - \sum_i E_i^{\text{atom}} = & \sum_i \Delta \widetilde{E}_i(\bar{n}_i, [\Delta n_i]) + \tfrac{1}{2} \sum_{\langle ij \rangle} \int \int{}' \frac{\Delta \rho_i \Delta \rho_j'}{|\mathbf{r} - \mathbf{r}'|} \\
& + \int \left[f_{\text{xc}}(n) - \sum_i [f_{\text{xc}}(\bar{n}_i + \Delta n_i) - f_{\text{xc}}(\bar{n}_i)] \right] \\
& + \int \left[t([n,v]) - \sum_i \Delta \widetilde{t}_i([\Delta n_i, \Delta v_i]) \right],
\end{aligned}
\tag{4.9}
$$

where $\langle ij \rangle$ indicates that only the terms with $i \neq j$ are included in the sum. The electrostatic term can be rewritten (see Appendix B for details)

$$
\begin{aligned}
\tfrac{1}{2} \sum_{\langle ij \rangle} \int \int \frac{\Delta \rho_i \Delta \rho_j'}{|\mathbf{r} - \mathbf{r}'|} = & E_{\text{Madelung}} - \sum_i \alpha_i \bar{n}_i + \tfrac{1}{2} \sum_i \left[\int_{a_i} \int_{a_i'} \frac{\Delta \rho_{-i} \Delta \rho_{-i}'}{|\mathbf{r} - \mathbf{r}'|} - \int_{a_{-i}} \int_{a_{-i}'} \frac{\Delta \rho_i \Delta \rho_i'}{|\mathbf{r} - \mathbf{r}'|} \right] \\
& - \sum_i \int_{a_i} \int_{a_{-i}'} \frac{(\bar{n}_i + \Delta \rho_i)\Delta \rho_i'}{|\mathbf{r} - \mathbf{r}'|} + \sum_i \int_{a_i} \int_{a_i'} \frac{\Delta \rho_i (\Delta \rho_{-i}' - \bar{n}_i')}{|\mathbf{r} - \mathbf{r}'|}.
\end{aligned}
\tag{4.10}
$$

In this expression E_{Madelung} is the Madelung energy

$$
E_{\text{Madelung}} = \tfrac{1}{2} \sum_{\langle ij \rangle} \int_{a_i} \int_{a_j'} \frac{\rho \rho'}{|\mathbf{r} - \mathbf{r}'|}, \tag{4.11}
$$

α_i is defined by

$$
\alpha_i = - \int_{a_i} \int_{\Omega'} \frac{\Delta \rho_i'}{|\mathbf{r} - \mathbf{r}'|} = - \int_{a_i} \Delta \phi_i, \tag{4.12}
$$

$a_{-i} = \Omega - a_i$ is the region outside a_i, and $\Delta \rho_{-i}$ is a short notation for the tail sum $\sum_{j \neq i} \Delta \rho_j$. In the atomic-sphere approximation the second last term in Eq. (4.10) vanishes and the Madelung energy is of second order in $\bar{n}_i - \Delta n_{-i}$ in cell a_i and should be neglected.

The exchange-correlation term in Eq. (4.9) may to first order in $\bar{n}_i - \Delta n_{-i}$ in cell a_i be written

$$
\begin{aligned}
\sum_i \Bigg[& \int_{a_i} f_{\text{xc}}(\Delta n_{-i}) - \int_{a_{-i}} [f_{\text{xc}}(\Delta n_i + \bar{n}_i) - f_{\text{xc}}(\bar{n}_i)] \\
& + \int_{a_i} [v_{\text{xc}}(\Delta n_i + \bar{n}_i) - v_{\text{xc}}(\bar{n}_i)](\Delta n_{-i} - \bar{n}_i) \Bigg]. \tag{4.13}
\end{aligned}
$$

The kinetic energy in a WS cell a_i of the solid may be divided in two parts,

$$
\int_{a_i} t([n,v]) = \int_{a_i} t_i^{\text{vac}}([n,v]) + \int_{a_i} \Delta t_i([n,v]), \tag{4.14}
$$

where $\int_{a_i} t_i^{\text{vac}}$ is the kinetic energy in cell a_i when atom i

is absent (i.e., $v = 0$ in a_i) and $\int_{a_i} \Delta t_i$ is the induced change in cell a_i when the atom is added.

We shall assume that the density in a_i when atom i is absent is given by Δn_{-i}. In the comparison between the atom-induced change in the kinetic energy of the solid and of the homogeneous gas, we want to take the difference between this background density and the background density $\bar{n}_i$ in the homogeneous gas into account to first order and we therefore write [see Eq. (3.6)]

$$
\begin{aligned}
\int_{a_i} \Delta \widetilde{t}_i(\bar{n}_i, [\Delta n_i, \Delta v_i]) = & \int_{a_i} \Delta \widetilde{t}_i(\Delta n_{-i}, [\Delta n_i, \Delta v_i]) \\
& + \int_{a_i} \Delta v_i(\Delta n_{-i} - \bar{n}_i). \tag{4.15}
\end{aligned}
$$

Using the expressions Eqs. (4.10)–(4.15) and the relation Eq. (3.5) between Δv_i and Δn_i, we obtain

$$
\begin{aligned}
\Delta E = & \sum_i E_{c,i}(\bar{n}_i) + E_{\text{Madelung}} - \sum_i \int_{a_i} \int_{a_{-i}'} \frac{\rho \Delta \rho_i'}{|\mathbf{r} - \mathbf{r}'|} \\
& + \sum_i \int_{a_i} [\Delta e_i([v]) - \Delta \widetilde{e}_i(\Delta n_{-i}, [\Delta v_i])] + \Delta E_{\text{tail}}^{\text{corr}}, \tag{4.16}
\end{aligned}
$$

where we have defined the energy function $E_{c,i}(\bar{n}_i)$ by

$$
E_{c,i}(\bar{n}_i) = \Delta E_i^{\text{hom}}(\bar{n}_i) - \alpha_i \bar{n}_i \tag{4.17}
$$

and

$$\Delta E_{\text{tail}}^{\text{corr}} = \sum_i \left[\int_{a_i} t_i^{\text{vac}}([n,v]) - \int_{a_{-i}} \Delta \tilde{t}_i(\bar{n}_i, [\Delta n_i, \Delta v_i]) \right.$$

$$\left. + \frac{1}{2} \left[\int_{a_i} \int_{a_i'} \frac{\Delta \rho_{-i} \Delta \rho_{-i}'}{|\mathbf{r} - \mathbf{r}'|} - \int_{a_{-i}} \int_{a_{-i}'} \frac{\Delta \rho_i \Delta \rho_i'}{|\mathbf{r} - \mathbf{r}'|} \right] + \int_{a_i} f_{\text{xc}}(\Delta n_{-i}) - \int_{a_{-i}} [f_{\text{xc}}(\Delta n_i + \bar{n}_i) - f_{\text{xc}}(\bar{n}_i)] \right].$$

$$(4.18)$$

The tail correction energy consists of a sum of a kinetic energy, an electrostatic energy, and an exchange-correlation energy all of the same general structure. There are differences between the energies in a vacancy constituted by the tails sticking into the cell and the energies of the tails sticking out of the cell. Because the cell is neutral the same number of electrons is in the vacancy as in the tails sticking out. This leads to a fairly complete cancellation in the tail correction term and this may therefore often be neglected.

Because of the modification $\bar{n}_i \rightarrow \Delta n_{-i}$ we made in $\Delta \tilde{t}_i$ the nv part of the kinetic energy $\Delta \tilde{t}_i$ is canceled by the same part of Δt_i and we are left with only the difference $\Delta e_i - \Delta \tilde{e}_i$ in Eq. (4.16).

In the atomic-sphere approximation the Madelung energy should be neglected (being of second order in $\bar{n}_i - \Delta n_{-i}$ in a_i) and the succeeding term vanishes.

To summarize: The expression Eq. (4.16) for the binding energy has been obtained under the assumption that the density can be represented as a superposition of atom-induced densities in a homogeneous electron gas. For each atom the density of the associated homogeneous gas is chosen to equal the average over the WS cell of the tails coming from the other atoms. The further assumptions that the sum over the density tails and Hartree potential tails sticking into a cell are nearly constant over the cell lead to the possibility of "freezing" the potential in each cell as the one in the corresponding homogeneous gas. Due to the variational properties Eq. (3.9) and Eq. (4.6), errors in the densities and potentials do only contribute to the energy in second and higher order.

V. THE ONE-ELECTRON ENERGY PARAMETERS

As indicated by the force theorem[11] a total-energy change may under certain circumstances be reduced to only the change in the sum over the one-electron energy parameters. Consider as an example the total-energy change due to a structural change of a solid from, say, a bcc to an fcc lattice in the atomic-sphere approximation. If we assume that the density and potential in an atomic cell in the two structures are almost identical, we can freeze them in changing from one structure to the other and the structural energy change may then be calculated solely from the change in the one-electron energy parameter spectrum.[14]

The effective-medium result, Eq. (4.16), can be regarded as a generalization of the force theorem. Here an atom with a frozen induced density and potential is moved from the reference host, the homogeneous electron gas, to the system under investigation. It is seen from Eq.

(4.16) that the binding energy in the atomic-sphere approximation then is given as a sum of a term that is associated with the atom in the homogeneous gas and a term that has to do with the change in the one-electron energy parameter spectrum. In the example mentioned above with the structural energy change the environment of the atom is very similar in the two different situations. In the effective-medium theory presented here the environment is parametrized by a single parameter: The density of the homogeneous electron gas is chosen so that it is reasonable to freeze the density and potential when comparing with the investigated system. The effective-medium theory provides in this way a framework to understand why some observed total-energy trends as, say, the binding energy of the transition metals as a function of d-band filling, can be explained solely from a consideration of the one-electron energy parameter spectrum.[14]

To calculate the total binding energy of a system of atoms from the expression (4.16) we must for each atom (i) estimate the difference between the atom-induced change in the one-electron energy sum (projected onto the atomic sphere) Δe_i in the studied system and the analogous quantity $\Delta \tilde{e}_i$ associated with the embedding of atom i in a homogeneous electron gas of the appropriate density. We will show that for simple metals the one-electron energy difference $\Delta e_i - \Delta \tilde{e}_i$ can be neglected, whereas for transition metals and other systems with two or more atoms showing sharp resonances in the one-electron spectrum when embedded in a homogeneous electron gas, $\Delta e_i - \Delta \tilde{e}_i$ will give an important contribution to the total energy. We shall be basing the discussion on the resonant level model or the $U = 0$ Anderson model.[15] The arguments are therefore mainly qualitative. We will, however, discuss one limit where the results can be used quantitatively towards the end of this section. (For a discussion of the quantitative applicability of the resonant level model see Anderson and McMillan,[15] Penn,[16] and Moriarty.[17])

In order to get Δe_i and $\Delta \tilde{e}_i$ we must consider the local density of states $\Delta n_i(\epsilon)$ and $\Delta \bar{n}_i(\epsilon)$ induced by atom i when embedded in an empty cell (a vacancy) in the system studied and in the reference system, respectively. Consider first an atom i embedded in a homogeneous electron gas. The resonant level Hamiltonian is

$$\tilde{H} = \epsilon_i n_i + \sum_k \epsilon_k n_k + \sum_k [W_{ik}(\epsilon) c_i^\dagger c_k + \text{H.c.}], \quad (5.1)$$

where we use an energy-dependent matrix element given by

$$W_{ik}(\epsilon) = \langle i | T + V_i - \epsilon | \mathbf{k} \rangle = V_{ik} + (\epsilon_k - \epsilon) \langle i | \mathbf{k} \rangle. \quad (5.2)$$

Instead of the local induced density of states $\Delta \tilde{n}_i(\epsilon)$ we shall be considering the projected density of states

$$\tilde{n}_i(\epsilon) = -\frac{1}{\pi} \text{Im} \langle i \mid \tilde{G}(\epsilon) \mid i \rangle = -\frac{1}{\pi} \text{Im} \tilde{G}_i(\epsilon). \quad (5.3)$$

Here $\tilde{G}$ is the Green's function of the system. Since $\tilde{n}_i(\epsilon)$ is also a local density of states it will closely resemble $\Delta \tilde{n}_i(\epsilon)$. In particular, the difference $n_i(\epsilon) - \tilde{n}_i(\epsilon)$ is expected to be very close to $\Delta n_i(\epsilon) - \Delta \tilde{n}_i(\epsilon)$.

The atom projected Green's function is given by

$$\tilde{G}_i(\epsilon) = \frac{1}{\epsilon - \epsilon_i - \tilde{q}_i(\epsilon)}, \quad (5.4)$$

where

$$\tilde{q}_i(\epsilon) = \sum_{\mathbf{k}} W_{i\mathbf{k}} G_{\mathbf{k}}^0 W_{\mathbf{k}i} = \sum_{\mathbf{k}} \frac{|W_{i\mathbf{k}}(\epsilon)|^2}{\epsilon - \epsilon_k + i\delta}$$

$$= \Lambda_i(\epsilon) - i\Delta_i(\epsilon). \quad (5.5)$$

The atom projected density of states is then

$$\tilde{n}_i(\epsilon) = \frac{1}{\pi} \frac{\Delta_i(\epsilon)}{[\epsilon - \epsilon_i - \Lambda_i(\epsilon)]^2 + \Delta_i(\epsilon)^2}, \quad (5.6)$$

with

$$\Delta_i(\epsilon) = \pi \sum_{\mathbf{k}} |W_{i\mathbf{k}}(\epsilon)|^2 \delta(\epsilon - \epsilon_k) \quad (5.7)$$

and

$$\Lambda_i(\epsilon) = P \sum_{\mathbf{k}} \frac{|W_{i\mathbf{k}}(\epsilon)|^2}{\epsilon - \epsilon_k + i\delta}. \quad (5.8)$$

The system of interacting atoms we describe by the Hamiltonian

$$H = \sum_i \epsilon_i n_i + \sum_k \epsilon_k n_k + \sum_{i,\mathbf{k}} [W_{i\mathbf{k}}(\epsilon) c_i^\dagger c_{\mathbf{k}} + \text{H.c.}]. \quad (5.9)$$

It describes a set of atomic states $\mid i \rangle$ coupled to each other through the free-electron states $\mid k \rangle$ in the interstitial region between the atomic cells. The energy levels ϵ_i and the coupling matrix elements $W_{i\mathbf{k}}$ are quantities determined by the potential in the cell with atom i and we can therefore "freeze" these parameters when going from considering the atom embedded in the homogeneous gas to the interacting system of atoms.

The i-projected Green's function $G_i(\epsilon)$ for this Hamiltonian can be written as Eq. (5.3) with $\tilde{q}_i$ exchanged for

$$q_i = \sum_{\mathbf{k}} W_{i\mathbf{k}} G_{\mathbf{k}}^0 W_{\mathbf{k}i}$$

$$+ \sum_{\mathbf{k},\mathbf{k}',j \neq i} W_{i\mathbf{k}} G_{\mathbf{k}}^0 W_{\mathbf{k}j} G_j^0 W_{j\mathbf{k}'} G_{\mathbf{k}'}^0 W_{\mathbf{k}'i} + \cdots$$

$$= \tilde{q}_i + \sum_{j \neq i} q_{ij} G_j^0 q_{ji} + \cdots . \quad (5.10)$$

The effective medium for atom i is a homogeneous electron gas of a density equal to the average of the density in cell a_i when the atom is not there. The choice of potential Eq. (4.5) implies that the bottom of the band for the effective medium is equal to the average value of the

effective potential inside the cell a_i. This is illustrated in Fig. 1. Guided by this observation we choose the free-electron states in the interstitial region used in Eq. (5.10) to be exactly those of the effective medium. The $\tilde{q}_i$ in Eq. (5.10) is then identical to that in Eq. (5.5). This means that if the multiple-scattering terms in Eq. (5.10) can be neglected the projected densities of states $n_i(\epsilon)$ and $\tilde{n}_i(\epsilon)$ are identical and $\Delta e_i - \Delta \tilde{e}_i$ vanishes. For the simple metals this is a reasonable approximation. This is not because the coupling matrix elements W_{jk} are negligible for the simple metals. As indicated in Fig. 1 the potential in one of the occupied cells differs by at least a constant shift from that in the homogeneous electron gas. It is the fact that only the local projection of q on $\mid i \rangle$ enters the expression for G_i and $n_i(\epsilon)$ combined with a phase shift that varies smoothly with energy that is the reason why the multiple scattering can be neglected for simple metals. This is seen most clearly by noting that $\text{Im} q_i$ and $\text{Im} \tilde{q}_i$ are basically local densities of states in cell a_i without the atom i present [cf. Eq. (5.7)]. If there are no strong scattering resonances in the surrounding atoms the local density of states in a vacancy is small for energies below the value V_0 of the effective potential in the vacancy, rises sharply around V_0, and approaches the free-electron value at the highest energies. This has been discussed in more detail by Inglesfield,[18] by Heine,[12] and by Gunnarsson et al.[19] It is shown schematically in Fig. 1. The two local densities of states in the figure contain the same number of electrons when integrated to the Fermi level. The main difference is that in the vacancy some of the low-lying states have been shifted down. Extending these arguments to $\text{Im} q_i(\epsilon)$ and $\text{Im} \tilde{q}_i(\epsilon)$ it is clear that $n_i(\epsilon)$ and $\tilde{n}_i(\epsilon)$ will not be identical. In particular, if $\tilde{n}_i(\epsilon)$ has a bound state just below the bottom of the band it will be broadened in the vacancy because $\text{Im} q_i(\epsilon)$ does not vanish in this energy region. It is, however, clear from Eq. (5.6) that in comparing the first moments (up to the Fermi energy) of $\tilde{n}_i(\epsilon)$ and $n_i(\epsilon)$ these differences will be small, in particular since, by construction, the zeroth moments are the same [charge neutrality, this only holds identically for $\Delta n_i(\epsilon)$ and $\Delta \tilde{n}_i(\epsilon)$].

If, on the other hand, the surrounding atoms have strong scattering resonances, then the local density of states in the vacancy will not vary as smoothly as in Fig. 1
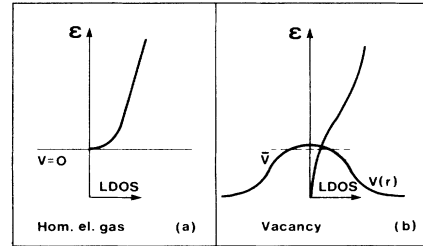

FIG. 1. The potential in the homogeneous electron gas (a) chosen as the average of the potential in the cell in the real system (the vacancy) (b). The density of states in the cell is similar in the two situations, but in the vacancy states near the bottom of the band is shifted downwards.

and cannot be approximated by the free-electron values. This means that we must include the multiple-scattering part in Eq. (5.10). This is, for instance, the case for the transition metals which show strong d resonances. Calculating the multiple-scattering terms in Eq. (5.10) for a perfect transition metal is equivalent to solving the d-band-structure problem with effective interatomic coupling matrix elements q_{ij}.

The q_{ij}'s can in a certain limit be related to the resonance half widths Δ, Eq. (5.7), in the homogeneous electron gas. To see this, first consider the coupling matrix element V_{ik}:

$$V_{ik} = \langle i \mid V_i \mid \mathbf{k} \rangle = \frac{i^l}{\Omega^{1/2}} 4\pi V_{il}(k) Y_{lm}(\hat{\mathbf{k}}) e^{i\mathbf{k}\cdot\mathbf{r}_i}, \quad (5.11)$$

where

$$V_{il}(k) = \int_0^{s_i} dr\, r^2 \phi_{il}(r) V_i(r) j_l(kr), \quad (5.12)$$

with s_i being the radius of the atomic sphere a_i. Furthermore, $\mid i \rangle = \phi_{il}(r) Y_{lm}(\hat{\mathbf{r}})$ and it is used that the potential inside the atomic sphere a_i is assumed spherically symmetric.

In terms of $V_{il}(k)$ the half width of the resonance is from Eq. (5.7)

$$\Delta_{il}(\kappa) = 2\kappa \mid V_{il}(\kappa) \mid^2, \quad (5.13)$$

with $\kappa = (2\epsilon)^{1/2}$. For narrow resonances like d resonances we can use $\Delta_d(\kappa) \simeq \Delta_d(\kappa_d)$, where κ_d is the wave vector at the d resonance.

In calculating the coupling matrix element q_{ij}^r at the resonance energy ϵ_r we make use of the observation first made by Andersen,[1] that the potential in the interstitial region can be chosen freely because the interstitial volume is small (zero in the atomic-sphere approximation). If we take the potential in the interstitial region as equal to the resonance energy, we get

$$q_{ilm,jl'm'}^r = \sum_{\mathbf{k}} W_{ik}(\epsilon_r) G_{\mathbf{k}}^0(\epsilon = 0) W_{kj}(\epsilon_r)$$

$$= -M_{il} \eta_{lml'm'} M_{jl'} r_{ij}^{-(l+l'+1)}, \quad (5.14)$$

where M_{il} and $M_{jl'}$ are matrix elements defined by

$$M_{il} = \frac{-1}{(2l+1)} \int_0^{s_i} dr\, r^2 \phi_{il}(r) [V(r) - \epsilon_r] r^l, \quad (5.15)$$

and $\eta_{lml'm'}$ are numerical constants equal to the Andersen structure constants[1] with the distance dependence taken out. For the d-d interaction, $\eta_{dd(\sigma,\pi,\delta)} = (-60, 40, -10)$. The matrix element M_{il} is related to the Andersen band-width parameter $\Delta_l^{\text{Andersen}}$ through

$$M_{il} = (s_i^{(2l+1)} \Delta_l^{\text{Andersen}})^{1/2}. \quad (5.16)$$

To see how the coupling matrix element q_{ij} is given by the resonance width we follow Harrison and Froyen[20] and Heine[12] and use the small kr approximation where the spherical Bessel function in Eq. (5.12) is expanded to lowest order and the resonance energy in Eq. (5.15) is

neglected. This leads to the relation

$$M_{il} \simeq -(2l-1)!! \frac{V_{il}(\kappa_r)}{\kappa_r^l}$$

$$= (2l-1)!! \left[\frac{\Delta_{il}(\kappa_r)}{2\kappa_r^{(2l+1)}} \right]^{1/2}, \quad (5.17)$$

and accordingly for an l-l interaction between identical atoms

$$q_{ilm,jlm'}^r \simeq -\eta_{lmlm'} \frac{[(2l-1)!!]^2}{2} \frac{\Delta_{il}(\kappa_r)}{(\kappa_r r_{ij})^{(2l+1)}}. \quad (5.18)$$

The result that the interatomic matrix element q_{ij} is given by an intra-atomic property (M or Δ) has been discussed in detail previously by Pettifor,[21] by Heine,[12] and by Moriarty.[22]

VI. EFFECTIVE-MEDIUM THEORY: THE GENERAL CASE

In the perfect solid discussed in Sec. IV we had the possibility of dividing space into WS cells and within each cell to freeze the potential as the one induced by an atom in a homogeneous gas. The background density of the corresponding homogeneous gas was chosen by averaging the density tails in a given WS cell over the cell volume. This procedure cannot simply be carried over to a situation with lower symmetry as can easily be seen. If, for example, we consider an atom situated at a surface site, the WS cell containing this atom will stretch to the far infinity and the average over this cell of the density tails from the other atoms will clearly vanish. We therefore have to choose the cells we average over in a different way. Having in mind that the reference system for our approximations is an atom embedded in a homogeneous electron gas, where we have perfect spherical symmetry, it seems natural to work with spheres. Given the ansatz Eq. (4.1) for the density we therefore associate a sphere s_i with each atom i and we choose the radius of each sphere so that the total charge within the sphere vanishes. Furthermore, the background density $\bar{n}_i$ is now defined as an average over the sphere s_i:

$$\bar{n}_i \equiv \left\langle \sum_{j \neq i} \Delta n_j \right\rangle_{s_i} = \langle \Delta n_{-i} \rangle_{s_i}. \quad (6.1)$$

As in Sec. IV we can define the averaged Hartree potential tail Eq. (4.4), but now the averaging is over s_i, and we shall also work here to first order in the quantities $\bar{n}_i - \Delta n_{-i}$ (in s_i), $\bar{\phi}_i - \Delta\phi_{-i}$ (in s_i), $\bar{n}_i - \bar{n}_j$ ($i \neq j$), $\bar{\phi}_i - \bar{\phi}_j$ ($i \neq j$), and $n - n_0$, where n_0 is the true ground-state density. The potential $\bar{v}$ [see Eq. (4.2)] is again shifted by the amount $-[\bar{\phi}_{i_0} + v_{xc}(\bar{n}_{i_0})]$ for some i_0 and the invariance of the local kinetic energy under first-order changes in the potential then allows us to freeze the potential in the sphere s_i as Δv_i. Even though the spheres s_i and s_j may overlap, there is, due to the variational property of the kinetic energy and the order to which we work, no conflict in fixing the potential in the overlap region as Δv_i when

dealing with the sphere s_i and as Δv_j when dealing with the sphere s_j.

The expression Eq. (4.9) for the binding energy still holds but the rearrangement of the terms done in Eqs.

(4.10)—(4.15) now involves some extra terms having to do with the spheres overlapping and not covering all of the space. For example, the expression analogous to Eq. (4.13) for the exchange correlation term now becomes

$$\sum_i \left[\int_{s_i} f_{xc}(\Delta n_{-i}) - \int_{s_{-i}} [f_{xc}(\bar{n}_i + \Delta n_i) - f_{xc}(\bar{n}_i)] + \int_{s_i} [v_{xc}(\bar{n}_i + \Delta n_i) - v_{xc}(\bar{n}_i)](\Delta n_{-i} - \bar{n}_i) \right]$$

$$+ \int f_{xc}(n) - \sum_i \int_{s_i} f_{xc}(n), \quad (6.2)$$

where $s_{-i} = \Omega - s_i$. The last two terms do not cancel because the spheres do not constitute a disjoint covering of all of the space.

The kinetic energy may be treated analogously to the exchange-correlation energy [the nonlocality of the kinetic energy is in principle still included because $t(\mathbf{r}, [n, v])$ is treated as a functional of n and v] and for a discussion of the electrostatic term the reader is referred to Appendix B. The main result of this paper can then be written

$$\Delta E[n,v] = \sum_i E_{c,i}(\bar{n}_i)$$

$$+ \sum_i \int_{s_i} \{ \Delta e_i[(v = \Delta v_i \text{ in } s_i)] - \Delta \tilde{e}_i[\Delta v_i] \}$$

$$+ \Delta E_{\text{tail}}^{\text{corr}} + \Delta E_{\text{AS}}^{\text{corr}}, \quad (6.3)$$

where the α_i that occurs in the definition of $E_{c,i}(\bar{n}_i)$ [Eq. (4.17)] and $\Delta E_{\text{tail}}^{\text{corr}}$ are given by Eqs. (4.12) and (4.17), respectively, with the substitutions $a_i \rightarrow s_i$ and $a_{-i} \rightarrow s_{-i}$. The tail correction term is often negligible as discussed after Eq. (4.18).

The atomic-sphere correction term $\Delta E_{\text{AS}}^{\text{corr}}$ is given by

$$\Delta E_{\text{AS}}^{\text{corr}} = \int t([n,v]) - \sum_i \int_{s_i} t([n,v])$$

$$+ \frac{1}{2} \left[\int \int' \frac{\rho \rho'}{|\mathbf{r} - \mathbf{r}'|} - \sum_i \int_{s_i} \int_{s_i'} \frac{\rho \rho'}{|\mathbf{r} - \mathbf{r}'|} \right]$$

$$+ \int f_{xc}(n) - \sum_i \int_{s_i} f_{xc}(n). \quad (6.4)$$

This term would vanish in the atomic-sphere approximation.

Define an overlap function $O(\mathbf{r})$ to be n-1 if $\mathbf{r}$ lies in n spheres (n=0,1,2,...). Due to the neutrality of the spheres the overlap function obeys

$$\int O\rho = \int On = 0, \quad (6.5)$$

where we have assumed that the overlap region does not contain any nuclei. Using this function the atomic sphere correction can be written

$$\Delta E_{\text{AS}}^{\text{corr}} = - \int O\{ t([n,v]) + \frac{1}{2}\rho\phi + f_{xc}(n) \}$$

$$+ \frac{1}{2} \sum_i \int_{s_i} \int_{s_{-i}'} \frac{\rho \rho'}{|\mathbf{r} - \mathbf{r}'|}, \quad (6.6)$$

where ϕ is the Hartree potential from the total charge

density. We notice that the atomic-sphere correction term $\Delta E_{\text{AS}}^{\text{corr}}$ is not restricted to the specific ansatz for the density that we take here but can be applied in other atomic-sphere approaches as well.

We notice that if we are interested in the embedding energy of, say, an impurity atom in some metallic host, and the contribution of the impurity density to the density in the neighboring metal cells can be neglected, we only need to consider the impurity cell. The present formulation then coincides with the earlier effective-medium theory[5,7] except for a slightly different definition of the average density. We expect that this is a reasonable approximation for small gas impurities such as H, O, or C.

VII. APPLICATIONS

In this section we illustrate the applicability of the theory developed in Secs. II—VI by using it to calculate the cohesive properties, phonon dispersion relations, and surface energies for a number of systems. Before getting to the results we first present the input into the calculations, all of which come from a self-consistent solution for the atom in question in a homogeneous electron gas.

A. An atom in a homogeneous electron gas

The calculations of the embedding energy and electron structure of an atom in a homogeneous electron gas are done within the local density approximation[23] using the methods described in Ref. 13. The treatment of the $3d$-transition-metal atoms requires some special care, because in an electron gas they introduce a narrow resonance peak in the change of the density of states. Therefore, up to ~ 600 energy points were needed to describe the continuous part of the energy eigenvalue spectrum and in the stabilization of the iterative process the feedback method introduced by Anderson[24] proved to work very efficiently. Moreover, in order to avoid large total energies corresponding to the free atom and the same atom in the electron gas to be subtracted, the frozen core approximation[25] has been used for the $3d$ transition metals.

In Fig. 2 the embedding energies $E_c(n)$ are shown for the simple metals Li, Na, and Al and in Fig. 3 the same functions are shown for the $3d$ metals. The $E_c(n)$ functions are all seen to have the same general form. The decrease in energy for low density is due to the hybridization between the atomic and the electron gas states and, for the metals in particular, due to the electrostatic term $-\alpha \bar{n}$ in
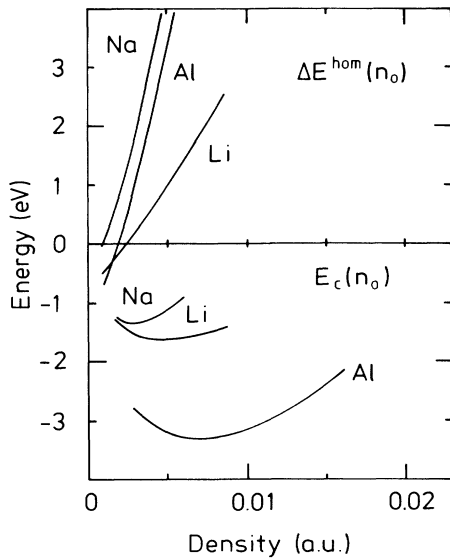
FIG. 2. The energy functions $\Delta E^{hom}(n)$ and $E_c(n)$ [Eq. (4.17)] for Li, Na, and Al calculated within the local density approximation

Eq. (4.17). At higher densities the kinetic energy repulsion, which is a consequence of the orthogonality requirement between electron gas states and the atomic states, starts to dominate, resulting in a minimum in $E_c(n)$.

The atom-induced density $\Delta n(r)$ for Al in an electron gas with $r_s = 3$ is compared with the free-atom density in Fig. 4. The electron density is enhanced in the electron gas near the Al nucleus resulting in a local overscreening. The Friedel oscillations seen for large r are of no impor-
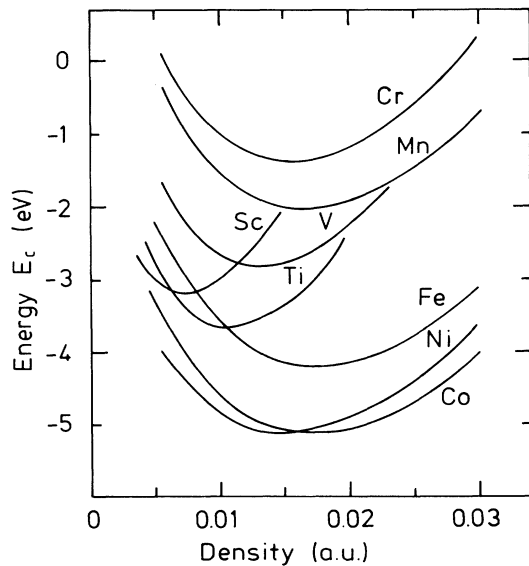

FIG. 3. The energy function $E_c(n)$ [Eq. (4.17)] for all the $3d$ transition metals, calculated within the local density approximation.
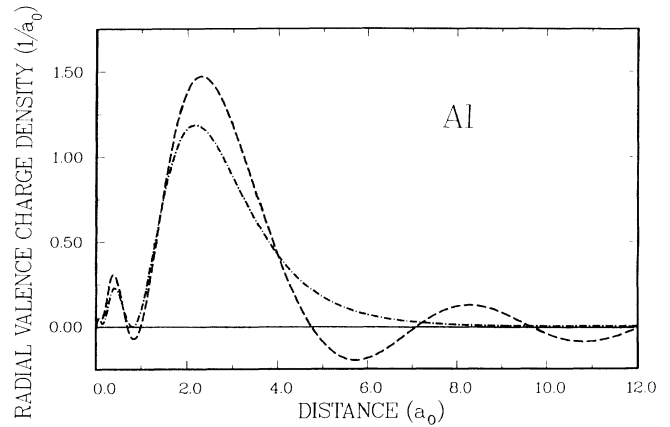

FIG. 4. The induced electron density of an Al atom in a homogeneous electron gas with $r_s = 3.0$ (dashed) compared with the free-atom density (dotted-dashed line).

tance here. Indeed, as discussed in Sec. IV, due to the stationary property of the total energy with respect to small variations in the density we could smear out these oscillations even in the ansatz density Eq. (4.1). It is seen that the free-atom density represents a good "smeared out" version of $\Delta n(r)$ in the tail region beyond $r = 3$, provided it is rescaled to contain the correct number of electrons. Inside the Wigner-Seitz cell the true induced density must be used.

The quality of the ansatz Eq. (4.1) can be judged from Fig. 5 where it is compared to the result of a self-consistent linear muffin-tin orbital (LMTO) calculation[1,14] for Al. Again it should be kept in mind that errors in the density only enter the total energy to second order.

For the transition metals the sharp d resonances require special attention as discussed in Sec. V. In Fig. 6 the induced (local) densities of states are shown for the transition metals in a $r_s = 2.5$ electron gas. The d resonances,
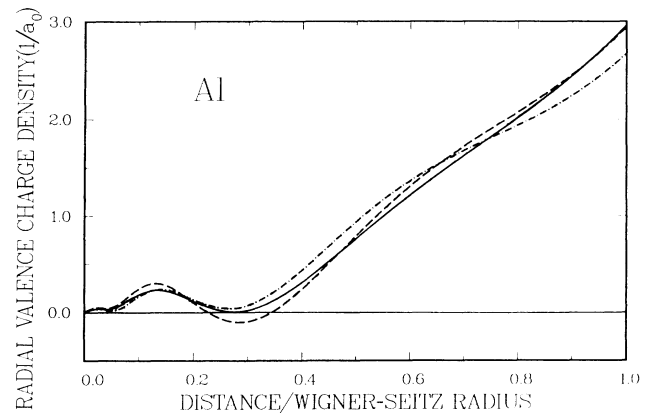

FIG. 5. A comparison between the ansatz of overlapping densities [Eq. (4.1)] (dashed) and the result of a self-consistent LMTO calculation for Al (solid line). Also included is a superposition of free-atom densities (dotted-dashed line).
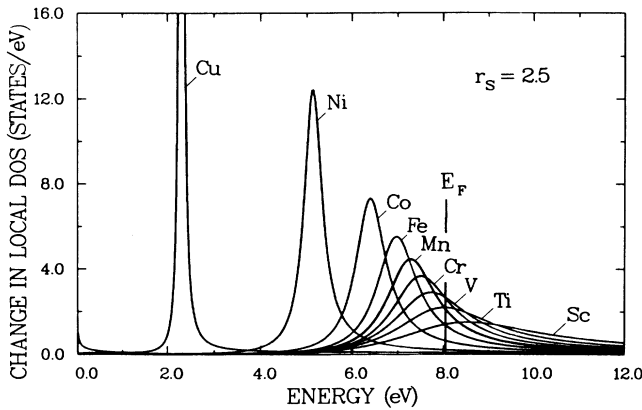
FIG. 6. The induced density of states for the $3d$ transition-metal atoms embedded in an $r_s = 2.5$ electron gas.

gradually filling as one passes through the transition metal series from K to Cu, are clearly seen. The parameters describing the d resonances and other parameters describing the atoms in a homogeneous electron gas are summarized in Table I.

B. Cohesive properties of a perfect solid

For a close packed monatomic solid the atomic-sphere correction Eq. (6.6) can be neglected, except if we are interested in the very small differences in energy between the various crystal structures. In Sec. III it was argued that the tail correction ΔE_{tail}^{corr} should be small in general. We have checked this by evaluating ΔE_{tail}^{corr} approximately for Na and Al. The evaluation can only be approximate because the kinetic energy difference in Eq. (4.16) cannot be calculated directly. The other two terms in Eq. (4.16) can, given the ansatz density Eq. (4.1). We have used the local (Thomas-Fermi) expression plus the first gradient correction in our estimate of the kinetic energy. Moreover, the integrals in Eq. (4.18) are evaluated approximating the true charge density by a spherical average. Within these approximations the value of ΔE_{tail}^{corr} for Na at the equilibrium lattice constant is 0.25 eV, whereas for Al it is 0.15 eV. This sets the scale for the absolute accuracy to be expected in the calculated binding energy when ΔE_{tail}^{corr} is neglected, which we shall do in the following. Energy differences are expected to be more accurate, though. Using the atomic-sphere approximation so that the two electrostatic contributions to Eq. (4.16) also disappear the expression for the cohesive energy (binding energy per atom) that we shall use is

$$E_{coh} = E_c(\bar{n}) + \int_a (\Delta e - \Delta \bar{e}).$$ (7.1)

For the simple atoms we argued in Sec. V that even the last term in Eq. (7.1) can be neglected, so that only the density-dependent energy $E_c(n)$ is left. The cohesive properties of the simple metals are therefore totally given by the properties of $E_c(n)$. The position and depth of the minimum in $E_c(n)$ gives the equilibrium lattice constant and cohesive energy, whereas the bulk modulus B is given by the curvature at the minimum. The latter is seen by

evaluating B directly:

$$B = \frac{1}{12\pi s} \frac{d^2 E_c}{ds^2},$$ (7.2)

where s is the Wigner-Seitz radius, and

$$\frac{d^2 E_c}{ds^2} = \frac{d^2 E_c}{d\bar{n}^2} \left[\frac{d\bar{n}}{ds} \right]^2.$$ (7.3)

The results for Na, Li, and Al from Fig. 2 are compared to the KKR calculations of Moruzzi, Janak, and Williams[26] and to experiment in Table II.

The understanding of the general form of the $E_c(n)$ curves of Figs. 2 and 3 outlined in Sec. VII A above can be transferred directly into a picture of the bonding in simple metals. The equilibrium configuration is a result of a competition between an inter-atomic electrostatic attraction $(-\alpha \bar{n})$ and the kinetic energy repulsion [which dominates $\Delta E^{hom}(\bar{n})$].

For the transition metals the interaction between the d resonances must be included as outlined in Sec. V. Given the d-d matrix elements Eq. (5.14) this in principle involves the solution of the tight-binding band-structure problem. For the perfect lattice this has been done.[1] For a less symmetrical situation one could imagine solving the problem by, e.g., the recursion method,[27] which does not rely on the translational symmetry. The simplest thing one can do is to assume a form for the d density of states (d-DOS) and then determine the parameters from the lowest moments.[28] This is the approach we shall take here even for the perfect lattice. Following Friedel,[29] Pettifor,[2] and Williams et al.,[3] we assume a square d band:

$$n_d(\epsilon) = 10/W \quad \text{for} \quad \epsilon_d - W/2 \le \epsilon \le \epsilon_d + W/2$$

$$= 0 \quad \text{otherwise.}$$ (7.4)

The center of the band ϵ_d (the first moment of the DOS) is given by the position of the d resonance, whereas the bandwidth W (the second moment) is given by the d-d coupling matrix element. We shall use the simple Wigner-Seitz result relating the coupling matrix element in Eqs. (5.14)—(5.15) to the bandwidth:

$$W = 25 \frac{M_d^2}{s^5}.$$ (7.5)

The appealing result Eq. (5.17) of the small kr approximation that expresses the matrix element M_d in terms of the resonance half width Δ_d works to the right in the periodic system, but further to the left this approximation breaks down and we shall therefore in the following use the expression Eq. (5.15) for M_d. Using the Wronskian theorem the matrix element M_l can be obtained directly from the value at the atomic sphere of the wave function normalized within the sphere and with logarithmic derivative $-(l+1)$ at the sphere.[1] This is the method we have used to get the M_d's (Table I).

Using the relation Eq. (5.16) we can compare the $\Delta_d^{Andersen}$ that we obtain with the potential taken from the calculation in the homogeneous electron gas with the one obtained from a fully self-consistent LMTO calculation[1] for the solid. At a fixed Wigner-Seitz radius they agree

TABLE I. Effective-medium-theory parameters for Al and $3d$ transition-metal atoms. E_c is given by Eq. (4.17), s is the radius of the neutral atomic sphere, ϵ_d is the position of the d resonance, Γ_d is the full d-resonance width ($\Gamma_d = 2\Delta_d$), N_d is the number of d electrons in the atomic sphere, and M_d is the matrix element Eq. (5.15). r_s and s are in units of bohr; E_c, ϵ_d, and Γ_d are in units of eV; and M_d is in units of (eV bohr^5)$^{1/2}$.

Atom	r_s	E_c	s	ϵ_d	Γ_d	N_d	M_d
Al	2.50	-2.30	2.623				
	2.75	-2.94	2.761				
	3.00	-3.20	2.889				
	3.25	-3.28	3.008				
	3.50	-3.24	3.119				
	3.75	-3.14	3.224				
	4.00	-3.00	3.323				
Sc	2.50	-1.99	2.767	8.921	4.019	2.165	8.53
	2.75	-2.82	2.962	7.346	2.840	2.044	9.00
	3.00	-3.13	3.142	6.147	2.042	1.926	9.37
	3.25	-3.19	3.308	5.214	1.487	1.816	9.68
	3.50	-3.08	3.462	4.742	1.097	1.733	9.97
	3.75	-2.90	3.603	3.876	0.820	1.659	10.16
	4.00	-2.68	3.734	3.390	0.620	1.591	10.33
Ti	2.50	-3.33	2.701	8.218	2.703	3.149	7.50
	2.75	-3.62	2.876	6.806	1.870	3.054	7.72
	3.00	-3.55	3.038	5.724	1.322	2.973	8.07
	3.25	-3.31	3.189	4.877	0.952	2.898	8.28
	3.50	-3.02	3.327	4.202	0.699	2.846	8.46
V	2.00	-0.34	2.279	11.929	4.727	4.300	6.13
	2.25	-2.11	2.466	9.583	3.060	4.205	6.46
	2.50	-2.78	2.641	7.852	2.044	4.131	6.74
	2.75	-2.77	2.803	6.543	1.405	4.051	6.98
	3.00	-2.49	2.953	5.528	0.988	3.997	7.16
Cr	2.00	+ 0.24	2.244	11.330	3.766	5.234	5.64
	2.20	-0.96	2.385	9.572	2.646	5.181	5.85
	2.50	-1.38	2.581	7.591	1.617	5.121	6.10
	3.00	-0.80	2.873	5.399	0.780	5.033	6.44
	3.50	+ 0.10	3.121	4.017	0.413	4.971	6.69
Mn	2.00	-0.80	2.217	10.738	3.078	6.160	5.24
	2.25	-1.89	2.381	8.815	1.989	6.106	5.45
	2.50	-2.02	2.534	7.341	1.326	6.087	5.62
	2.75	-1.73	2.677	6.192	0.910	6.056	5.79
	3.00	-1.29	2.808	5.282	0.645	6.037	5.91
	3.50	-0.35	3.041	3.957	0.342	5.999	6.09
Fe	2.00	-3.16	2.189	9.994	2.445	7.067	4.86
	2.20	-4.02	2.312	8.625	1.732	7.075	5.00
	2.50	-4.15	2.485	7.013	1.072	7.074	5.17
	3.00	-3.36	2.742	5.129	0.526	7.056	5.39
Co	2.00	-4.09	2.167	8.846	1.775	7.979	4.50
	2.25	-5.04	2.309	7.503	1.181	7.995	4.63
	2.50	-5.11	2.442	6.427	0.811	8.018	4.75
	2.75	-4.80	2.565	5.551	0.571	8.035	4.85
	3.00	-4.39	2.678	4.829	0.412	8.057	4.93
	3.50	-3.54	2.878	3.726	0.225	8.071	5.06

TABLE I. (Continued).

Atom	r_s	E_c	s	ϵ_d	Γ_d	N_d	M_d
Ni	2.00	-3.68	2.171	6.915	1.008	8.760	4.18
	2.20	-4.72	2.279	6.104	0.735	8.809	4.26
	2.50	-5.12	2.429	5.137	0.476	8.871	4.37
	2.75	-4.98	2.544	4.499	0.342	8.914	4.46
	3.00	-4.69	2.648	3.975	0.253	8.953	4.53
	3.50	-4.01	2.830	3.174	0.148	9.014	4.65
Cu	2.00	-1.14	2.201				
	2.25	-2.80	2.339				
	2.50	-3.41	2.464				
	2.75	-3.57	2.579				
	3.00	-3.49	2.685				

within approximately 10% for the $3d$ transition metals indicating that the potential we use is good.

In the present treatment we refine the picture with the square d band slightly by including the hybridization of the d bands with the free-electron-like bands. In the case of a single transition metal atom this is what gives the broadening of the d levels in a homogeneous electron gas. In accordance with this we will include the hybridization as if the d bands were infinitely narrow. The ansatz d-DOS is then a Lorentzian tail identical to the d-DOS of the atom in a homogeneous gas outside the bands. Within the d-band limits the square DOS of Eq. (7.4) is still used, properly renormalized to take into account the weight in the tails. Let

$$N_d^{\mathrm{tot}} = \int_{\epsilon_d - W/2}^{\epsilon_d + W/2} n_d^0(\epsilon)d\epsilon, \tag{7.6}$$

with

$$n_d^0 = \frac{10}{\pi} \frac{\Delta_d}{(\epsilon - \epsilon_d)^2 + \Delta_d^2} \tag{7.7}$$

denote the amount of weight inside the band limits. The one-electron energy difference in Eq. (7.1) is then

$$\int_a (\Delta e - \Delta \tilde{e}) \simeq \int_{\epsilon_d - W/2}^{\epsilon_F} \epsilon n_d(\epsilon)d\epsilon - \int_{\epsilon_d - W/2}^{\epsilon_F^0} \epsilon n_d^0(\epsilon)d\epsilon$$

$$= -\frac{N_d'(N_d^{\mathrm{tot}} - N_d')}{2N_d^{\mathrm{tot}}} W$$

$$-\frac{5}{\pi}\Delta_d \ln\left[\frac{(\epsilon_F^0 - \epsilon_d)^2 + \Delta_d^2}{(W/2)^2 + \Delta_d^2}\right], \tag{7.8}$$

where

$$N_d' = N_d - (10 - N_d^{\mathrm{tot}})/2 \tag{7.9}$$

is the number of d electrons in the band itself. Furthermore, N_d is the total number of d electrons in the resonance (inside region a) and can be taken from the calculation of the atom in a homogeneous electron gas (Table I), and ϵ_F^0 is then defined by the relation

$$N_d = \int_{-\infty}^{\epsilon_F^0} n_d^0(\epsilon)d\epsilon. \tag{7.10}$$

Equation (7.8) is obviously a gross oversimplification. It is, however, good enough to look at the *trends* in the cohesive properties along the transition metal series. Figure 7 shows the results for the cohesive energies and the equilibrium Wigner-Seitz radii for the entire $3d$ series. The present treatment clearly includes most of the trends. The largest deviations in the cohesive energies are in the middle of the series, whereas there seems to be a general underestimate of the equilibrium lattice constants. The latter deficiency of the present calculations must be attributed to the E_c term, since it is present, for instance, for Cu where the one-electron energy term is zero. Presumably it reflects an underestimate of the kinetic energy repulsion. The differences seen in Fig. 7 for the cohesive energy can be ascribed to a too large d-d interaction. The differences are therefore largest in the middle of the series where the d-d interaction is most important. There are two main reasons for the too large d-d interaction. The first is related to the too small lattice constants and therefore to $E_c(\bar{n})$ as discussed above. Because the bandwidth

TABLE II. The calculated Wigner-Seitz radius R_{WS}, cohesive energy E_{coh}, and bulk modulus B for Li, Na, and Al. The results are compared to the experimental ones (Ref. 40) and to the results of the self-consistent band-structure calculations of Moruzzi, Janak, and Williams (Ref. 26) (MJW).

	Li			Na			Al		
	This work	Expt.[a]	MJW[b]	This work	Expt.[a]	MJW[b]	This work	Expt.[a]	MJW[b]
$R_{\mathrm{WS}}(a_0)$	3.04	3.26	3.16	3.48	3.94	3.79	3.01	2.99	2.97
$E_{\mathrm{coh}}(\mathrm{eV})$	-1.6	-1.65	-1.65	-1.3	-1.13	-1.12	-3.3	-3.34	-3.79
$B(\mathrm{Mbar})$	0.19	0.11	0.15	0.2	0.07	0.09	0.8	0.7	0.8

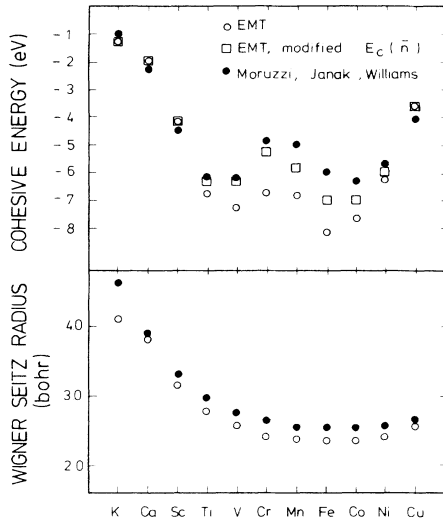[a] See Ref. 40.
[b] See Ref. 26.

FIG. 7. Comparison of calculated cohesive energies and equilibrium Wigner-Seitz radii for the $3d$ transition metals with the results of self-consistent KKR calculations of Moruzzi, Janak, and Williams (Ref. 23). Also included are the results for the cohesive energies, where the E_c functions have been shifted to lower densities, so that the equilibrium Wigner-Seitz radii are equal to those of Ref. 23.

W grows rapidly with decreasing s, W is too large around the equilibrium value of s and consequently the d-d interaction is too large. If we shift the minimum of the $E_c(\bar{n})$ functions to the density $\bar{n}$ that gives an equilibrium lattice constant in agreement with that of Moruzzi, Janak, and Williams, then the agreement for the cohesive energies becomes considerably better. This is also illustrated in Fig. 7. The remaining disagreement in Fig. 7 is to a large extent due to the fact that our bandwidths W are generally found to be larger than the self-consistently determined ones by 5—10 %. The results shown in Fig. 7 are for the nonmagnetic solutions. There are magnetic solutions with lower energy for the transition metals in the middle of the series. These will be discussed in a later publication.

The presence of the d-d interaction changes the picture of the cohesion somewhat from the simple metal case. The d-d interaction is always attractive tending to contract the system relative to what would be found if only the E_c term was included. This is illustrated in Fig. 8. The maximum in the cohesive energy around the middle of the series is given by the d-d interaction, in agreement
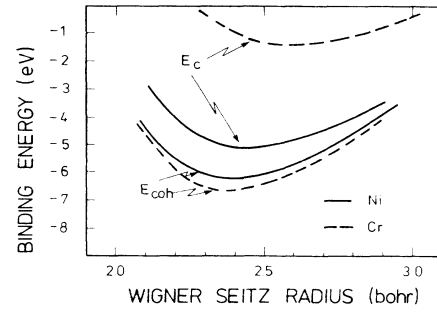

FIG. 8. The cohesive energy for Ni and Cr as a function of Wigner-Seitz radius. It is seen that for Ni most of the energy comes from $E_c(n)$, whereas for Cr the d-d interaction is very important.

with earlier suggestions.[29] It is the kinetic energy repulsion that prevents the lattice from collapsing, on the other hand. The notion of a density-dependent contribution E_c, which is common to all metals, and an extra d-d interaction for the transition metals is very appealing from the point of view that all metals are treated within the same framework.

C. Evaluating the atomic sphere correction

To consider situations where the translational symmetry of the solid is destroyed, the atomic-sphere correction ΔE_{AS}^{corr} of Eq. (6.6) must be included. Before treating examples of such low-symmetry systems we therefore first discuss the evaluation of this term in some detail.

The first integral in Eq. (6.6) is dominated by the electrostatic part. This is illustrated in Fig. 9, where $\frac{1}{2}\rho\phi$ is compared to $t + f_{xc}$ at a distance of 3 bohr from one to four Al atoms. A local (Thomas-Fermi) expression for t is used here. Since the O integral in Eq. (6.6) basically involves differences between $(t + \frac{1}{2}\rho\phi + f_{xc})$ at different sites, it is dominated by the electrostatic term which has the largest gradient in Fig. 9. This is a general phenomenon: t and f_{xc} vary approximately as $n^{5/3}$ and $n^{4/3}$, respectively, whereas $\frac{1}{2}\rho\phi$ varies faster than n^2. In the following we shall therefore use the approximation

$$\Delta E_{AS}^{corr} \simeq \Delta E_{AS}^{es} = -\frac{1}{2}\int O\rho\phi + \frac{1}{2}\sum_i \int_{s_i}\int_{s'_{-i}} \frac{\rho\rho'}{|\mathbf{r}-\mathbf{r}'|}.$$

(7.11)

According to Eq. (B8) we have

$$\Delta E_{AS}^{es} - \sum_i \alpha_i \bar{n}_i = \frac{1}{2}\sum_{\langle ij\rangle}\int\int \frac{\Delta\rho_i\Delta\rho_j}{|\mathbf{r}-\mathbf{r}'|} + \sum_i \left[\frac{1}{2}\int_{s_i}\int_{s'_i} \frac{\Delta\rho_{-i}\Delta\rho'_{-i}}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{2}\int_{s_{-i}}\int_{s'_{-i}} \frac{\Delta\rho_i\Delta\rho'_i}{|\mathbf{r}-\mathbf{r}'|} + \int_{s_i}\int_{s'_i} \frac{\Delta\rho_i(\Delta\rho'_{-i}-\bar{n}'_i)}{|\mathbf{r}-\mathbf{r}'|} \right].$$

(7.12)

For a given pair of densities $\Delta\rho_i$ and $\Delta\rho_j$ the first term on the right-hand side is a pair potential. The rest of the terms are small compared to the first. The first two of these are of the type tail out minus tail in entering ΔE_{tail}^{corr},

while the last is first order in the small quantity $\Delta\rho_{-i} - \bar{n}_i$. In calculating the small energy ΔE_{AS}^{es} we shall be including these terms only to the extent that they can be represented by a pair potential. This means that we can
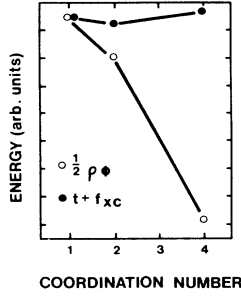
FIG. 9. A comparison of $t + f_{xc}$ and $\frac{1}{2}\rho\phi$ at a distance of 3 bohr from 1, 2, and 4 Al atoms.

write

$$\Delta E_{AS}^{es} = \sum_i \alpha_i \bar{n}_i + \frac{1}{2} \sum_{\langle ij \rangle} V_{ij}(\mathbf{r}_i - \mathbf{r}_j). \qquad (7.13)$$

The pair potential V_{ij} can be calculated by placing the densities $\Delta\rho_i$ and $\Delta\rho_j$ on an fcc lattice and noting that for a close-packed fcc crystal $\Delta E_{AS}^{es} \simeq 0$. If only the 12 nearest neighbors contribute to $\bar{n}_i$ we have

$$V_{ij}(r_{ij}) = -[\alpha_i \Delta\bar{n}_j^{fcc}(r_{ij}) + \alpha_j \Delta\bar{n}_i^{fcc}(r_{ij})],$$

where $\Delta\bar{n}_i^{fcc}(r_{ij})$ is the average density for a perfect fcc crystal made up of i-type densities, that is, the average is over a sphere of a radius s_{fcc} related to the interatomic distance r_{ij} by

$$r_{ij} = (16\pi/3)^{1/3}2^{-1/2}s_{fcc} = \beta s_{fcc} .$$

The atomic sphere correction is then

$$\Delta E_{AS}^{corr} \simeq \sum_i \alpha_i \left[\bar{n}_i - \sum_{j \neq i} \Delta\bar{n}_j^{fcc}(r_{ij}) \right]. \qquad (7.14)$$

The average density from one atom over a sphere of radius s centered a distance r away is defined as

$$\Delta\bar{n}(s,r,\sigma) = \frac{1}{\frac{4\pi}{3}s^3} \int_s \Delta n_\sigma(|\mathbf{r}' - \mathbf{r}|)d\mathbf{r}'. \qquad (7.15)$$

Here σ is a parameter describing the electron gas density from which Δn_σ is taken. Because there is a unique relationship between the electron gas density and the radius within which the embedded atom is neutral (the Wigner-Seitz radius) we use the equivalent radius as the density parameter. For the self-consistent ansatz density we thus always have $\sigma_i = s_i$.

In actual evaluations of the total energy and in particular if one is aiming at dynamics simulations, it is useful to parametrize the s and r dependence of $\Delta\bar{n}(s,r,\sigma)$. A very convenient form is an exponential

$$\Delta\bar{n}(s,r,\sigma) = \Delta n_0 \exp(\eta_1 s - \eta_2 r + \eta_3 \sigma). \qquad (7.16)$$

With this form the choice of s to be the radius for which the sphere is neutral becomes particularly simple. If we only consider nearest neighbors and again use the fcc structure as a reference system where the spheres are assumed to be space filling, the self-consistency requirement

$$\sum_{j \neq i} \Delta\bar{n}(s_i, r_{ij}, \sigma_j) = \bar{n}_{WS}(s_i) = 12\Delta\bar{n}(s_i, \beta s_i, s_i) \qquad (7.17)$$

becomes

$$s_i = \frac{-1}{\beta\eta_2 - \eta_3} \ln \left[\frac{1}{12} \sum_{j \neq i} \exp(-\eta_2 r_{ij} + \eta_3 s_j) \right]. \qquad (7.18)$$

The density argument in $E_c(\bar{n}_i)$ then becomes

$$\bar{n}_i = 12\Delta n_0 \exp(-\eta s_i) = n_0 \exp[-\eta(s_i - s_0)], \qquad (7.19)$$

where $\eta = \beta\eta_2 - \eta_1 - \eta_3$, $n_0 = 12\Delta n_0 \exp(-\eta s_0)$, and the atomic sphere correction Eq. (7.14) is

$$\Delta E_{AS}^{corr} \simeq \sum_i \alpha_i \left[\bar{n}_i - \Delta n_0 \sum_{j \neq i} \exp[-\eta r_{ij}/\beta + \eta_3(s_j - r_{ij}/\beta)] \right].$$

$$(7.20)$$

The final expression for the total binding energy using the exponential ansatz is then

$$\Delta E_{tot} = \sum_i [E_c(\bar{n}_i) + \alpha_i(\bar{n}_i - \bar{n}_i^{fcc})], \qquad (7.21)$$

where $\bar{n}_i$ is given by Eq. (7.19) and $\bar{n}_i^{fcc}$ is the last term in the square brackets in Eq. (7.20).

The expressions for $\bar{n}_i$ and $\bar{n}_i^{fcc}$ in Eq. (7.21) may easily be generalized to include more than the nearest neighbors as discussed in Appendix C.

The exponential dependence [Eq. (7.19)] of $\bar{n}_i$ on s is well obeyed by the results of the self-consistent calculations for Al in a homogeneous electron gas with $\eta = 2.00$ bohr^{-1}, $n_0 = 0.007$ bohr^{-3}, and $s_0 = 3.0$ bohr. Assuming an exponential form for $\Delta\bar{n}(r,s,\sigma)$ [Eq. (7.16)] is not so well obeyed. Using an exponential form is equivalent to a smearing out of the tail of $\Delta n(r)$ (cf. Fig. 4) so that the Friedel oscillations disappear. As discussed in Secs. IV and VII A above this is not unreasonable. It does, however, mean that η_1, η_2, and η_3 cannot be determined uniquely from $\Delta n(r)$ in the homogeneous electron gas. In the present, preliminary applications of the theory we make a very simple choice of the η parameters. We make use of the observation that the form of the free-atom density is a reasonable smeared out representation of the *tail* density. We therefore take $\eta_3 = 0$ and $\eta_2 = 1.27$ bohr^{-1} from here. The parameter η_3 describes the dependence of the induced density on the background density, and to take $\eta_3 = 0$ is therefore equivalent to neglecting this dependence and the self-consistency problem associated with it. This has the simplifying consequence that Eq. (7.18), that in general is a set of implicit equations for the radii s_i, reduces to an explicit nearest-neighbor sum. We notice that other procedures to obtain η_2 are possible and that the present determination is therefore not unique. Together with the E_c function, which to a good approximation is given by

$$E_c(n) = -3.28 + 1.12(n/0.007 - 1)^2$$

$$-0.35(n/0.007 - 1)^3, \qquad (7.22)$$

(in units of eV) and the value of $\alpha_i = 1280$ eV bohr^3, the Al potential, is completely specified.

With $\eta_3 = 0$, the form of the interaction Eq. (7.21) is

identical to the one *assumed* by Daw and Baskes.[8] The present derivation thus supports their applications to a number of situations. It must, however, be stressed that for, e.g., transition metals there is an additional term in the energy expression as discussed in Sec. VII B.

We notice that with the exponential density the expression Eq. (7.3) entering the bulk modulus Eq. (7.2) becomes

$$\frac{d^2E_c}{ds^2} = \frac{d^2E_c}{dn^2} n_0^2\eta^2, \tag{7.23}$$

where n_0 is the equilibrium density.

In the following we shall be using the expressions above derived on the basis of the exponential form Eq. (7.16) for the averaged density and the values for the parameters quoted. This is not necessarily the most accurate choice. It is, however, very convenient and will serve to illustrate the applicability of the method.

D. Phonons in Al

The calculation of the phonon spectra is done by displacing layers in the crystal, determining the inter-layer force constants from the corresponding change in the total energy. The simple problem of a one-dimensional harmonic chain is then solved to get the dispersion relations. In the present calculation we only include charge density from nearest neighbors. In all cases considered here, except the [110] longitudinal branch, we also only include the nearest-neighbor interlayer force constants. With the exponential density Eq. (7.16) the force constants can be calculated analytically. For instance, in the case of a Brillouin-zone phonon, where the layers are moved alternatively in the plus and minus z direction, we have (for $\eta_3=0$)

$$\frac{d^2E}{dz^2} = \alpha_i n_0 \frac{2\eta\eta_1}{3\beta^2} N_1 \left| \frac{z}{r} \right|^2, \tag{7.24}$$

where N_1 is the number of nearest neighbors in the next layer, n_0 is the equilibrium density, $\beta \simeq 1.81$ is the fcc interatomic spacing to Wigner-Seitz radius ratio, and z/r is the ratio of the interlayer spacing to the interatomic distance. Only the latter and N_1 will vary from one phonon branch to another.

Using the parameters for Al quoted in the preceding section this gives the dispersion relations shown in Fig. 10. It must be pointed out that this is only a first estimate which can be improved by including in the density contributions from more distant neighbors.

Only the atomic-sphere correction term contributes to Eq. (7.24). The second derivative of the density-dependent term is zero for a volume conserving phonon. The interatomic interactions giving rise to the (zone-boundary) phonons are thus electrostatic in character. They stem from the fact that when the atoms are squeezed together the ion cores are not completely screened from each other. We notice that the atomic-sphere correction has a pair potential form as long as the density is kept constant. In the description of zone-boundary phonons it may thus be appropriate to use a pair potential description. For distortions involving changes in volume, on the other hand, the
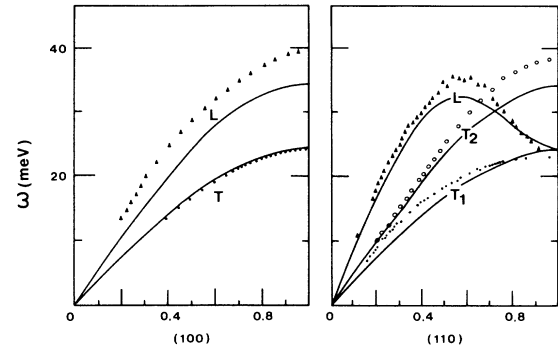

FIG. 10. Comparison of calculated and experimental phonon dispersion relations for Al. The experimental points are taken from Ref. 39.

density-dependent term becomes important as illustrated by the expression for the bulk modulus Eq. (7.23). It is impossible to describe this term with a pair potential.

E. Surface energies and relaxations for Al

The surface energies of various Al surfaces have been calculated as a function of the interlayer spacings. The layers have not been allowed to reconstruct in the present calculation, but this could easily be included. We have again used the exponential density and the parameters quoted in Sec. VII C. Because the densities fall off rapidly it is only necessary to consider a small number of lattice planes. In the calculations reported here only nearest-neighbor contributions to the density are included, meaning that at most one layer more than the number of layers allowed to relax has to be considered. The lower-lying layers will not be different from bulk layers and therefore do not contribute to the surface energy.

In Table III the equilibrium surface energy and the corresponding lattice relaxations are compared to experiment. Considering the simplicity of the approach the agreement is quite good. The agreement with the much more involved calculations of Ho and Bohnen[30] is similarly good. In comparing the magnitude of the relaxations to experiment and to other calculations it must be kept in mind that the energies involved in the relaxations are of the order 10 meV.

With the exponential density Eq. (7.16) and including only nearest-neighbor contributions to the density, the surface energy of the unrelaxed surface can be calculated very easily. If an atom has only N nearest neighbors at the surface instead of 12 in the bulk, its energy relative to that of a bulk atom is

$$E_s(N) = C \left[1 - \left[\frac{N}{12} \right]^{\eta/\beta\eta_2} \right]^2$$
$$+ \alpha_i n_0 \left[\left[\frac{N}{12} \right]^{\eta/\beta\eta_2} - \frac{N}{12} \right]. \tag{7.25}$$

Here we only include the quadratic term in the expression for E_c Eq. (7.22) and $C = 1.12$ is the corresponding coefficient.

TABLE III. Comparison of calculated equilibrium relaxations d_{12} (between first and second layer) and d_{23} (between second and third layer) and the surface energies for various Al surfaces to experiment and to other local density calculations by Ho and Bohnen (Ref. 30) and by Lang (Ref. 35). The experimental value for E_S represents some average over the various crystal planes.

		Al(110)	Al(100)	Al(111)
Δd_{12} (%)	This work	-7	-3	-1
	Ho and Bohnen[a]	-6.8		
	Expt.[b,c]	-8.5	0	
	Expt.[d,e]	-8.8		+ 0.9
Δd_{23} (%)	This work	+ 1	0	0
	Ho and Bohnen[a]	+ 3.5		
	Expt.[b]	+ 5.5		
	Expt.[d]	+ 5.0		
E_S (erg/cm^2)	This work	883	830	701
	Ho and Bohnen[a]	1090		
	Lang[f]		835	
	Expt.[g]		1180	

[a] See Ref. 30.
[b] See Ref. 33.
[c] See Ref. 37.
[d] See Ref. 34.
[e] See Ref. 38.
[f] See Ref. 35.
[g] See Ref. 36.

The inwards relaxations seen in Table III for the most open (110) surface are seen quite generally for fcc metals. It is also generally found that the second layer relaxes outwards. For more open surfaces the relaxations are larger and even the second layer may move inwards giving rise to a $- - +$ relaxation pattern. The effective-medium theory expression Eq. (7.21) for the total energy gives a conceptually simple way of rationalizing these observations. The driving force behind the inwards relaxations of the first lattice plane is the attempt of these atoms to place themselves in the optimum electron density as defined by the minimum of the $E_c(n)$ curve in Fig. 2. The atoms in the first plane have fewer nearest neighbors and consequently sample a too low density. This is compensated for by moving closer to the atoms in the second plane. The atomic sphere correction ΔE_{AS}^{corr} opposes the tendency to move atoms closer to each other and therefore tends to diminish the relaxations. It is also this term that, in combination with an increased density from the first layer, is responsible for the outwards relaxation of the second layer. For the most close-packed surfaces the two terms nearly cancel, but the more open the surface is, the more nearest neighbors the surface atoms will have lost and the stronger the driving force from the $E_c(n)$ term will be. One can also easily see from this argument how surfaces that are so open that the second layer atoms have lost a significant number of nearest neighbors may develop a $- - +$ or even more complicated relaxation sequences. Since there is an E_c function like that of Al for every metal (cf. Fig. 3) the arguments presented here are of a very general nature, although the inclusion of the d-d interactions for the transition metals may complicate the picture somewhat.

Because the minimum in the $E_c(n)$ function comes from a competition between an attractive interatomic electrostatic interaction and a repulsive kinetic energy term, the inwards relaxations of the first lattice plane can also be ascribed to the decrease in the kinetic energy of the first layer atoms which have fewer nearest neighbors and therefore less confined electrons. This allows the atoms to move closer to the second layer atoms to take advantage of the attractive electrostatic interaction. In this way the present picture makes contact with the picture of Finnis and Heine[31] and Barnett, Landman, and Cleveland.[32]

VIII. SUMMARY

The main result of the present paper is the derivation of an expression Eq. (6.3) for the total energy of a system of interacting atoms. The result is valid to second order in the deviation of the ansatz density Eq. (4.1) from the true ground-state density of the system. With a set of further approximations this result has been turned into a form for the total energy Eq. (7.21) simple enough for, e.g., molecular dynamics simulations. The applicability of the method has been illustrated by calculations of the cohesive properties for a long row of metals, and of phonon dispersion relations and surface properties of Al. It is also shown that the total-energy expression provides a convenient way of understanding these phenomena.

ACKNOWLEDGMENT

APPENDIX A

As a simple illustration of the usefulness of the generalized energy functional (2.14) we can prove the so-called *force theorem* first shown by Andersen.[11]

Consider a solid where the ions in a half-space B are translated a distance δa relative to the ions in half-space A. The aim is to calculate the force between regions A and B or equivalently the first-order change in the total energy due to the translation by δa. Imagine that the density and the potential in the undistorted solid have been calculated self-consistently. Because of the variational property (2.15) it is sufficient to use a density and a potential in the distorted solid that is correct to zeroth order in δa to get a correct first-order change in the total energy.

One possible choice for the density and potential in the distorted solid is to take them equal to what they are in the undistorted solid. The change in the total energy is then given by the electrostatic energy change involved in moving the bare nuclei to their distorted positions in the fixed electronic cloud. This is just the result of the Hellmann-Feynman theorem.

Another choice for the density and potential in the distorted solid is to use the same density and potential as in the undistorted solid but this time shifted rigidly together with the nuclei. In this way a "gap region" C opens up between regions A and B and the potential and the density can be taken to continue smoothly over this region.

Due to the "freezing" of the density and potential in the regions A and B the vn term in the change in the kinetic energy vanishes for these regions and we are left with

$$\delta T = \delta \left[\sum_\alpha \epsilon_\alpha \right] - \int_C vn . \tag{A1}$$

The electrostatic interaction *within* region A and *within* region B is also unchanged so

$$\delta E^{\mathrm{es}} = \delta E^{\mathrm{es}}_{A \leftrightarrow B} + \int_C n\phi_{A+B}, \tag{A2}$$

where $E^{\mathrm{es}}_{A \leftrightarrow B}$ is the change in the electrostatic interaction *between* the regions A and B and ϕ_{A+B} is the Hartree potential from the charge in regions A and B.

The change in the exchange correlation energy is

$$\delta E_{\mathrm{xc}} = \int_C f_{\mathrm{xc}}(n) = \int_C n\epsilon_{\mathrm{xc}}(n), \tag{A3}$$

and the total energy change is therefore given by the *force theorem*

$$\delta E = \delta \left[\sum_\alpha \epsilon_\alpha \right] + \delta E^{\mathrm{es}}_{A \leftrightarrow B} + \int_C n[\phi_{A+B} + \epsilon_{\mathrm{xc}}(n) - v] . \tag{A4}$$

The last term may be included in the single-particle energy sum by changing the potential in region C to

$$v = \phi_{A+B} + \epsilon_{\mathrm{xc}}(n), \tag{A5}$$

that is by giving the potential a discontinuity of the size $\epsilon_{\mathrm{xc}}(n) - v_{\mathrm{xc}}(n)$.

APPENDIX B

In this appendix we consider the electrostatic terms used in Secs. IV, VI, and VII. The starting point is the electrostatic energy E^{es} defined by

$$E^{\mathrm{es}} = \frac{1}{2} \sum_{\langle ij \rangle} \int \int' \frac{\Delta\rho_i \Delta\rho'_j}{|\mathbf{r} - \mathbf{r}'|}$$

$$= \frac{1}{2} \int \int' \frac{\rho\rho'}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \sum_i \int \int' \frac{\Delta\rho_i \Delta\rho'_i}{|\mathbf{r} - \mathbf{r}'|} . \tag{B1}$$

Let $\{s_i\}$ denote a set of regions of the total space Ω and let $s_{-i} = \Omega - s_i$. We rewrite the two terms on the right-hand side of Eq. (B1) as

$$\frac{1}{2} \int \int' \frac{\rho\rho'}{|\mathbf{r} - \mathbf{r}'|} = E' + \frac{1}{2} \sum_i \int_{s_i} \int_{s'_i} \frac{(\Delta\rho_i + \Delta\rho_{-i})(\Delta\rho_i + \Delta\rho_{-i})'}{|\mathbf{r} - \mathbf{r}'|} , \tag{B2}$$

where

$$E' = \frac{1}{2} \left[\int \int' \frac{\rho\rho'}{|\mathbf{r} - \mathbf{r}'|} - \sum_i \int_{s_i} \int_{s'_i} \frac{\rho\rho'}{|\mathbf{r} - \mathbf{r}'|} \right] \tag{B3}$$

and

$$\frac{1}{2} \sum_i \int \int' \frac{\Delta\rho_i \Delta\rho'_i}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2} \sum_i \int_{s_i + s_{-i}} \int_{(s_i + s_{-i})'} \frac{\Delta\rho_i \Delta\rho'_i}{|\mathbf{r} - \mathbf{r}'|} . \tag{B4}$$

Subtraction of (B4) from (B2) leads to

$$E^{\mathrm{es}} = E' + \frac{1}{2} \sum_i \left[\int_{s_i} \int_{s'_i} \frac{\Delta\rho_{-i} \Delta\rho'_{-i}}{|\mathbf{r} - \mathbf{r}'|} - \int_{s_{-i}} \int_{s'_{-i}} \frac{\Delta\rho_i \Delta\rho'_i}{|\mathbf{r} - \mathbf{r}'|} \right] + \sum_i \int_{s_i} \int_{s'_i} \frac{\Delta\rho_i \Delta\rho'_{-i}}{|\mathbf{r} - \mathbf{r}'|} - \sum_i \int_{s_i} \int_{s'_{-i}} \frac{\Delta\rho_i \Delta\rho'_i}{|\mathbf{r} - \mathbf{r}'|} . \tag{B5}$$

The last two terms in this expression may for an arbitrary set of numbers $\bar{n}_i$ be rewritten

$$\sum_i \int_{s_i} \int_{s'_i} \frac{\Delta\rho_i \Delta\rho'_{-i}}{|\mathbf{r} - \mathbf{r}'|} = \sum_i \int_{s_i} \int_{s'_i} \frac{\Delta\rho_i \bar{n}'_i}{|\mathbf{r} - \mathbf{r}'|} + \sum_i \int_{s_i} \int_{s'_i} \frac{\Delta\rho_i (\Delta\rho_{-i} - \bar{n}_i)'}{|\mathbf{r} - \mathbf{r}'|} \tag{B6}$$

and

$$\sum_i \int_{s_i} \int_{s'_{-i}} \frac{\Delta\rho_i \Delta\rho'_i}{|\mathbf{r}-\mathbf{r}'|} = \sum_i \int_{s_i} \int_{s'_{-i}} \frac{(\Delta\rho_i+\bar{n}_i)\Delta\rho'_i}{|\mathbf{r}-\mathbf{r}'|} - \sum_i \int_{s_i} \int_{s'_{-i}} \frac{\bar{n}_i \Delta\rho'_i}{|\mathbf{r}-\mathbf{r}'|}.$$ (B7)

Collecting the terms, we get the following expression for the electrostatic energy:

$$E^{\mathrm{es}} = E' - \sum_i \alpha_i \bar{n}_i$$

$$+ \frac{1}{2}\sum_i \left[\int_{s_i}\int_{s'_i} \frac{\Delta\rho_{-i}\Delta\rho'_{-i}}{|\mathbf{r}-\mathbf{r}'|} - \int_{s_{-i}}\int_{s'_{-i}} \frac{\Delta\rho_i\Delta\rho'_i}{|\mathbf{r}-\mathbf{r}'|} \right] + \sum_i \int_{s_i}\int_{s'_i} \frac{\Delta\rho_i(\Delta\rho_{-i}-\bar{n}_i)'}{|\mathbf{r}-\mathbf{r}'|} - \sum_i \int_{s_i}\int_{s'_{-i}} \frac{(\Delta\rho_i+\bar{n}_i)\Delta\rho'_i}{|\mathbf{r}-\mathbf{r}'|},$$ (B8)

where α_i is defined as in Eq. (4.12) with a_i replaced by s_i.

If the s_i's are assumed to be neutral spheres and $\bar{n}_i$ is chosen as the average over the density tails the last term in Eq. (B8) vanishes.

If we take $s_i = a_i$ to be a disjoint covering of all of space the quantity E' reduces to the Madelung energy

$$E' = E_{\mathrm{Madelung}} = \frac{1}{2}\sum_{\langle ij \rangle} \int_{a_i}\int_{a'_j} \frac{\rho\rho'}{|\mathbf{r}-\mathbf{r}'|}.$$ (B9)

APPENDIX C

In this appendix we generalize the expression for the total energy [Eq. (7.21)] to include more than the nearest neighbors. This generalization is only approximate but is essential if one is to do molecular dynamic simulations.

As in the case with only nearest-neighbor contributions, we have that the background density $\bar{n}(s)$ depends exponentially on the radius s [Eq. (7.19)]

$$\bar{n}(s) = n_0 e^{-\eta(s-s_0)},$$ (C1)

and we take the exponential ansatz Eq. (7.16) for the average density $\Delta\bar{n}(s,r)$ with $\eta_3 = 0$

$$\Delta\bar{n}(s,r) = \Delta n_0 e^{\eta_1 s - \eta_2 r}.$$ (C2)

If we assume, as we did in the case with only nearest neighbors included, that an fcc lattice is space filling we get the relation

$$\bar{n}(s) = 12\Delta\bar{n}(s,\beta s) + 6\Delta\bar{n}(s,2^{1/2}\beta s) + \cdots$$ (C3)

or

$$n_0 e^{\eta s_0} e^{-\eta s} = 12\Delta n_0 e^{-\eta_1 s_0}(1 + \tfrac{1}{2}e^{(1-2^{1/2})\eta_2\beta s} + \cdots)$$

$$\times e^{-(\beta\eta_2 - \eta_1)s}.$$ (C4)

This relation cannot be strictly fulfilled because the left-

hand side is an exponential and the right-hand side is a sum of different exponentials. It can, however, be approximately satisfied if we keep the relation $\eta = \beta\eta_2 - \eta_1$ and take

$$\Delta n_0 = \frac{1}{12\gamma_1}n_0 e^{\eta s_0},$$ (C5)

with the constant γ_1 given by

$$\gamma_1 = 1 + \tfrac{1}{2}e^{-(2^{1/2}-1)\beta\eta_2 s_0} + \cdots.$$ (C6)

The radii can now be determined by solving

$$\bar{n}(s_i) = \sum_{j\neq i}\Delta\bar{n}(s_i,r_{ij}),$$ (C7)

and we obtain

$$s_i = -\frac{1}{\beta\eta_2}\ln\left[\frac{1}{12\gamma_1}\sum_{j\neq i}e^{-\eta_2 r_{ij}}\right].$$ (C8)

The atomic-sphere correction can be determined analogously to the case with only nearest neighbors taken into account by using an exponential form of the pair potential part. The assumption that the atomic-sphere correction vanishes for all fcc lattices again leads to a total-energy expression of the form Eq. (7.21) with $\bar{n}$ related to s via the exponential expression Eq. (C1) and the radii s_i determined by Eq. (C8). Furthermore $\bar{n}_i^{\mathrm{fcc}}$ is now given by

$$\bar{n}_i^{\mathrm{fcc}} = \frac{1}{12\gamma_2}n_0 \sum_{j\neq i}e^{-\eta(r_{ij}/\beta - s_0)},$$ (C9)

with

$$\gamma_2 = 1 + \tfrac{1}{2}e^{-(2^{1/2}-1)\eta s_0} + \cdots.$$ (C10)

We point out that to get reasonable results with more than nearest neighbors included it is essential that the same number of atoms is included everywhere in the calculation, and it may be necessary to use the actual s_0 in Eqs. (C6) and (C10).

[1] O. K. Andersen, O. Jepsen, and D. Glötzel, in *Proceedings of the Enrico Fermi International School for Physics*, Course LXXXIX, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985).

[2] D. G. Pettifor, Phys. Rev. Lett. **42**, 846 (1979).

[3] A. R. Williams, C. D. Gelatt, and V. L. Moruzzi, Phys. Rev. Lett. **44**, 429 (1980).

[4] J. K. Nørskov and N. D. Lang, Phys. Rev. B **21**, 2131 (1980).

[5]J. K. Nørskov, Phys. Rev. B 26, 2875 (1982).

[6]M. J. Stott and E. Zaremba, Phys. Rev. B 22, 1564 (1980).

[7]P. Nordlander, S. Holloway, and J. K. Nørskov, Surf. Sci. 136, 59 (1984); B. Chakraborty, S. Holloway, and J. K. Nørskov, ibid. 152/153, 660 (1985); K. W. Jacobsen and J. K. Nørskov, ibid. 166, 539 (1986); P. Nordlander, J. K. Nørskov, and F. Besenbacher, J. Phys. F 16,1161 (1986).

[8]M. S. Daw and M. I. Baskes, Phys. Rev. Lett. 50, 1285 (1983); Phys. Rev. B 29, 6443 (1984); S. M. Foiles, ibid. 36, 3409 (1985).

[9]H. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[10]W. Kohn and L. Sham, Phys. Rev. 140, A1133 (1965).

[11]A. R. Mackintosh and O. K. Andersen, in Electrons at the Fermi Surface, edited by M. Springford (Cambridge University Press, Cambridge, England, 1980).

[12]V. Heine, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[13]M. J. Puska, R. M. Nieminen, and M. Manninen, Phys. Rev. B 24, 3037 (1981).

[14]H. L. Skriver, Phys. Rev. B 31, 1909 (1985); H. L. Skriver, The LMTO Method (Springer, New York, 1984).

[15]P. W. Anderson and W. L. McMillan, in Proceedings of the Enrico Fermi International School for Physics, Course XXXVII, edited by W. Marshall (Academic, New York 1967).

[16]D. R. Penn, Phys. Rev. B 9, 839 (1974).

[17]J. A. Moriarty, Phys. Rev. B 5, 2066 (1972).

[18]J. E. Inglesfield, J. Phys. F 2, 878 (1972); 3, 1921 (1973); and 9, 1551 (1979).

[19]O. Gunnarsson, H. Hjelmberg, and J. K. Nørskov, Phys. Scr. 22, 165 (1980).

[20]W. A. Harrison and S. Froyen, Phys. Rev. B 21, 3214 (1980)

[21]D. G. Pettifor, J. Phys. C 5, 97 (1972).

[22]J. A. Moriarty, J. Phys. F 5, 873 (1975).

[23]D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[24]D. G. Anderson, J. Assoc. Comput. Mach. 12, 547 (1965).

[25]O. Gunnarsson, O. Jepsen, and O. K. Andersen, Phys. Rev. B 27, 7144 (1983).

[26]V. L. Moruzzi, J. F. Janak, and A. R. Williams, Calculated Electronic Properties of Metals (Pergamon, New York, 1978).

[27]R. Haydock, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[28]F. Cyrot-Lackmann, Surf. Sci. 15, 535 (1969); F. Ducastelle and F. Cyrot-Lackmann, J. Phys. Chem. Solids 31, 1295 (1970); 32, 285 (1971).

[29]J. Friedel, in The Physics of Metals, edited by J. M. Ziman (Cambridge University Press, Cambridge, England, 1978), Vol. I.

[30]K. M. Ho and K. P. Bohnen, Phys. Rev. B 32, 3446 (1985).

[31]M. W. Finnis and V. Heine, J. Phys. F 4, L37 (1974).

[32]R. N. Barnett, U. Landman, and C. L. Cleveland, Phys. Rev. B 27, 6534 (1983).

[33]J. R. Noonan and H. L. Davis, Phys. Rev. B 29, 4349 (1984).

[34]J. N. Andersen, H. B. Nielsen, L. Petersen, and D. L. Adams, J. Phys. C 17, 173 (1984).

[35]N. D. Lang, in Theory of the Inhomogeneous Electron Gas, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[36]W. R. Tyson and W. A. Miller, Surf. Sci. 62, 267 (1977).

[37]D. W. Jepsen, P. M. Markus, and F. Jona, Phys. Rev. B 6, 3684 (1972).

[38]H. B. Nielsen and D. L. Adams, J. Phys. C 15, 615 (1982).

[39]J. Yarnell et al., in Lattice Dynamics, edited by R. F. Wallis (Pergamon, New York, 1965).

[40]C. Kittel, Introduction to Solid State Physics (Wiley, New York, 1971).