PHYSICAL REVIEW B VOLUME 46, NUMBER 7 15 AUGUST 1992-I

Ab initio potential for solids

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(Received 21 February 1992)

A total-energy theory for a solid is presented. It is based on density-functional theory and consists of a succession of approximations. At the most accurate level, the theory consists of a systematic derivation of an ansatz for the electron density which is best suited for the Harris functional. At the most approximate level, the theory is equivalent to the usual effective-medium theory. At all levels of approximation, every term in the total-energy expression is calculated *ab initio*, that is, without any fitting to experiment or to other calculations. Every step in the approximation procedure can thus be tested independently. The theory is applied to calculations of the surface energies and vacancy formation energy of Al. At the most accurate level, the theory gives results that are in almost complete agreement with self-consistent calculations. At the more approximate, but also computationally much less demanding, level, the theory gives results that are still in excellent agreement with the self-consistent results.

I. INTRODUCTION

With advanced numerical methods and increasingly faster computers, it is now possible to do *ab initio* calculations of the energetics of solids. Even though the local-density approximation (LDA) is usually made in order to treat exchange and correlation effects, the results for elastic properties, phonon frequencies, surface energies, etc., are typically in very good agreement with experiment.[1] The methods are, however, still so time consuming that only systems with rather few atoms per unit cell can be treated. For many problems, for example involving extended defects, one needs to consider larger systems in order to include the important physics, and the present methods are not sufficiently efficient. The same is true in simulations of finite temperature or time-dependent problems, and in problems where the equilibrium configuration of a system involves the variation of many atom coordinates. Substantial progress has been made with the Car-Parrinello method,[2] but there still is a need for simpler methods to treat such problems.

The usual approach has been to use pairwise interactions between the atoms. This is computationally very efficient, but unfortunately gives a rather poor description of the bonding in most solids. A number of empirical, semiempirical, or nearly *ab initio* methods have been proposed[3–9] which include the many-body interactions in an approximate way. There is, however, a need for methods that are faster, accurate enough to give sensible results and, at the same time, do not require experimental input into the calculation. Furthermore, a good model demands a greater understanding of the nature of the approximations thus leading to a physically more meaningful picture of the essential interactions.

In this paper we present a theory which allows us to calculate the total energy of a solid using different levels of approximation. The main point of the theory is that at each level of approximation, each part of the energy is calculated *ab initio*, that is, without fitting to other calculations or to experiment. This ensures that we can test every approximation in detail, and we can make sure that the physical picture behind the theory is correct and that we are not being misled by errors that cancel due to any fitting procedure. We test the theory by calculating surface energies for the three simple surfaces of Al and the vacancy formation energy. Comparisons to a fully self-consistent calculation show the method to give good results even at the level of approximation where the energy calculation is very much faster than with conventional self-consistent methods. We will show that in its most approximate form, the theory is equivalent to the effective-medium theory[8] and thereby mathematically similar to a number of frequently used and very effective semiempirical methods, such as the embedded-atom method,[5] the Finnis-Sinclair method,[6] or the glue model.[7]

II. THE FIRST LEVEL OF APPROXIMATION: THE OPTIMIZED UNIVERSAL ELECTRON-DENSITY ANSATZ

A. General remarks

The starting point is the density-functional theory of Hohenberg and Kohn,[10] and we shall be working within the local-density approximation (LDA) for the exchange and correlation energies although the theory may be generalized to more elaborate schemes for treating these effects. The total energy of a system of atoms is a unique functional $E[n]$ of the electron density $n(\mathbf{r})$ of the system, and $E[n]$ is variational around the ground-state electron density. Usually the ground state density is determined by a self-consistent solution of the Kohn-Sham equations.[10]

An equally good energy expression is the Harris functional[11,12] which is stationary but not necessarily variational at the ground-state energy.[13,14] A useful attribute of the Harris functional is that it depends only on the input charge density, whereas the Kohn-Sham functional also depends on the output density. It has been shown that overlapping free-atom densities constitutes a good input to the Harris functional for molecular systems and bulk systems where, in the latter, cohesive energies, lattice constants, phonon frequencies, and bulk moduli can be accurately determined.[15] A well-known problem using this ansatz for the input density, however, is the complete failure to determine surface energies.[16] Finnis[17] resolved this difficulty by a two-parameter variation of the input density until the stationary value of the Harris functional was attained which gave the correct surface energy compared with the self-consistent result. The long-wavelength components of the density are especially important for the surface because of the long-range nature of the Coulomb interaction, so the Finnis procedure, which results in a contraction of the charge density, had evidently addressed this issue albeit in an *ad hoc* way.

If the ansatz density for the Harris functional is good enough, then this will give a total-energy calculation which is considerably faster than a self-consistent solution because only one iteration is needed in the Kohn-Sham equations. In a recent paper,[18] it was shown that there exists a systematic decomposition of the self-consistent electron density for bulk Al and the Al(111) surface into overlapping-atom-like densities, and it was claimed that this procedure gave the optimized choice input density for the Harris functional.[19] In Sec. II B we will discuss this means of determining optimized atomiclike densities from first-principles calculations of the crystalline solid that are transferable to different chemical environments, and we will give specific results for Al.

B. The optimized density

The total density n_{tot} in a crystal of overlapping free atomic densities Δn_{atom} is given by

$$n_{\text{tot}}(\mathbf{r}) = \sum_{\mathbf{R}_\mu} \Delta n_{\text{atom}}(\mathbf{r} - \mathbf{R}_\mu), \tag{1}$$

where $\{\mathbf{R}_\mu\}$ is the set of lattice vectors, and we consider only one type of atom for convenience. Our arguments are most transparent in reciprocal space: the corresponding expression for the Fourier-transformed densities is

$$n_{\text{tot}}(\mathbf{G}) = S(\mathbf{G})\Delta n_{\text{atom}}(\mathbf{G}), \tag{2}$$

where $\mathbf{G}$ is a reciprocal-lattice vector and $S(\mathbf{G})$ is the structure factor.[20] This density may be used to construct the input potential for the iteration of the Kohn-Sham equations[10] to a self-consistent density $n_{\text{tot}}^{\text{sc}}$. From this result, we can extract an atomiclike density Δn_{op} (optimized) which is related to $n_{\text{tot}}^{\text{sc}}$ by the structure factor as in Eq. (2). This optimized density depends on the crystal structure and volume, and is only determined on the discrete set of reciprocal-lattice vectors for which the structure factor is nonzero. Overlapping such densities in the solid is designed to reproduce the correct density only for those components for which the structure factor is nonzero. The construction of $\Delta n_{\text{op}}(\mathbf{r})$ therefore first requires an analytical continuation in reciprocal space of $\Delta n_{\text{op}}(\mathbf{G})$ to $\Delta n_{\text{op}}(\mathbf{k})$, where $\mathbf{k}$ is a continuous variable, before inversion to real space.

We have studied bulk Al using the plane-wave pseudopotential method,[21,22] and in Fig. 1 we show the deviation of $\Delta n_{\text{op}}(\mathbf{G})$ from $\Delta n_{\text{atom}}(\mathbf{G})$ for the discrete shells in reciprocal space that the fcc lattice [$S(\mathbf{G}) = 1$ for all $\mathbf{G}$] samples. Charge conservation fixes the $\mathbf{G}=0$ term, and the short-wavelength components converge rapidly to the atomic value of zero so that the essential physics of bulk Al is determined in the intermediate wavelength region. By varying the lattice constant, the optimized density components evolve parallel to the free-atom density,[18] which justifies the success of using overlapping free-atom densities in calculating the elastic properties and phonon frequencies of the bulk.[16,23] The long-wavelength contributions are especially important for the surface problem which we consider next.

We first observe that for a lattice with a basis of *dissimilar* atoms, it is not possible to resolve atomiclike densities for each atom. We studied the Al(111) ideal surface in a supercell geometry oriented along the **z** direction with four atomic layers and two vacuum layers. We made the simplifying assumption that all four Al atoms in the supercell are *identical* so that we extract a representative atomiclike density for the surface problem. We will see that this works well largely because the surface and bulk are decoupled in reciprocal-space with the main contribution to the surface energy being the long-wavelength components which are not present in the bulk.

We have plotted in Fig. 1 the results for the spherically averaged $\Delta n_{\text{op}}(\mathbf{G})$ which we extracted from the Al(111) surface calculation. We note that the short-

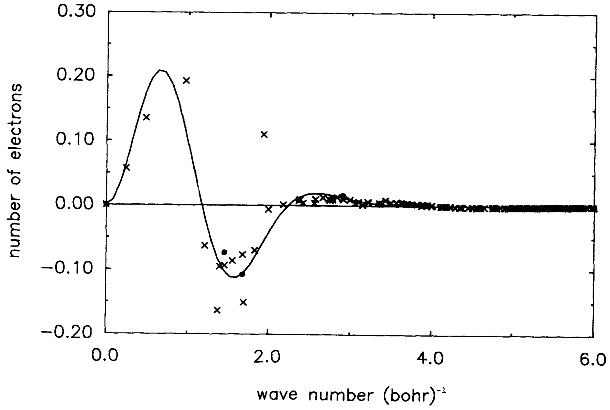

FIG. 1. The solid dots are the deviation of $\Delta n_{\text{op}}(G)$ from $\Delta n_{\text{atom}}(G)$ for the discrete shells in reciprocal space that the fcc lattice (the lattice constant is 3.96 Å) samples. The crosses are the corresponding components for the Al(111) ideal surface, and the solid line is the least-squares fit of the data to a product function (Appendix).

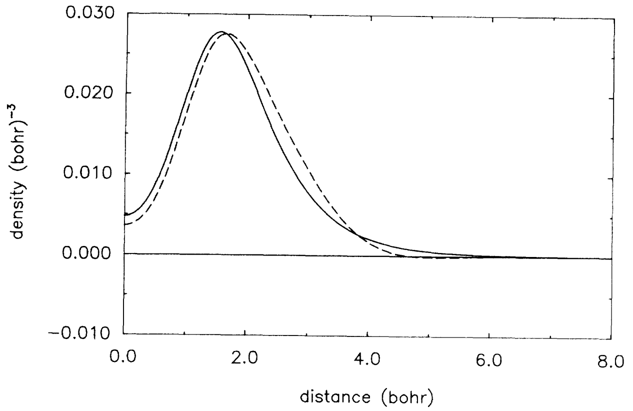

FIG. 2. The real-space pseudodensity $n_{\text{atom}}(r)$ (solid line) and $n_{\text{op}}(r)$ (dashed line).

wavelength components for the surface relax to the bulk result in reciprocal space — which it must to be able to recover in real space the bulklike properties away from the surface. The components with the wave vector perpendicular to the surface are surface sensitive and mark significant deviations away from the free-atom result in the long-wavelength region. We now continue the components $\Delta n_{\text{op}}(\mathbf{G})$ using a least-squares fit to a product function (see the Appendix) incorporating the surface-sensitive long-wavelength components and the bulk information in the short-wavelength region as shown in Fig. 1.

In Fig. 2 we show the densities in real space, noting the contraction of the density toward the core region compared with the free-atom density and the resulting sharper attenuation of the density tail, a feature present in the atom embedded in a homogeneous electron gas and the Finnis renormalized atom. The optimized density exhibits oscillations in the tail region that are due to screening and which are also present in the atom embedded in a homogeneous electron gas. It is therefore not surprising that[18] the atom embedded in a homogeneous electron gas of a reasonable density gives results with the Harris functional of the same level of quality as with the optimized density.

We make the ansatz that $\Delta n_{\text{op}}(r)$ is a universal, transferable density, and in Sec. II C, we test this assumption by considering the Harris functional for different situations. It must be pointed out that the optimized density does not reproduce the entire self-consistent density even for the (111) surface (from which it was derived) because of reasons given above (zero structure factor, spherical averaging, numerical interpolation, etc.), but the stationary property of the Harris functional ensures a good estimate of the total energy.

C. Results and discussion

In Table I we give results for the bulk, the three principal unrelaxed surfaces of Al, and the unrelaxed vacancy using the optimized density as an input to the Harris functional, and we compare with the self-consistent calculations. We used a supercell with four slab layers plus two vacuum layers for the (111) and (100) surfaces, and a supercell with eight plus four layers for the (110) surface. The vacancy problem comprised of a 27-atom unit cell.

In the construction of the optimized density we used a functional form which gave a very localized density essentially only extending to the nearest neighbors. This constraint was imposed because we want to construct a nearest-neighbor model with which we can compare the more approximate schemes we shall introduce later. It can be seen from Table I that the localization of the optimized density leads to a slight overestimate of the surface and vacancy energies compared with the self-consistent ones and also with the earlier published results for an optimized density where the localization was not imposed.[18] However, the Harris-functional results with the localized

TABLE I. (a) Nearest-neighbor distance (d_1^0), cohesive energy (E_c), and bulk modulus (B) for Al in the fcc lattice using the self-consistent (SC) and Harris (H) methods and the various different levels of approximation of the present theory: EMT_1 includes the potential-energy Δv contribution to the kinetic-energy difference (see Sec. III D), and EMT_2 and EMT_3 include two different estimates to the one-electron energy difference (see Sec. III E). (b) Energy of formation of Al for the three principal unrelaxed surfaces and the ideal vacancy. The energies are per surface atom or per atom around the vacancy. The vacancy formation energy is then 12 (the number nearest neighbors to the vacancy) times the vacancy number in the table.

Quantity	SC	H	EMT_1	EMT_2	EMT_3
		(a) Bulk			
d_1^0 (bohr)	5.284	5.292	5.292	5.292	5.292
E_c (eV)	4.22	4.22	4.22	4.22	4.22
B (Mbar)	0.89	0.89	0.89	0.89	0.89
		(b) Surface and vacancy			
(111) (eV)	0.43	0.46	0.60	0.47	0.45
(100) (eV)	0.52	0.55	0.75	0.53	0.60
(110) (eV)	0.80	0.86	1.10	0.81	0.87
Vacancy	0.053	0.060	0.123	0.072	0.043

optimized densities must still be considered in excellent agreement with the self-consistent results, and supports our claim that $\Delta n_{\mathrm{op}}(r)$ is universal and transferable to the extent that a single function is enough to give a good description of both the bulk metal at various lattice parameters and in various structures and of the surface of the metal.

Although faster than the self-consistent calculation, the total-energy calculation at this level of approximation is still rather time consuming due to the fact that the eigenvalues ε_i of the Kohn-Sham equations

$$[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \tag{3}$$

must still be calculated once to get the kinetic-energy contribution[24]

$$T[n] = \sum_{\alpha} \varepsilon_\alpha - \int n(\mathbf{r}) v_{\mathrm{eff}}(\mathbf{r}) d\mathbf{r} \tag{4}$$

to the total energy

$$E[n] = T[n] + G[n] \, . \tag{5}$$

Here, $v_{\mathrm{eff}}(\mathbf{r})$ is the effective potential which is given by a sum of the external potential, the Hartree potential, and the exchange-correlation potential,[20] and G contains the electrostatic and exchange-correlation energies. In order to find a really efficient total-energy method, one would need a more effective method for calculating the kinetic energy.

III. THE SECOND LEVEL OF APPROXIMATION: THE KINETIC-ENERGY FUNCTION

A. General remarks

In order to proceed, we introduce the concept of an effective medium or reference system.[25] The idea is that for each atom i in the system, we look for a reference system where the atom is in "similar" surroundings, but where the symmetry is higher so that the total-energy calculation is simpler. We then write the total energy of the system of interest

$$E = E + \sum_i e_i^{\mathrm{ref}}(s_i) - \sum_i e_i^{\mathrm{ref}}(s_i) \tag{6}$$

$$= \sum_i e_i^{\mathrm{ref}}(s_i) + \Delta T + \Delta G. \tag{7}$$

Here e_i^{ref} is the energy of atom i in the reference system characterized by some parameter s_i, and the kinetic, electrostatic, and exchange-correlation energy differences are given by

$$\Delta T = T - \sum_i t_i^{\mathrm{ref}}, \tag{8}$$

$$\Delta G = G - \sum_i g_i^{\mathrm{ref}}. \tag{9}$$

The small e, t, and g denote energies per atom whereas the capital E, T, and G denote energies for the whole system.

We propose the following approach: Given the ansatz optimized density $\Delta n_{\mathrm{op}}(r)$, the electrostatic and the exchange-correlation energies of the system are exactly determined by first overlapping $\Delta n_{\mathrm{op}}(r)$ in the configuration under investigation. The aim, then, is to find *that* reference system for which $|\Delta T|$ is small and easily calculated, so that the quantum kinetic interactions are taken into account to good measure in the reference calculation which is done just once and for all times.

In our work we choose the effective medium or reference system to be a fcc crystal of an appropriate volume, although an equally good reference system that one may choose is the atom embedded in a homogeneous electron gas. In Fig. 3 we have plotted the total energy per atom (e) of Al in the fcc lattice, and the separate contributions of the kinetic (t) and the electrostatic plus exchange-correlation energy (g) as a function of the nearest-neighbor distance.

Now consider an arbitrary configuration of Al atoms. In order to find the reference system for any of these atoms, say atom i, one must specify the lattice constant of the reference fcc crystal. In principle, any lattice constant will do, but obviously some choices are more sensible than others. The most sensible ones are those where $|\Delta T|$ is small and can be calculated in low-order perturbation theory. The choice we make here is that a fcc crystal which has the *same* neutral-sphere radius s_i as the atom i in the system under study. This choice is the one that is made in the usual effective-medium theory,[8] and ensures that the atom is immersed in the same average electron density. With this choice of determining the reference volume, we at least ensure that there is no long-range Coulomb interaction between the atomic spheres and, as we shall see in Sec. III D, there are also a number of numerical problems that are avoided with this choice. In Sec. III B we give the explicit construction for determining the neutral spheres about each atom and the results for the three principal surface orientations and the ideal vacancy.

B. The embedding density function

For an arbitrary configuration of Al atoms, we determine the neutral-sphere radius s_N for each atom by solving the equation

$$\int_{s_N} d\mathbf{r}\, n(\mathbf{r}) \;=\; Z \tag{10}$$

about each atom, where $Z = 3.0$ corresponds to the total valence charge of atomic Al, and n is the superposition of the optimized atomic densities. In Fig. 4 we have shown s_N as a function of the nearest-neighbor distance for the fcc lattice and, for comparison, we also included the Wigner-Seitz radius s_W.

It is useful to resolve (10) into contributions from successive shells of atoms and to this end, we define the embedding function

$$\Gamma(s,d) \;=\; \int_s d\mathbf{r}\, \Delta n_{\mathrm{op}}(|\mathbf{r} - \mathbf{d}|) \, . \tag{11}$$

In Fig. 5 we have plotted $\Gamma(s,0)$ and $\Gamma(s,d)$ for s and d in our range of interest.

Equation (10) may now be written as

$$\sum_j n_j \Gamma(s_N, d_j) = Z, \tag{12}$$

where the sum is over all shells of atoms around a given atom and n_j is the number of lattice vectors in the jth shell with length d_j.

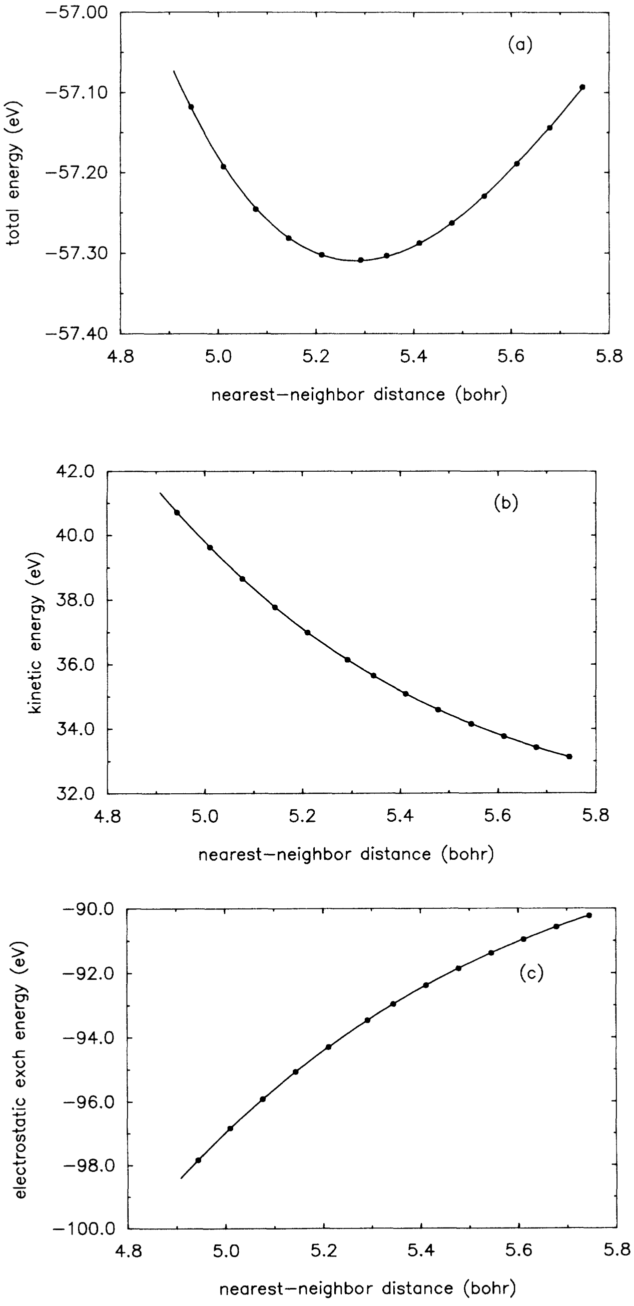

FIG. 3. The (a) total energy, (b) kinetic energy, and (c) electrostatic plus exchange-correlation energy of Al in the fcc structure as a function of the nearest-neighbor distance d_1. The solid lines are cubic fits to the data points (dots).

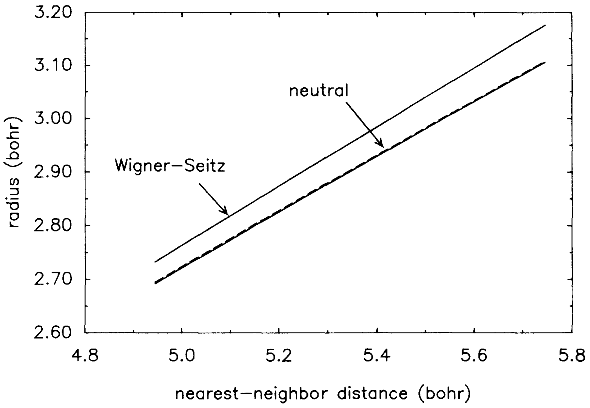

FIG. 4. The neutral-sphere radius S_N as a function of the nearest-neighbor distance d_1 for Al in the fcc structure. The Wigner-Seitz radius $S_W = [\frac{3}{4\pi\sqrt{2}}]^{1/3} d_1$ is also included for comparison. The dashed line is S_N calculated including only up to nearest-neighbor contributions.

Using Eq. (12) we now determine s_N for the fcc lattice, but include contributions only up to the nearest-neighbor shell (n_1=12); the result plotted in Fig. 4 compares very well with the exact result calculated from Eq. (10). It is clear that the optimized density is reasonably well localized in real space and that a nearest-neighbor model is

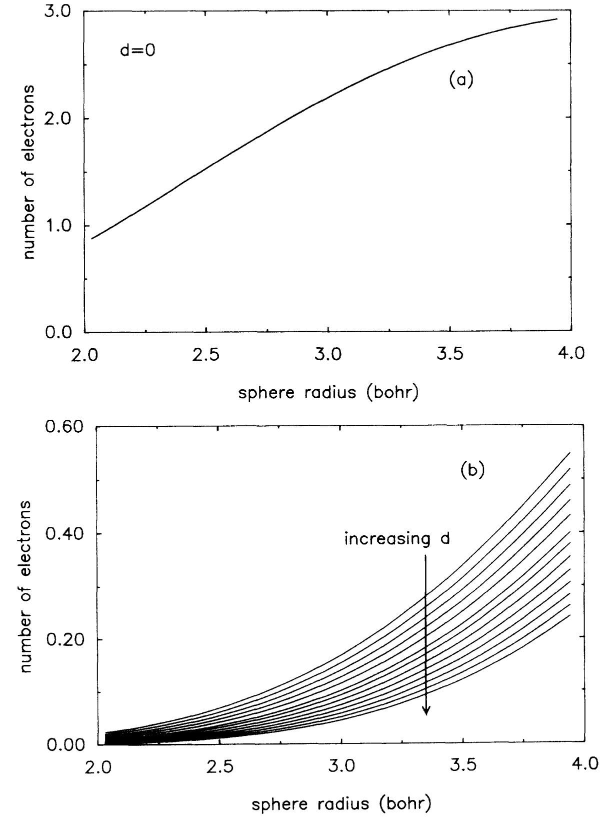

FIG. 5. The embedding function as defined in the text as a function of the sphere radius s for (a) $d = 0$ and (b) $\sqrt{2} d a_0$ in the range 3.70–4.30 Å in increments of 0.05 Å.

TABLE II. The neutral-sphere radius for surface atoms for the three principal unrelaxed surfaces of Al and the ideal vacancy, and the corresponding energies. Note that the results for the (110) surface include the combined contributions from the first-layer (1) and second-layer (2) atoms.

Surface orientation	s_N (bohr)	e^s (eV)	t^s (eV)	g^s (eV)
(111)	2.959	-56.89	34.90	-91.79
(100)	2.995	-56.74	34.54	-91.28
(110) (1), (2)	3.035, 2.897	-113.74	69.93	-183.67
Vacancy	2.897	-57.254	35.707	-92.961

adequate in describing the essential interactions, and so in subsequent calculations, we will only include contributions to this order.

We now solve for the neutral-sphere radii of the atom(s) at the three ideal surfaces

$$\Gamma(s_N,0) + n_1\Gamma(s_N,d_1^0) = 3.0\,, \tag{13}$$

where $d_1^0 = 5.292$ bohr is the fcc lattice equilibrium nearest-neighbor distance, and where for the (111) and (100) surface atoms, n_1 is 9 and 8, respectively, and for the (110) surface, n_1 is 7 for the first-layer atom and 11 for the second-layer atom. The atom at the ideal vacancy is identical to the second layer (110) surface atom — within a nearest-neighbor model — since both have lost a single nearest neighbor.

In Table II we tabulate the results for s_N for the surface atoms and, using the results in Fig. 4, we determine the corresponding reference fcc volumes which have the same neutral-sphere radii, and these results together with the corresponding energies are listed in Table III.

We now turn to looking at the individual energy contributions in Sec. III C.

C. Results

In the nearest-neighbor model, we can easily resolve

$$T = \sum_i t_i \tag{14}$$

and

$$G = \sum_i g_i \tag{15}$$

into contributions from each atom in our surface supercell. We do this by assigning bulk energies to all those atoms that are bulklike within this model (i.e., those atoms that have retained their bulk coordination number of 12), and we attribute all deviations of energies from the bulk values to the surface atom in question. In Table II we tabulate the individual energies e^s, t^s, and g^s for each of the three surfaces and the ideal vacancy under consideration. Note that the results for the (110) surface include the combined contributions from the first-layer and second-layer atoms, both atoms of which have lost the bulk coordination number.

In order to illustrate the usefulness of the effective medium or reference system, it is instructive to consider the deviation of the kinetic energies t^s from the bulk equilibrium value t_0. $t^s - t_0$ is the kinetic-energy contribution to the surface energy. In Table IV the calculated value of $t^s - t_0$ is compared to $t^{\rm ref}(s_N) - t_0$, the kinetic-energy of an atom in the reference system at the appropriate neutral-sphere radius. It can be seen that the use of a reference system with the same neutral sphere reduces the problem of calculating the kinetic-energy contribution to the surface energy by an order of magnitude.

Now we define

$$\Delta t = t^s - t^{\rm ref}\,, \tag{16}$$

$$\Delta g = g^s - g^{\rm ref} \tag{17}$$

as the energy differences between the real and the reference systems. The surface energy can then be written as[26]

$$\sigma = e^{\rm ref} - e_0 + \Delta t + \Delta g\,, \tag{18}$$

where $e^0 = -57.31$ eV is the bulk energy per atom of the fcc lattice at the equilibrium volume. It is simple to calculate Δg from the density ansatz. In Sec. III D, we will describe how to estimate the the small quantity Δt using low-order perturbation theory.

TABLE III. The fcc equilibrium bulk and reference volumes, and the associated energies.

		fcc reference volumes		
s_N (bohr)	d_1^0 (bohr)	$e^{\rm ref}$ (eV)	$t^{\rm ref}$ (eV)	$g^{\rm ref}$ (eV)
2.876	5.292	-57.31	36.15	-93.46
2.959	5.465	-57.27	34.68	-91.95
2.995	5.536	-57.23	34.21	-91.44
3.035	5.614	-57.19	33.75	-90.94
2.897	5.345	-57.304	35.645	-92.949

TABLE IV. The kinetic-energy difference between the surface and bulk $t^s - t_0$ compared with that between the reference system and the bulk $t^{\text{ref}} - t_0$. EMT_1, EMT_2, and EMT_3 are successive inclusions of the potential energy Δv and two different approximations to the one-electron energy $\Delta\varepsilon$ contributions to the difference in the kinetic energy between the reference system and the bulk. The units are in eV.

Surface orientation	$t^s - t_0$	$t^{\text{ref}}(s_N) - t_0$	EMT_1	EMT_2	EMT_3
(111)	-1.25	-1.47	-1.07	-1.20	-1.22
(100)	-1.61	-1.94	-1.43	-1.65	-1.58
(110)	-2.37	-2.91	-2.16	-2.45	-2.39
Vacancy	-0.443	-0.505	-0.375	-0.426	-0.455

D. Calculating the difference in the kinetic energy to first order

We have asserted above that the atom i in the system under consideration is similar to the atom in its corresponding reference fcc system provided that both have the same average electron density or neutral-sphere radius s_N. We shall be exploiting this similarity in calculating the kinetic-energy difference Δt to first order in the difference between the reference and the real systems. In order to do this, we make two independent approximations. First, we calculate Δt within the atomic-sphere approximation (ASA). In the ASA, the Wigner-Seitz cell of atom i is replaced by the neutral sphere s_N, and the effective potential inside the neutral sphere is spherically averaged. In order to see the effect of the ASA on the kinetic-energy contribution, we show in Fig. 6 the fully anisotropic potential contribution to the kinetic energy

$$\int_{\text{WS}} d\mathbf{r}\, v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) \tag{19}$$

for Al in the fcc lattice as a function of the nearest-neighbor distance d_1^0, where WS is the Wigner-Seitz unit cell, and we compare this with the ASA result

$$\int_{s_N} d\mathbf{r}\, \bar{v}_{\text{eff}}(r) n(\mathbf{r})\,, \tag{20}$$

where $\bar{v}_{\text{eff}}(r)$ is the spherically averaged potential. The curves appear to be shifted by a constant amount relative to each other, so that *differences* in energies can be computed reliably in the ASA.

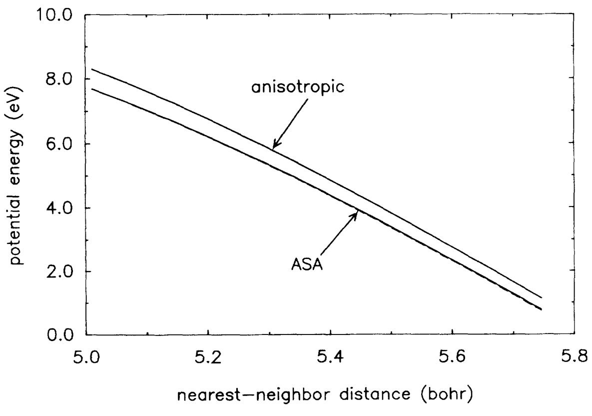

FIG. 6. The effective potential contribution to the kinetic energy for the fcc lattice as a function of the nearest-neighbor distance d_1 for the fully anisotropic potential and that calculated in the ASA. The dashed line includes only up to nearest-neighbor contributions.

The second approximation we make is to treat the difference between the real and the reference system to first order. We make use of the fact that the kinetic energy, when considered a functional of the effective potential, is stationary with respect to deviations around the ground state.[8] This means that to first order in the difference between the effective potential in the real and the reference systems, the kinetic energy due to atom i, as given by Eq. (4), can be written (in the ASA) as

$$t_i = \sum_\alpha \varepsilon_\alpha[v_{\text{eff}}]|_i - \int_{s_N} d\mathbf{r}\, \bar{v}_{\text{eff}}(r) n(\mathbf{r}) \tag{21}$$

$$\approx \sum_\alpha \varepsilon_\alpha[v_{\text{eff}}^{\text{ref}}]|_i - \int_{s_N} d\mathbf{r}\, \bar{v}_{\text{eff}}^{\text{ref}}(r) n(\mathbf{r})\,, \tag{22}$$

where the sum over the eigenvalues is projected on the sphere at site i. Notice that in Eq. (22) the last term only depends on the potential in cell i, whereas the eigenvalue sum depends on the potential in the surroundings too.

The difference in the kinetic energies between the atom in question and the atom in its associated reference system is now given in the ASA by

$$\Delta t = \sum_\alpha \varepsilon_\alpha[\bar{v}_{\text{eff}}^{\text{ref}}]|_i - \sum_\alpha \varepsilon_\alpha[\bar{v}_{\text{eff}}^{\text{ref}}] \tag{23}$$

$$- \int_{s_N} d\mathbf{r}\, \bar{v}_{\text{eff}}^{\text{ref}}(r)[n(\mathbf{r}) - n^{\text{ref}}(\mathbf{r})] \tag{24}$$

$$= \Delta\varepsilon + \Delta v\,. \tag{25}$$

The first term, $\Delta\varepsilon$, we call the one-electron correction term, and it is truly quantum mechanical in nature; for example, it includes hybridization effects and changes in the density of states at the Fermi level. This term will be discussed more fully in Sec. III E.

For now, we consider the second term Δv. Note, firstly, that this quantity is independent of the arbitrary constant to which the effective potential is defined; the uniqueness of Δv is a consequence of the condition of charge neutrality in each of the spheres about the atoms.

In analogy with the definition of the embedding density function in Sec. III B, we resolve expression (20) into contributions from successive shells of atoms by defining the potential-weighted embedding function

$$\Lambda(s,d) = \int_{s_N} d\mathbf{r}\, \bar{v}^{\mathrm{ref}}_{\mathrm{eff}}(r)\, \Delta n_{\mathrm{op}}(|\mathbf{r}-\mathbf{d}|)\,, \tag{26}$$

where $\bar{v}^{\mathrm{ref}}_{\mathrm{eff}}(r)$ is the potential associated with that fcc lattice with neutral-sphere radius s_N. In Fig. 7 we have plotted $\Lambda(s_N,0)$ and $\Lambda(s_N,d)$ for s_N and d in our range of interest. Expression (20) may be written as

$$\sum_j n_j\, \Lambda(s_N,d_j)\,. \tag{27}$$

As before, we only consider up to nearest-neighbor contributions. The result for the fcc lattice in Fig. 6 shows, once again, the adequacy of this approximation for the very localized optimized density used here.

The difference Δv for the three ideal surfaces can now be simply written as

$$\Delta v = 12.0\, \Lambda(s_N,d_1) - n_1\, \Lambda(s_N,d_1^0)\,. \tag{28}$$

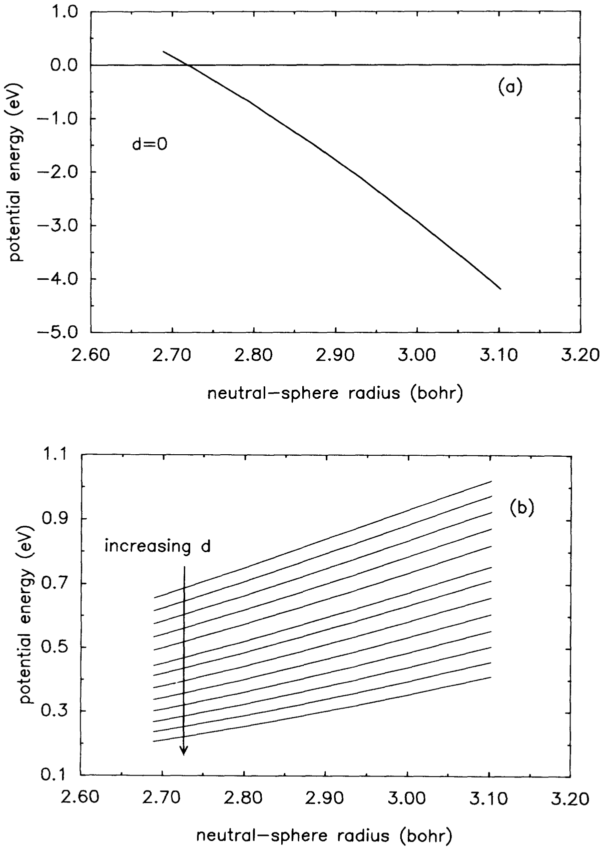

FIG. 7. The potential-weighted embedding function as defined in the text as a function of the neutral-sphere radius s_N for (a) $d = 0$ and (b) $\sqrt{2}d a_0$ in the range 3.70–4.30 Å in increments of 0.05 Å.

In Table IV the effect of including Δv in the estimate of $t^s - t_0$ is seen to reduce the error. At this level of approximation, and omitting the one-electron contribution, the surface energies and the vacancy formation energy defined as

$$\sigma^{EMT_1} = \Delta e + \Delta v + \Delta g\,, \tag{29}$$

are consistently overestimated compared with the correct result in Table I. Both the absolute value of the surface energies and the qualitative result of increasing energy with increasing "openness" of the surface is, however, included at this level of approximation. Moreover, the results do meet the requirement of being expressible in terms of simply calculable quantities.

E. The one-electron correction

The treatment in Sec. III D of the energy difference between, for example, a surface atom and the atom in the reference system, was done to first order within the atomic-sphere approximation. However, we are left with a term, the one-electron correction, which we shall now discuss. The one-electron correction is the difference in the sum over the Kohn-Sham eigenvalues projected onto an atomic sphere in the real system and the reference system, respectively. The potential to be used in the Kohn-Sham equations [Eq. (3)] for the real system has to be "frozen" to be the same as that in the reference system within the atomic sphere. In terms of the densities of states (DOS) projected onto the atomic spheres [$\rho(\varepsilon)$ and $\rho^{\mathrm{ref}}(\varepsilon)$ in the real system and the reference system, respectively] the one-electron correction can be written as the difference of the first moments of the DOS to the Fermi level[27]

$$\Delta\varepsilon = \int^{\varepsilon_F} d\varepsilon\, \varepsilon\rho(\varepsilon) - \int^{\varepsilon_F^{\mathrm{ref}}} d\varepsilon\, \varepsilon\rho^{\mathrm{ref}}(\varepsilon). \tag{30}$$

A complete evaluation of the state densities in this equation would involve the solution of the Kohn-Sham equations, and not much would be gained over a full calculation using the Harris functional with the input density constructed as a superposition of optimized densities. However, a very detailed knowledge of the DOS is in many cases not necessary to get a good estimate of the one-electron correction, and an approximate evaluation is often adequate for the following reasons: The one-electron correction involves only the first moments to the Fermi energy of the densities of states, which are much smoother functions than the DOS themselves, and we only need to evaluate the *difference* between the atom in the real system and in the reference system, and this evaluation should be performed with a frozen potential. This means that if the environment of the atom in the real system is similar to the one in the reference system, the one-electron correction is only a small correction and it does not have to be calculated with great accuracy.

For the evaluation of the one-electron correction, we shall use a simple nearest-neighbor tight-binding model with one s and three p states on each atomic site. The projection of the DOS onto an atomic sphere of a given atom in Eq. (30) is then substituted by a projection onto the states associated with that atom. We shall discuss the details of how the model is constructed below but first some general comments on the use of tight-binding models for this purpose. The one-electron correction is a difference between the band energy in the real system and that in the reference fcc crystal, and we therefore have to establish a way of defining the appropriate lattice constant for the reference crystal in the context of the tight-binding model. As the lattice constant of an fcc aluminum crystal is varied, the bandwidth changes and a one-to-one correspondence between the lattice constant and the second moment μ_2^{fcc} of the DOS exists. Therefore, we can equally well define the reference crystal by specifying the second moment μ_2^{fcc}. The information available in the model that can be used to define the reference system of an atom is the density of states projected onto that atom, and this information can be expressed through the second- and higher-order moments $\mu_2, \mu_3, \mu_4, \ldots$ of the DOS. (The zeroth and first moments are defined through the normalization and the freezing of the potential as discussed below. The second- and higher-order moments are calculated relative to the first moment.) If we express the higher-order moments through the dimensionless quantities $\gamma_n = \mu_n/\mu_2^{(n/2)}$ the second moment of the reference crystal can therefore be regarded as a function of $\mu_2, \gamma_3, \gamma_4, \ldots$. Since μ_2 is the only quantity with units of energy squared, the second moment μ_2^{fcc} of the reference fcc crystal can be written

$$\mu_2^{\text{fcc}} = \mu_2 f(\gamma_3, \gamma_4, \ldots), \tag{31}$$

where f is a dimensionless function to be determined. Since we naturally want the reference system for an atom in a perfect fcc crystal of a given lattice constant to be the fcc crystal itself, the function f must be equal to one if γ_3 and the other higher-order moments take on their fcc values. In fact, the function f has to be taken identical to one for all values of the higher-order moments for the following reason: In the effective-medium construction, the reference system is determined from the neutral-sphere radius or equivalently the embedding density of the atom. The embedding density is determined from the ansatz density, which is a superposition of atomic densities and therefore it contains information about pairs of atoms only, i.e., if the atoms surrounding a given atom change positions in a way that keep the distances to the given atom unchanged, the embedding density will remain the same. Therefore the reference system will also remain the same. In order to keep this property in the tight-binding model, the choice of reference system cannot depend on the higher moments $\gamma_3, \gamma_4, \ldots$ because all of these contain information about clusters with more than two atoms. Therefore, the reference system has to be defined as the fcc crystal with *the same second moment* of the DOS projected onto the atom as in the real system.

The tight-binding model for aluminum is constructed based on the linear muffin-tin orbital (LMTO) method[28,29] in the following way. The Hamiltonian H is of the form

$$H_{RL,R'L'} = C_{RL}^{\alpha_I}\delta_{RR'}\delta_{LL'} + (\Delta_{RL}^{\alpha_I})^{1/2} S_{RL,R'L'}^{\alpha_I} (\Delta_{R'L'}^{\alpha_I})^{1/2}, \tag{32}$$

where R is the atomic position and L denotes the angular-momentum state. The screening parameters α_I are chosen as in Ref. 29 to localize the hopping integrals using monopoles (s) and dipoles (p), and we use the exponential interpolation form for the off-diagonal elements of the structure constants as given in Table I of Ref. 29. However, for simplicity we truncate the hopping integrals to nearest-neighbors only. The on-site elements of the structure constants are calculated from the off-diagonal elements using the Dyson equation [Eq. (6) in Ref. 29] where we again truncate to nearest-neighbor contributions for consistency. We neglect the overlap between the states.

The potential parameters $C_{RL}^{\alpha_I}$ and $\Delta_{RL}^{\alpha_I}$ for an aluminum fcc crystal at the equilibrium lattice constant are determined from a fully self-consistent LMTO calculation.[30] Since the reference systems are fcc crystals with different lattice constants, we also need the potential parameters for varying lattice constant or equivalently for varying bandwidth (second moment) of the crystal. For simplicity, we shall assume a simple scaling of both $C_{RL}^{\alpha_I}$ and $\Delta_{RL}^{\alpha_I}$ as being proportional to the square root of the second moment of the DOS. This scaling is exact in the case of a free-electron gas where the parameters vary inversely proportional to the square of the lattice constant and it is therefore a reasonable approximation for aluminum. The scaling leads to an overall variation of the band energy with varying lattice constant for a fcc crystal proportional to the square root of the second moment.

The construction of the Hamiltonian for a surface or a vacancy now proceeds in the following way: The interatomic hopping matrix elements are kept fixed at the equilibrium bulk value because the interatomic distances are unchanged. The band-center parameters $C_{RL}^{\alpha_I}$ are taken from the reference system separately for each atom. This determines the separation between C_p and C_s on a given atom. The band-center parameters for the different atoms are positioned relative to each other by aligning the Fermi levels of their reference systems. The diagonal elements (the on-site values) of the Hamiltonian are given by the band-center parameters plus a contribution coming from the on-site elements of the structure constants. The latter are calculated from the interatomic hopping matrix elements by using the above-mentioned Dyson equation for the structure constants.

The one-electron correction comes about as a difference in the band energy of, say, the surface system and the band energy (per atom) for all the atoms in their respective reference fcc crystals, and we therefore have to specify a common energy zero for an atom in the surface structure and the reference atom. Guided by the fact that we have to use the same potential for the atom in the two calculations we line up the first moments of the density of states projected onto the atom in the surface calculation and in the reference system.

We find the projected densities of states and the corresponding energies using the recursion method.[31] This gives a systematic expansion in contributions from higher and higher moments of the densities of states, and we shall in the following discuss two different levels of approximations. In the first one, called EMT_2, the one-electron correction is calculated by diagonalizing the model Hamiltonian exactly, i.e., the recursion expansion is carried to complete convergence. In the second approximation, EMT_3, the recursion expansion is truncated after two levels (which is equivalent to expanding to the fourth moment) and a terminator is substituted for the remaining part of the recursion expansion. The terminator we use is defined in the following way: The recursion expansion coefficients [denoted a_n ($n = 0, 1, 2, \ldots$) and b_n ($n = 1, 2, 3, \ldots$) for the on-site and hopping elements, respectively] converge in the limit of n going to infinity to values determined by the upper (ε_+) and lower (ε_-) band edges,

$$a_n \rightarrow \tfrac{1}{2}(\varepsilon_+ + \varepsilon_-), \tag{33}$$

$$b_n \rightarrow \tfrac{1}{4}(\varepsilon_+ - \varepsilon_-). \tag{34}$$

The convergence to these limiting values goes as $1/n^2$ in a three-dimensional ordered system,[32] and the terminator we use is defined to interpolate between the second level values a_1 and b_2, and the bulk fcc values using this $1/n^2$ form.

It should be pointed out that in the fourth-moment approximation, EMT_3, the calculation of the one-electron energy involves only paths in the lattice with up to four legs connecting nearest-neighbor atoms, so only information about the surroundings of an atom up to a distance of two nearest-neighbor distances is used.

The kinetic-energy estimates in the EMT_2 and EMT_3 approximations for the surfaces and the vacancy are shown in Table IV. The inclusion of the one-electron correction leads to a clear improvement over the EMT_1 approximation in comparison with the Harris results.

The resulting surface and vacancy energies calculated in the EMT_2 and EMT_3 approximations are shown in Table I. It is seen that the one-electron energy leads to a decrease in the surface energy of a few tenths of an eV, and the resulting surface energies are in good agreement with the ones obtained by the Harris calculation. The results of the complete diagonalization (EMT_2) and the fourth-moment approximation (EMT_3) are also very close to each other for the surfaces, indicating that the information from only two neighbor shells of a given atom is sufficient to give a reasonable estimate of the one-electron energy correction for a surface.

Even though the one-electron correction is quite small for the the atoms around a vacancy, it adds up to a substantial correction to the vacancy formation energy of the order 0.6 eV. This perhaps unexpectedly large correction comes about as a sum of 12 contributions from the 12 atoms which are neighbors to the vacancy. For each of these atoms the correction is therefore only of the order 0.05 eV, which is not unreasonable compared to the correction of about 0.2 eV for a surface atom. The resulting vacancy formation energies are in reasonable agreement with the result of the Harris calculation.

IV. THE MOST APPROXIMATE LEVEL: CONNECTION TO THE USUAL EFFECTIVE-MEDIUM THEORY

The whole philosophy of the approach outlined above is that of the effective-medium theory.[3,4,8] The main idea is to find a reference system — an effective medium — in which the energy of a given atom can be calculated readily, but is still sufficiently similar to the surroundings of the atom in the real system that the difference between the energy in the real and the reference systems can be calculated in low-order perturbation theory.

Usually, the effective medium has been chosen to be a homogeneous electron gas, but other effective mediums have been used, including a fcc crystal of the atom in question.[9,33,34] The total-energy expression in the usual effective-medium theory has the form[8]

$$E = \sum_i E_{c,i}(\bar{n}_i) + \Delta E_{AS} + \Delta E_{1\,\mathrm{el}}, \tag{35}$$

where the first term on the right-hand side is the cohesive function which, like in Eq.(7), is the energy of atom i in the reference system. The second term is the so-called atomic-sphere correction and the last is the one-electron energy correction. The latter is exactly $\sum_i \Delta\varepsilon$ from Eq. (25), and ΔE_{AS} can thus be associted with $\Delta G + \sum_i \Delta v_i$ from Eqs. (7) and (25).

The main aspect of the present treatment is twofold. Firstly, *all* terms are calculated *ab initio*, that is there is no fitting to experimental or calculated results. Secondly, ΔE_{AS} in the usual effective-medium theory has always been calculated assuming that it could be written as the difference between a sum of pair interactions in the real and the reference systems. If the reference system is a fcc lattice of the atom in question where each atom has 12 nearest neighbors, then in a nearest-neighbor description ΔE_{AS} has been written as

$$\Delta E_{AS} = \sum_i \left[\sum_{j \neq i} V(r_{ij}) - 12 V(r_{\mathrm{fcc}}(\bar{n}_i)) \right] . \tag{36}$$

Here $V(r)$ is the pair potential, and $r_{\mathrm{fcc}}(\bar{n}_i)$ is the nearest-neighbor distance in the reference fcc lattice corresponding to the average density $\bar{n}_i$ of atom i. We thus obtain the old effective-medium theory by assuming the functional form Eq. (36) for $\Delta G + \sum_i \Delta v_i$. It turns out that this is a reasonable, but far from exact, approximation to the real situation.

The most approximate level, which is equivalent to the usual effective-medium theory, and thereby mathematically similar to other methods like the embedded-atom method,[5] the Finnis-Sinclair method,[6] or the glue model,[7] thus consists in approximating $\Delta G + \sum_i \Delta v_i$ as a difference between pairwise interactions.

It is worth pointing out that the largest one-electron correction $\Delta\varepsilon$ is found for the vacancy formation energy. Since $\Delta\varepsilon$ is intrinsically *not* a pair interaction, one therefore cannot expect to be able to reproduce both the vacancy formation energy and the surface energies in a semiempirical theory that does not include the one-electron correction. Consequently, if the potential is fitted to give the correct vacancy formation energy as with the embedded-atom method, for instance, the surface-energy will be underestimated and vice versa. This explains why, in these approaches, it has never been possible to get surface energies that are large enough. This does not mean that surface-energy differences are necessarily calculated incorrectly (cf. the constancy of the one-electron correction in Table IV), so calculations of reconstruction energies and other energy differences may still be very accurate.

The focus on a nonpairwise description of the exchange-correlation contribution to Δg and the kinetic-energy difference Δt has been introduced previously in the so-called corrected effective-medium theory (CEM).[9] The approach taken in the present work both in terms of the density ansatz and the treatment of Δt is, however, different compared to the CEM: these authors use a free-atom density ansatz, whereas we stress the importance of using a screened optimized density. Indeed, if one uses the free-atom density as an input to the Harris functional, the surface energies come out completely wrong.[16–18] This may not be a problem in the CEM since other terms in the energy expression are adjusted with this density. Secondly, in the CEM, the kinetic-energy difference is estimated without referring to the one-electron spectrum as is done in the present work.

V. CONCLUSIONS

We have developed a theory of bonding in a solid which consists of a series of approximations. The basis of the approach is the effective-medium idea in which the total energy of an atom in some general configuration is calculated by referring it to a situation which is similar but calculationally simpler, and then treating the difference between the real system and the reference system or effective medium in low-order perturbation theory.

At the highest level of accuracy in the hierarchy of approximations that has been developed, we have devised a method for decomposing the self-consistent electron density for a solid into an atomlike electron density. This optimized density is universal and transferable to the extent that it can be used in conjunction with the Harris functional to give very accurate total energies without a self-consistent calculation for a series of tried configurations.

At the next level, we introduce the effective medium and thus have a method that does not require the solution of an eigenvalue problem to determine the kinetic energy, but is still accurate enough to give meaningful results. As in the previous level of approximation, everything is calculated from the input density and we can therefore test every aspect of the theory in detail. When the one-electron energy correction is included — even in a simple fourth-moment expansion — results in almost quantitative agreement with the full Harris or self-consistent calculations are obtained.

At the lowest level, we have a theory which is equivalent to the usual effective-medium theory and thus mathematically similar to such semiempirical methods as the embedded-atom method,[5] the Finnis-Sinclair method,[6] or the glue model.[7]

ACKNOWLEDGMENTS

We are grateful to K. Kunc, O.H. Nielsen, R.J. Needs, and R.M. Martin whose solid-state programs we have used, and to E.L. Shirley who developed the pseudopotential routines. We are thankful to Lars Hansen and H. Skriver for many useful discussions.This work was in part supported by the Danish Research Councils through the Center for Surface Reactivity.

APPENDIX: PARAMETRIZATION OF OPTIMIZED DENSITY

We have

$$\Delta n_{\mathrm{op}}(k) = \Delta n_{\mathrm{atom}}(k) + a_1 k^2 (k - a_2)(k - a_3) \times \exp(a_4 k - a_5 k^2), \qquad \text{(A1)}$$

where $a_1 = 0.497, a_2 = 1.174, a_3 = 2.237, a_4 = 0.950, a_5 = 1.032$.

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