Intra-atomic correlation energies in cubic metals with canonical d bands

P. Thalmeier and L. M. Falicov

Department of Physics, University of California, Berkeley, California 94720

(Received 4 June 1979)

A calculation of the intra-atomic d-band correlation energies on the basis of a Hubbard interaction between d electrons is presented. The calculations are performed for canonical d bands in the face-centered and body-centered cubic structures. It is shown that using a single-particle approximation of the ground state, the correlation energy can be represented as a function of the occupation numbers of the five canonical subbands. The correlation energies are calculated as a function of the average number of d electrons. It is shown that the results are very different from Friedel's simple model of correlation energies which neglects band-structure effects.

I. INTRODUCTION

There are mainly two methods for dealing with the problem of correlation energies due to electron-electron interactions in d-electron metals. The first one, well known as the density functional (DF) formalism[1] and its extension, the spin-density functional (SDF) formalism[2] show that the contribution of electron-electron interaction to the ground-state energy of an inhomogeneous electron gas can exactly be expressed as a functional of the electron density (spin-density matrix for SDF). In order to make quantitative calculations, however, one is forced to assume that the exchange and correlation functional is local in the density. For nontransition metals this approach is very successful in explaining the ground-state properties. For transition metals, with their highly localized d orbitals and hence strong variations in the d-electron density, it is more questionable whether it represents an equally satisfactory theory. The second and older method puts more emphasis on the localized nature of the d electrons: in the Hubbard model[3,4] it is assumed that the electronic Coulomb interaction can be replaced by a "Hubbard" interaction which contains only interactions of d electrons that occupy Wannier states at the same atomic site. However, most of the quantitative calculations in this case have been restricted to unrealistic model calculations with the d band replaced by a single s band.

In this work we want a more realistic approach. We will calculate the intra-atomic correlation energy of d electrons whose interaction is described by the Hubbard Hamiltonian and which are assumed to be in a ground state described by the canonical d bands of Andersen *et al.*[5-7] We present this correlation energy as a function of the average number of d electrons and for the two cubic structures, the face-centered (fcc) and the body-centered (bcc) ones. The assumption of a one-electron ground-state im-

plies that this calculation is meaningful only in the case where the Hubbard interaction parameter U is smaller than the d-band width W. Our calculations can be considered as a quantitative extension of Friedel's old qualitative estimations[8,9] of intra-atomic correlation energies which do not take into account band-structure effects.

In Sec. II we present a short review of canonical d bands. Section III defines our model and describes the calculation of the correlation energy. In Sec. IV results are presented and Sec. V gives the conclusions.

II. CANONICAL BANDS AND DENSITY OF STATES

In our approach to calculate the intra-atomic correlation energy we have to start from single-particle states for the d electrons. We want to do the calculation for the complete $3d$ transition-metal series in a simplified way so that the correlation energy, except for a scaling factor U, depends only on the relevant crystal structure and the number of electrons in the d band. In order to achieve this we need to have a d-band structure whose overall shape depends only on the crystal structure and not on the valence of the particular element. Tight-binding schemes, like the one employed by Asdente and collaborators,[10,11] have the disadvantage of requiring at least four parameters (one splitting and three overlaps). Therefore our natural choice is to use the scheme developed by Andersen and collaborators[5,7] in which single-parameter canonical band structures were obtained. In this general band theory of transition metals Andersen has shown that the energy bands in closely packed crystals can be constructed by using canonical bands that depend only on the structure. They already contain the main topological features of the real bands which are easily obtained by specifying certain "potential

functions" for every type (s,p,d, etc.) of band. In our calculations we will neglect the effect of the s-d hybridization on the band structure and simply assume that the presence of a wide s band leads to a nonintegral number of electrons in the narrow and more correlated d bands.

We describe only the calculations for fcc and bcc structures, which have only one atom per unit cell and correspond to symmorphic space groups. The other common structure in transition metals, the hexagonal close packed, contains two atoms per cell and the nonsymmorphic character of the group makes determination of single-atom occupations much more difficult.

All the information we need is contained in the canonical structure matrix for the d band

$$S_{m'm}(\vec{k}) = \sum_{\vec{R} \neq 0} \exp(i\vec{k} \cdot \vec{R}) S_{m'm}(\vec{R}) \ . \qquad (2.1)$$

Here m,m' denote each of the five possible d states, $\vec{k}$ is a wave vector in the first Brillouin zone, and the summation runs over all lattice vectors of the first, second, and third nearest-neighbor shells. The structure matrix S in real space is given by

$$S_{m'm}(\vec{R}) = g_{m'm}(4\pi)^{1/2} Y_{4\mu}^{*}(\hat{R})(R/s)^{-5} \ , \qquad (2.2)$$

where

$$g_{m'm} = (-1)^{m+1}$$

$$\times \frac{10}{3} \left[\frac{(4+\mu)!(4-\mu)!}{(2+m')!(2-m')!(2+m)!(2-m)!} \right]^{1/2} ,$$

$$(2.3)$$

$\mu = m' - m$, $\hat{R} = \vec{R}/R$, and $s = (3\Omega_p/4\pi)^{1/3}$ is the Wigner-Seitz radius of the unit cell with Ω_p the primitive unit-cell volume. From Eq. (2.1) the canonical d-band energies can be obtained by simple diagonalization. If we denote the eigenvalues of Eq. (2.1) by $S_m(\vec{k})$, the d-band energies $E(\vec{k})$ of a specific transition metal are obtained by the scaling procedure

$$S_m(\vec{k}) = P(E) \ . \qquad (2.4)$$

Here P is the potential function for the d band. It is monotonically increasing and depends on the specific d metal under consideration. In the case of narrow d bands, the potential function will vary slowly over the width of the band and we can approximate it simply by a linear function of E

$$P(E) = (E - C_0)S_0/W(n) \ . \qquad (2.5)$$

Here S_0 is a dimensionless constant and denotes the width of the canonical band; $W(n)$ is the actual bandwidth in eV of a specific metal characterized by

an average number n of d electrons; and C_0 is the center of gravity for the d band. In the linear approximation for $P(E)$ these canonical bands can also be expressed in the familiar tight-binding language.[5-7,10,11] In this case the canonical structure matrix is proportional to an effective tight-binding Hamiltonian in the two-center approximation. If $U_{mm'}(\vec{k})$, considered as a matrix, is the m component of the m' eigenvector ($m,m' = 1,2,3,4,5$), then the d-band Bloch functions can be expressed as

$$\Psi_m(\vec{k},\vec{r}) = \sum_{m'} U_{mm'}(\vec{k}) \phi_{m'}(\vec{k},\vec{r}) \ , \qquad (2.6)$$

where $\phi_m(\vec{k},\vec{r})$ are suitable linear combinations of atomic orbitals.

As we will see later on, the calculation of correlation energies requires the knowledge of the occupancy of each individual d spin band $\nu (1 \leq \nu \leq 10)$ for a given Fermi energy. The band index ν labels the d bands according to increasing energy, i.e., $E_{1\vec{k}} \leq E_{2\vec{k}} \cdots \leq E_{10\vec{k}}$ for each $\vec{k}$ in the Brillouin zone. It is well known that this is identical to the analytical continuation scheme in which bands are defined by starting from any $\vec{k}$ point without degeneracy and analytically (e.g., with $\vec{k} \cdot \vec{p}$ perturbation theory) continuing to any other $\vec{k}$ points explicitly avoiding points or lines of degeneracy. The partial densities of states (PDOS) of these ordered bands are given by

$$D_\nu(E) = \frac{\Omega}{(2\pi)^3} \int_{E_{\nu\vec{k}}=E} |\vec{\nabla} E_{\nu\vec{k}}|^{-1} dS_E \ , \qquad (2.7)$$

where $\Omega = N\Omega_p$ is the crystal volume and S_E a constant energy surface. The total density of states (DOS) is simply the sum of the individual subband contributions

$$D(E) = \sum_{\nu=1}^{10} D_\nu(E) \ . \qquad (2.8)$$

The PDOS functions for bcc and fcc are shown in Figs. 1 and 2. Since we are dealing with the paramagnetic state, the ten spin bands coalesce into five pairs of subbands.

Main peaks in each of the five d subbands are clearly visible. For this calculation and all subsequent similar calculations we sampled the Brillouin zone by means of the tetrahedron method, described in Refs. 12 and 13, with a mesh of 1111 and 3333 microtetrahedra for bcc and fcc, respectively.

We also need the integrated PDOS, that is the partial number of states, $n_\nu(E_F)$, defined for each subband by

$$n_\nu(E_F) = \int_{-\infty}^{E_F} D_\nu(E) \, dE$$

$$= \frac{\Omega}{(2\pi)^3} \int_{-\infty}^{E_F} \Theta(E_F - E_{\nu\vec{k}}) \, d^3k \ . \qquad (2.9)$$

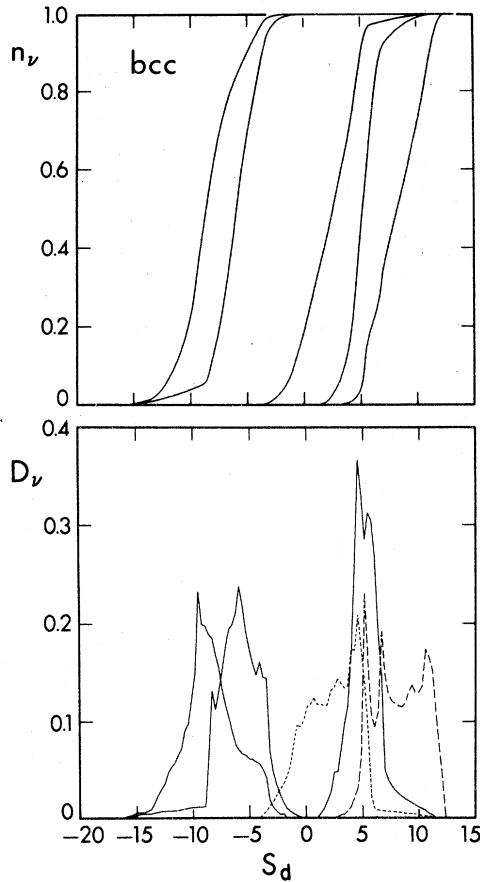For every subband ν, $n_\nu(E_F)$ is a monotonically in-

FIG. 1. Lower diagram: partial densities of states for the bcc canonical d bands. Upper diagram: integrated partial densities of states. The abscissas are the structure constant S_d, which is related to the Fermi energy by the linear transformation $E_F = S_d(W/28.5)$, where W is the bandwidth.
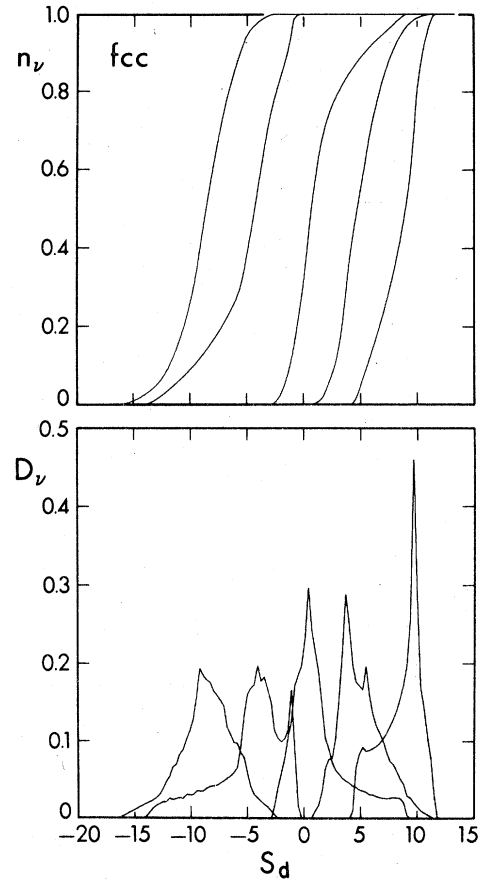
FIG. 2. Lower diagram: partial densities of state for the fcc canonical d bands. Upper diagram: integrated partial densities of state. The Fermi energy E_F is a linear function of S_d, the structure constant of the absicssas: $E_F = SC$ $\times (W/27.6)$, where W is the bandwidth.

creasing function with values between 0 and 1. Rather than performing the integration numerically over the PDOS, it is more accurate to integrate the individual contributions of every microtetrahedron and sum the integrated values.[13] The results of this calculation are shown in Figs. 1 and 2 for bcc and fcc, respectively. We note that for bcc the five subbands separate into two lower bands which have e_g-type symmetry at the center of the Brillouin zone Γ, and three upper bands of t_{2g}-type symmetry at Γ. The gap between the two groups of subbands can of course also be seen in the density of states.[7] For fcc, this e_g-t_{2g} separation is still present but is less pronounced than in bcc. The total number of states, $n(E_F)$, equal to the number of electrons in the d band determines the value of the Fermi level E_F

$$n(E_F) \equiv \sum_{\nu=1}^{10} n_\nu(E_F) = n \quad . \tag{2.10}$$

The monotonically increasing function $n(E_F)$ is

shown in Ref. 7 for the different structures. With the aid of Eq. (2.10) any function of the Fermi energy can easily be transformed into a function of the number of d electrons.

III. INTRA-ATOMIC CORRELATION ENERGY IN HUBBARD'S MODEL

A. Multiband Hubbard model

We assume that the Coulomb interaction between $3d$ electrons in a metal with a narrow d band is well described by the Hubbard Hamiltonian.[3,4] This Hamiltonian takes into account only interactions of electrons localized at the same lattice site. As a basis for the localized d states we take the Wannier functions defined by

$$w_n(\vec{r} - \vec{R}_i) = N^{-1/2} \sum_{\vec{k}} \exp(-i\vec{k} \cdot \vec{R}_i)\psi_n(\vec{k}, \vec{r}) \quad , \tag{3.1}$$

where R_i is the lattice site and $\psi_n(\vec{k}, \vec{r})$ is the Bloch function corresponding to the canonical subband $E_n(\vec{k})$. Because all the subbands are connected at points or along lines of degeneracy, the Bloch functions in Eq. (3.1) exhibit singularities at these degeneracies. Consequently the Wannier functions will not decay exponentially around their relevant sites but rather have tails decaying with a power-law behavior. However this problem can be controlled as shown in Refs. 14 and 15. Since we need the Wannier functions only for formal arguments, we will not discuss this further. In general the Wannier states defined by Eq. (3.1) have no definite symmetry. However it has been shown[15] that the freedom in choosing a phase factor for the Bloch functions can be used to give the Wannier orbitals a definite symmetry character. In fact an appropriate choice for the phase factor leads to Wannier orbitals which are one-dimensional representations of the point group of the crystal.

If the creation and destruction operators of Wannier states are denoted by $a_{\nu i}^\dagger$ and $a_{\nu i}$ the Hamiltonian for the d electrons reads

$$\mathcal{H} = T + V_c \quad , \tag{3.2}$$

$$T = \sum_{ij, \nu} T_{\nu ij} a_{\nu i}^\dagger a_{\nu j} \quad , \tag{3.3}$$

$$V_c = \frac{1}{2} U \sum_{i \nu \nu'} a_{\nu i}^\dagger a_{\nu' i}^\dagger a_{\nu' i} a_{\nu i} \quad . \tag{3.4}$$

Here T is the one-electron band energy in the Wannier representation, which we will not need explicitly in the following; V_c describes the electron repulsion in Hubbard's approximation, (ij) denote lattice sites, $(\nu \nu')$ denote one of the ten d-band spin states. The occupation number operators for these states are defined by

$$\hat{n}_{\nu i} = a_{\nu i}^\dagger a_{\nu i}, \quad \hat{n}_i = \sum_\nu \hat{n}_{\nu i} \quad . \tag{3.5}$$

With this definition and the anticommutation rules for Fermi operators, the interaction can be written

$$V_c = \frac{1}{2} U \sum_i \hat{n}_i (\hat{n}_i - 1) \quad . \tag{3.6}$$

B. Correlation energy

According to Eq. (3.2), the total ground-state energy of the d-electron system is given by

$$E_{gs}(n) = \langle T \rangle + \langle V_c \rangle \quad , \tag{3.7}$$

where the angular brackets denote the expectation value with respect to the ground state. This can be split into

$$E_{gs}(n) = E_0(n) + E_B(n) + E_c(n) \quad , \tag{3.8}$$

where

$$E_0(n) \equiv NC_0 n + V_{c0} = N[C_0 n + \frac{1}{2} U n (n-1)] \quad , \tag{3.9}$$

$$E_B(n) = \langle T \rangle - NC_0 n \quad , \tag{3.10}$$

$$E_c(n) = \langle V_c \rangle - V_{c0} \quad . \tag{3.11}$$

Here $E_0(n)$ denotes the sum of the atomic configuration energies of isolated d atoms: $V_{c0} \equiv \frac{1}{2} NUn(n-1)$ is the mean atomic interaction energy and C_0 is a negative constant so that the configuration energy is described by a quadratic function of n. This parabola defines our zero energy level for any number of d electrons, and all energies will be measured relative to this zero level in what follows. In the other two terms of Eq. (3.8), $E_B(n)$ is the total band energy and $E_c(n)$ is the total correlation energy in the d bands. In the atomic limit, when $T_{\nu ij} = C_0 \delta_{ij}$ in Eq. (3.3), both $E_B(n)$ and $E_c(n)$ vanish. For finite hopping elements $T_{\nu ij}$, $E_B(n)$ will be different from zero due to the d-band dispersion and $E_c(n)$ is nonzero because hopping processes lead to fluctuations in the number of d electrons in a given site, i.e., in this case the number of d electrons on a given site is no longer equal to a well-defined integral number but has to be described by a probability distribution around its mean value $\underline{x}$. In fact, the use of Eq. (3.5) and $n = \langle n_i \rangle$ yield

$$E_c(n) = \frac{1}{2} U \sum_i (\langle \hat{n}_i^2 \rangle - \langle \hat{n}_i \rangle^2) = \frac{1}{2} NU \sigma^2(n) \quad . \tag{3.12}$$

Therefore the correlation energy is simply proportional to σ^2, the square of the standard deviation for the probability distribution of the number of d electrons at a given site.

From Eq. (3.12) it is obvious that the energy $E_c(n)$ is minimized by choosing a ground state with a fixed number of electrons per site and allowing no fluctuations. Such a state however cannot minimize the band energy term (3.10) unless we have a full or empty d band, or the various subbands, either completely full or completely empty, are nonoverlapping.

An upper bound for this correlation can be obtained by means of a single determinantal wave function $|\phi_0\rangle$, which minimizes Eq. (3.10). This will overestimate the intra-atomic interaction energy because of the inherent large fluctuations $\sigma(n)$ attached to it. We will now prove that the calculation of $E_c(n)$ with $|\phi_0\rangle$ can be easily accomplished if we know the integrated PDOS functions $n_\nu(E_F)$ defined in Eq. (2.10). We first write $|\phi_0\rangle$ as a single antisymmetrized product of single-particle Bloch states

$$|\phi_0\rangle = \prod_{\substack{\nu, \vec{k} \\ E_{\nu \vec{k}} \leq E_F}} c_{\nu \vec{k}}^\dagger |0\rangle \quad . \tag{3.13}$$

Here $c_{\nu \vec{k}}^\dagger$ ($c_{\nu \vec{k}}$) are creation (destruction) operators

for a Bloch state with wave vector $\vec{k}$ and band index ν. They are connected to the Wannier operators $a_{\nu i}^\dagger$ ($a_{\nu i}$) via transformation (3.1)

$$a_{\nu i} = N^{-1/2} \sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_i) c_{\nu\vec{k}} \ . \tag{3.14}$$

To calculate for any operator $A(\hat{n}_i)$ the expectation value $\langle A \rangle \equiv \langle \phi_0 | A | \phi_0 \rangle$, we perform a Fourier transformation for the number operators:

$$\hat{n}_{\nu\vec{q}} = N^{-1/2} \sum_i \exp(i\vec{q}\cdot\vec{R}_i) \hat{n}_{\nu i} \ ,$$
$$\hat{n}_{\vec{q}} = \sum_\nu \hat{n}_{\nu\vec{q}} \ . \tag{3.15}$$

By means of Eq. (3.14) it is easy to show that

$$\hat{n}_{\nu\vec{q}} = N^{-1/2} \sum_{\vec{k}} c_{\nu\vec{k}}^\dagger c_{\nu(\vec{k}+\vec{q})} \tag{3.16}$$

and the use of Eqs. (3.15) and (3.12) yields

$$E_c(n) = \tfrac{1}{2} U \sum_{\vec{q}} (\langle \hat{n}_{\vec{q}}\hat{n}_{-\vec{q}} \rangle - \langle \hat{n}_{\vec{q}} \rangle \langle \hat{n}_{-\vec{q}} \rangle) \ . \tag{3.17}$$

Finally, since

$$\langle c_{\nu\vec{k}}^\dagger c_{\nu(\vec{k}+\vec{q})} \rangle = 0 \quad \text{for } \vec{q} \neq 0 \ , \tag{3.18}$$

we find

$$\langle \hat{n}_q \rangle = N^{-1/2}\delta_{\vec{q},0} \sum_{\nu,\vec{k}} \langle c_{\nu\vec{k}}^\dagger c_{\nu\vec{k}} \rangle \ . \tag{3.19}$$

In addition

$$N^{-1} \sum_{\vec{k}} \langle c_{\nu\vec{k}}^\dagger c_{\nu\vec{k}} \rangle = N^{-1} \sum_{\vec{k}} \Theta(E_F - E_{\nu\vec{k}})$$
$$= n_\nu(E_F) \ . \tag{3.20}$$

Consequently

$$\langle \hat{n}_{\vec{q}} \rangle = \langle \hat{n}_{-\vec{q}} \rangle = N^{1/2}\delta_{\vec{q},0} n(E_F) \ . \tag{3.21}$$

For the first term in Eq. (3.17) we use

$$\hat{n}_{\vec{q}}\hat{n}_{-\vec{q}} = \sum_{\nu\nu'} \hat{n}_{\nu\vec{q}}\hat{n}_{\nu'(-\vec{q})} = N^{-1} \sum_{\nu\vec{k},\nu'\vec{k}'} c_{\nu\vec{k}}^\dagger c_{\nu(\vec{k}+\vec{q})} c_{\nu'\vec{k}'}^\dagger c_{\nu'(\vec{k}'-\vec{q})} \ , \tag{3.22}$$

which, by standard use of anticommutation rules, yields

$$\langle \hat{n}_{\vec{q}}\hat{n}_{-\vec{q}} \rangle = N^{-1} \sum_{\nu\vec{k}} \langle c_{\nu\vec{k}}^\dagger c_{\nu\vec{k}} \rangle - N^{-1} \sum_{\nu\vec{k}} \langle c_{\nu\vec{k}}^\dagger c_{\nu\vec{k}} \rangle \langle c_{\nu(\vec{k}+\vec{q})}^\dagger c_{\nu(\vec{k}+\vec{q})} \rangle + N^{-1} \sum_{\nu\vec{k},\nu'\vec{k}'} \langle c_{\nu\vec{k}}^\dagger c_{\nu\vec{k}} \rangle \langle c_{\nu'\vec{k}'}^\dagger c_{\nu'\vec{k}'} \rangle \delta_{\vec{q},0} \ , \tag{3.23}$$

from which we finally obtain

$$E_c(n) = \tfrac{1}{2} NU \sum_\nu n_\nu(E_F)[1 - n_\nu(E_F)] \ . \tag{3.24}$$

Hence we find that the total correlation energy can be expressed as a sum of individual subband contributions, each of them having a quadratic dependence as a function of the integrated PDOS, $n_\nu(E_F)$. The contribution of a subband ν to E_c vanishes if $n_\nu = 0$ or $n_\nu = 1$, i.e., if the subband is either empty or completely filled, as one intuitively expects. It reaches a maximum of $\tfrac{1}{8}NU$ per spin band in the half-filled case, i.e., for $n_\nu = \tfrac{1}{2}$. Because $n_\nu(E_F)$ is an implicit function of n according to Eq. (2.10), E_c can be considered a function of n for the canonical bands. For completeness we also give the expression for the band energy $E_B(n)$

$$E_B(n) = \int_{-\infty}^{E_F} D(E)(E - C_0) dE \ , \tag{3.25}$$

where the density of states has been defined in Eqs. (2.7) and (2.8). It is instructive to discuss our fundamental formula (3.24) for two especially simple cases. In the first one let us assume that all ten d subbands are completely degenerate, i.e.,

$$E_{\nu\vec{k}} = E_{\vec{k}}, \quad n_\nu(E_F) = n/10 \quad \text{for all } \nu \ . \tag{3.26}$$

This leads to a correlation energy

$$E_{c1}(n) = \tfrac{1}{2} NUn(1 - \tfrac{1}{10}n), \quad E_{c1}(\max) = 1.25 NU \ . \tag{3.27}$$

This case corresponds essentially to Friedel's model,[8,9] and it is characterized by a binomial probability distribution for the number of d electrons at a given site. Comparison of Eqs. (3.25) and (3.11) yields $\sigma_1^2(n) = n(1 - 0.1n)$. This is indeed the square of the standard deviation for a binomial distribution function; $E_{c1}(n)$ has a simple parabolic shape as function of n. In the second, complementary case we consider d subbands that are completely separate in pairs (subbands which differ only in spin direction are still considered to be fully degenerate.) For a given number of electrons per site define $R(n) = \tfrac{1}{2}(n - n_0)$ where n_0 is the largest even integer smaller than n. Then we obtain

$$E_{c2}(n) = NUR(n)[1 - R(n)] \ , \tag{3.28}$$

$$E_{c2}(\max) = 0.25 NU \ .$$

Obviously this correlation energy is periodic in n with period 2. Comparison of Eqs. (3.27) and (3.28) shows that the maximum possible correlation energies differ by a factor of 5, the number of different spin band pairs. For a real band structure the situation is intermediate between the extreme cases discussed above. There will be an overlap between the subbands or groups of them which however, cannot be complete as in the degenerate case. Hence the following inequality for $E_c(n)$ of a real d band will be valid

$$E_{c1}(n) \leq E_c(n) \leq E_{c2}(n) \quad \text{for } 0 \leq n \leq 10 \ . \qquad (3.29)$$

With the values of $n_v(E_F)$ given in Sec. II, we can now calculate the correlation energy for a canonical d band, according to Eq. (3.24).

IV. RESULTS FOR THE CUBIC STRUCTURES

From the above considerations it is clear that the amount of intra-atomic correlation energy inherent in a certain band structure depends on how many of the spin band pairs are partially filled (or empty) at a given Fermi energy or equivalently at a given total number of electrons/atoms. The more bands are partially filled, the bigger the on-site fluctuation of d-electron numbers and hence the bigger the correlation energy will be. Every degenerate spin band pair can contribute a maximum amount of $0.25 U$ to the correlation energy.

We first discuss the bcc structure. As mentioned in Sec. II (see Fig. 1) the five d-subbands are separated into two groups of two subbands at lower energy and three subbands at higher energy. The overlap between the two groups of subbands is very small. Hence we expect maxima in the correlation energy when the Fermi level lies approximately in the middle of one of the groups and a pronounced minimum when the Fermi level lies in between the two groups. This is confirmed by the results of Fig. 3, which show maxima of the bcc correlation energy at $n \simeq 2.5$ and $n \simeq 7.5$. A sharp minimum in the correlation energy is observed at $n = 4$ where the lower four spin bands are completely filled and the upper group of six spin bands is still empty. Both maxima correspond to a correlation energy of about $0.4 U$. One might have expected that the second maximum at $n \simeq 7.5$ could be larger than the first one at $n \simeq 2.5$ because in the higher group there are three subbands which could be partially filled, but only two in the lower group. However, close inspection of Fig. 1 shows that the subband distance in the higher group is so large that effectively only two subbands can be partially filled for a given n, the remaining one has to be completely filled or empty. Therefore the height of the second maximum is similar to the first
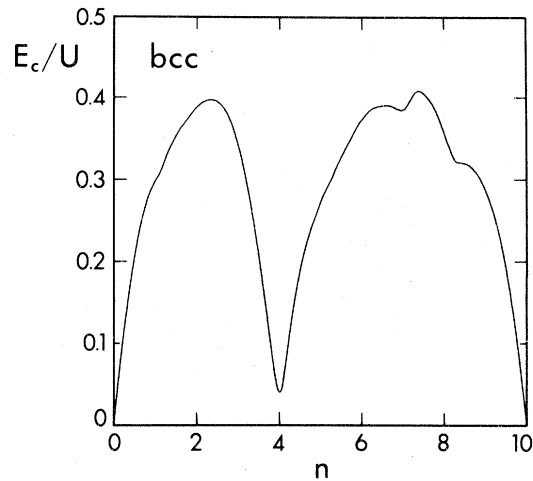

FIG. 3. Correlation energy for the bcc structure in units of U as a function of d-band occupation number n.

one. Because of the relatively large spacing between subbands in the second group, three structures in the correlation energy, which are due to individual subbands, can be clearly seen in the range $6 < n < 10$.

For the fcc case (Fig. 4) the overall behavior of the correlation energy looks similar to the bcc curve, although the details are somewhat different. Especially the minimum at $n = 4$ is less pronounced. This is because the separation between the two groups of subbands is smaller in the fcc structure than in the bcc case. We can again identify smaller structures arising from contributions of individual subbands. For example the small maximum at $n = 5$ is caused by the first subband of the second group. The height of the two maxima is not very different either from each other in the two cases or as compared between
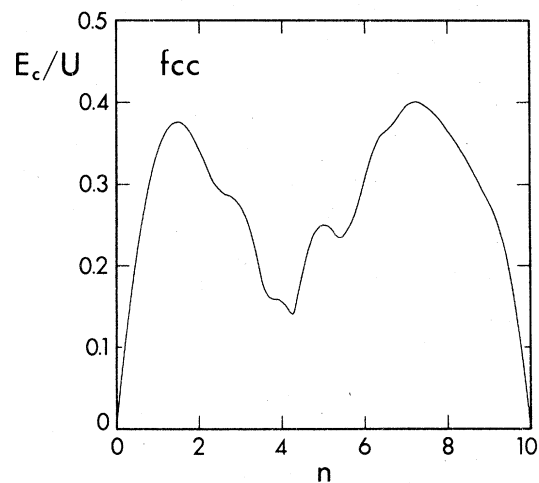

FIG. 4. Correlation energy for the fcc structure in units of U as a function of d-band occupation number n.

the fcc and bcc structures. The maximum value we
have calculated, $E_c(\max)/N \sim 0.4\,U$, is to be com-
pared with Friedel's maximum value of $1.25\,U$. Real
band-structure effects are thus responsible for
spreading out the d subbands and consequently they
reduce the interaction energy by approximately a fac-
tor of 3.

It is also instructive to look at the difference
$\Delta E_c(n)$ in the correlation energy between both cubic
structures (see Fig. 5). In regions with $\Delta E_c > 0$
($\Delta E_c < 0$) the correlation energy by itself would favor
bcc (fcc) structure. We can see that each structure is
favored by the correlation energy in roughly two in-
tervals. For $n > 8$ the two structures have approxi-
mately the same correlation energy. Of course which
kind of structure is actually preferred for a specific
number of d electrons is not determined by the corre-
lation energy alone but rather by the total ground-
state energy, i.e., the sum of band and correlation en-
ergies

$$E_t(n) = W(n)E_B'(n) + U(n)E_c'(n) \ . \qquad (4.1)$$

Here E_B' and E_c' are the band and correlation ener-
gies, in units of bandwidth $W(n)$ and on-site
Coulomb interaction $U(n)$, respectively. For any
specific d metal W, U can be determined by pho-
toelectron and Auger electron spectroscopy.[16] The
band energy $E_B'(n)$ has been already calculated in
Ref. 6. With our calculated correlation energy we
could now in principle discuss the question of relative
stability of the bcc and fcc structures as a function of
n and the parameter U/W. This is in fact an interest-
ing line for future investigations.

V. CONCLUSIONS

In our calculations we have shown that the intra-
atomic correlation energy in a d band with Hubbard
interactions is very different from the prediction of
the simple Friedel model which neglects band-
structure effects. On one hand the maximum value
of the correlation energy as a function of d-band oc-
cupation is reduced by approximately a factor of 3
with respect to Friedel's value. On the other hand it
has no longer a simple parabolic shape but rather
shows a two-peak structure due to the splitting of d
bands in e_g and t_{2g} symmetries of the cubic struc-
tures. Furthermore we have seen that the difference
of correlation energies between fcc and bcc structures
changes sign frequently as a function of d-band occu-
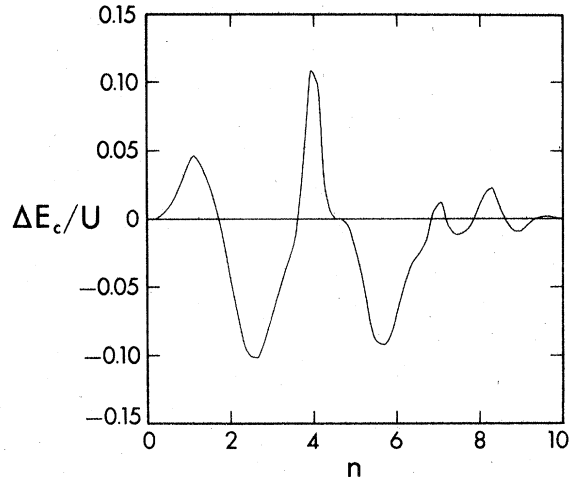

FIG. 5. Difference in the correlation energy of the fcc
and bcc structures. $\Delta E = E_c(\text{fcc}) - E_c(\text{bcc})$.

pation and hence the correlation energy alone would
prefer different structures for different d-electron oc-
cupation numbers.

Several extensions of our calculations are possible.
With the band energy calculated in Ref. 6 we can
determine the total ground-state energy and then one
definitely can consider the stability question for the
two cubic structures. Furthermore, by doing spin po-
larized calculations one can discuss the possibility of
a ferromagnetic ground state. In order to get rid of
our condition that the Hubbard parameter is appreci-
ably smaller than the bandwidth one could use a vari-
ational ground state for the calculation of band ener-
gy and correlation energy rather than the simple
determinantal state. In such a variational ground
state the components with large charge fluctuations
would be reduced, the reduction depending on a vari-
ational parameter which is determined by minimizing
the total ground-state energy. Such an approach has
been successfully used in calculations for finite Hub-
bard models[17] and could be also applicable to our
case.

[1]W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[2]O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274
    (1976).
[3]J. Hubbard, Proc. R. Soc. London Sect. A 276, 238 (1963).
[4]J. Hubbard, Proc. R. Soc. London Sect. A 277, 237 (1964).
[5]O. K. Andersen, Phys. Rev. B 12, 3060 (1975).

[6]A. R. Mackintosh and O. K. Andersen, in *Electrons in Metals*, (Festschrift for D. Shoenberg), edited by M. Springford (Cambridge University, Cambridge, England to be published).

[7]O. K. Andersen and O. Jepsen, Physica (Utrecht) B 91, 317 (1977).

[8]J. Friedel, Proc. Phys. Soc. London Sect. B 65, 769 (1952).

[9]J. Friedel, in *The Physics of Metals I. Electrons*, edited by J. M. Ziman (Cambridge University, Cambridge, England, 1969), p. 340.

[10]M. Asdente and J. Friedel, Phys. Rev. 124, 384 (1961).

[11]M. Asdente and M. D. Delitala, Phys. Rev. 163, 497 (1967).

[12]G. Lehmann, P. Rennert, M. Taut, and H. Wonn, Phys. Status Solidi 37, K27 (1970); G. Lehmann and M. Taut, *ibid.* 54, 469 (1972).

[13]O. Jepsen and O. K. Andersen, Solid State Commun. 9, 1763 (1977).

[14]E. I. Blount, Solid State Phys. 13, 305 (1962).

[15]G. Strinati, Phys. Rev. B 18, 4104 (1978).

[16]E. Antonides, C. E. Janse, and G. A. Sawatzky, Phys. Rev. B 15, 1669 (1977).

[17]G. Stollhoff and P. Fulde, Z. Phys. B 26, 257 (1977); B 29, 231 (1978).