

## Correlation effects in the cohesion and magnetic properties of transition metals

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The variational method of Stollhoff and Fulde is applied to a model Hamiltonian describing the  $d$  band of a transition metal to obtain the correlated ground state. The model used includes the Coulomb and exchange intra-atomic energies and is rotationally symmetric in orbital and spin space. The calculated cohesion energy has a minimum for a half-filled  $d$  band, which is connected with gradual localization of a magnetic moment in the presence of the Hund's-rule exchange interaction. At the same time the charge fluctuations are strongly suppressed and spin fluctuations enhanced. We have found a corrected Stoner criterion which gives a ferromagnetic ground state for realistic values of the model parameters for  $3d$  metals, and is in agreement with the exact result of Kanamori at very low electron and hole concentrations.

### I. INTRODUCTION

The dual nature of transition metals, which show both localized as well as itinerant properties, has been studied for many years. It is well known that the low-temperature specific heat, the susceptibility, and the transport properties are best understood within a band picture for partially filled  $d$  bands. On the other hand, it has been argued that such magnetic properties as hyperfine fields, the high-temperature Curie-like susceptibility, or existence of spin waves above the Curie temperature, indicate a more localized nature of the  $d$  electrons.<sup>1,2</sup>

Early treatments of correlations in transition metals dealt for simplicity with a one-band Hubbard model.<sup>3,4</sup> This model was very intensely studied over the last 16 years, but very few definite results were obtained (for a review see Ref. 5). The ground state was rigorously shown to be ferromagnetic for cubic lattices with almost one electron per atom and for infinite correlations.<sup>6</sup> It is therefore expected that a ferromagnetic ground state should exist for large enough correlations, and for not too low band filling, as also obtained in the spectral-density method.<sup>7</sup> But the model, as a one-band model, seems unrealistic for transition metals. The same holds true for the doubly degenerate Hubbard model,<sup>8</sup> which is useful for the understanding of some transition-metal compounds.

The second and complementary method, the spin-density-functional formalism,<sup>9</sup> is very useful in quantitative explanation of the ground-state properties of not only nontransition, but also transition metals. However, it does not allow us to get more insight into the nature of electronic states in transition metals, and does not help us to understand how the local

moments and magnetic properties do form in presence of the electron-electron interaction.

A model of a  $d$  band with its degeneracy fully included, which is more realistic for transition metals than the one-band or doubly degenerate Hubbard models, was considered by Friedel and Sayers who studied the role of  $d$ - $d$  correlations in the cohesion energy and stability of a ferromagnetic state.<sup>10</sup> Recent perturbation expansion of this model for the cubic lattices shows that the density of one-particle states is drastically changed in the presence of correlations for realistic values of the Coulomb interaction  $U$  and the bandwidth  $W$ .<sup>11</sup> In this paper we want to study in more detail the model of Friedel and Sayers,<sup>10</sup> which we solve in Sec. II with the help of a variational ansatz, analogous to that of Stollhoff and Fulde.<sup>12,13</sup> The variational ground state obtained in such a way allows for going beyond lowest-order perturbation theory in the calculation of the cohesion energy in Sec. III. Further, we give evidence for gradual localization of  $d$  electrons with increasing correlations and show how the Stoner criterion is changed (Sec. IV). The paper is summarized in Sec. V.

### II. LOCAL APPROACH TO CORRELATIONS IN A TRANSITION METAL

As Friedel and Sayers,<sup>10</sup> we restrict ourselves to a simplified picture of the  $d$  one-electron band, where all five  $d$  orbitals with different orbital moments ( $l = 2$  to  $-2$ ) are assumed equally populated at each energy. The total energy band is assumed symmetrical with respect to the atomic energy and rectangular, with the density of states for  $\sigma$ -spin electrons in  $i$ th

band

$$\rho_{l\sigma}(\omega) = \begin{cases} \frac{1}{W}, & \text{if } |\omega| \leq \frac{1}{2}W \\ 0, & \text{otherwise} \end{cases} \quad (2.1)$$

This density of states exhibits particle-hole symmetry, so in what follows we may limit ourselves to the less than or half-filled band case. Although a constant density of states may seem to be a rather crude approximation, it is not so as far as the influence of correlations is considered.<sup>14</sup>

Correlation between electrons is described by intra-atomic Coulomb and exchange interactions, i.e., by the most important local part. In fact, it is known for molecules that intra-atomic correlations are responsible for most of the correlation energy,<sup>12,13</sup> so this assumption should also be reasonable for a transition metal. The Coulomb interactions are characterized by the energy  $U_0$  when two electrons with opposite spins occupy the same  $d$  orbital, and  $U$  if they sit at the same site in two different orbitals while  $J$  is the exchange interaction (for electrons on different orbitals). These three energy parameters  $\{U_0, U, J\}$  are not independent. The orbital symmetry of the model Hamiltonian requires that  $U_0 = U + J$ , as has been discussed by Parmenter for the impurity problem,<sup>15</sup> and by Cyrot and Lyon-Caen in the degenerate Hubbard model.<sup>16</sup>

The model Hamiltonian used here for transition metals

$$H = \sum_{mn,i\sigma} t_{mn} a_{mi\sigma}^\dagger a_{ni\sigma} + (U + J) \sum_{mi} n_{mi\uparrow} n_{mi\downarrow} + (U - \frac{1}{2}J) \sum_{m,i < j; \sigma\sigma'} n_{mi\sigma} n_{mj\sigma'} - 2J \sum_{m,i < j} \vec{S}_{mi} \cdot \vec{S}_{mj}, \quad (2.2)$$

is completely symmetric in both spin and orbital subspaces.  $a_{mi\sigma}^\dagger$  ( $a_{mi\sigma}$ ) are creation (annihilation) operators of a  $\sigma$ -spin electron at orbital  $i$  ( $i = 1, \dots, 5$ ), and site  $m$  ( $m = 1, 2, \dots, N$ ).  $n_{mi}$  is a particle number operator ( $n_{mi\sigma} = a_{mi\sigma}^\dagger a_{mi\sigma}$ ), and  $\vec{S}_{mi} = (S_{mi}^+, S_{mi}^-, S_{mi}^z)$  is a spin operator, the components of which are related to electron operators in a usual way:  $S_{mi}^+ = a_{mi\uparrow}^\dagger a_{mi\downarrow}$ ,  $S_{mi}^- = a_{mi\downarrow}^\dagger a_{mi\uparrow}$ ,  $S_{mi}^z = \frac{1}{2}(n_{mi\uparrow} - n_{mi\downarrow})$ .

Let us calculate first charge and spin fluctuations, defined as

$$\sigma^2(n_m) = \langle n_m^2 \rangle - \langle n_m \rangle^2 \quad (2.3)$$

and

$$\sigma^2(S_m^z) = \langle (S_m^z)^2 \rangle - \langle S_m^z \rangle^2, \quad (2.4)$$

respectively, where

$$n_m = \sum_{i\sigma} n_{mi\sigma}, \quad S_m^z = \sum_i S_{mi}^z, \quad (2.5)$$

for exactly solvable limiting cases of the Hamiltonian Eq. (2.2). In the band limit ( $U = J = 0$ ) we get maximum of fluctuations in the number of particles

$$\sigma_B^2(n_m) = n(1 - \frac{1}{10}n) \quad (2.6)$$

and relatively small spin fluctuations

$$\sigma_B^2(S_m^z) = \frac{1}{4}n(1 - \frac{1}{10}n), \quad (2.7)$$

where  $n$  is the average number of electrons per site. In the opposite, atomic limit ( $t_{mn} = 0$ ), the  $d$  shell is built according to Hund's rule, as the exchange interaction  $J$  is positive ( $J > 0$ ). The energy per site is then

$$E_{AL} = \begin{cases} 0, & \text{if } n \leq 1 \\ \frac{1}{2}n(n-1)(U-J), & \text{if } 1 < n \leq 5 \end{cases} \quad (2.8)$$

There is no fluctuation in charge, and fluctuations in the  $z$ th spin component are just those of a free ion

$$\sigma_{AL}^2(S_m^z) = \frac{1}{2S+1} \sum_{l=-S}^S l^2, \quad (2.9)$$

where  $S = \frac{1}{2}n$  and  $n \leq 5$ . Thus we see that the actual values of charge and spin fluctuations contain information about degree of electron localization.

Unfortunately, an essential shortcoming of the Hartree-Fock approximation (HFA) is that it gives the band-limit values of charge and spin fluctuations Eqs. (2.6) and (2.7), independently of the values of  $U$  and  $J$ . Here we construct a more appropriate ground state of the Hamiltonian Eq. (2.2) by the local approach to correlations, which appeared to be very successful in the calculation of molecules.<sup>12,13</sup> The basic idea is that in the presence of correlations we expect that probabilities of such configurations of electrons in a solid, which have more correlation energy than the average for the actual filling, are reduced. Thus we propose the following ansatz for the correlated ground state  $|\Psi_C\rangle$

$$|\Psi_C\rangle = \prod_n (1 - \eta_n O_n) |\Phi_{HFA}\rangle, \quad (2.10)$$

where  $|\Phi_{HFA}\rangle$  is the HFA ground state, and any operator  $O_n$  can take one of the following three forms

$$O_n = \begin{cases} O_{mi}^{(1)} = n_{mi\uparrow} n_{mi\downarrow}, \\ O_{mij}^{(2)} = \sum_{\sigma\sigma'} n_{mi\sigma} n_{mj\sigma'}, \\ O_{mij}^{(3)} = \vec{S}_{mi} \cdot \vec{S}_{mj}. \end{cases} \quad (2.11)$$

$\eta_n$  are variational parameters to be found from minimization of the ground-state energy  $E_{GS}$ , which we normalize per one site

$$E_{GS} = \langle \Psi_C | H | \Psi_C \rangle / N \langle \Psi_C | \Psi_C \rangle . \quad (2.12)$$

$\langle \dots \rangle$  denotes the average over the HFA ground state. The projection operator  $P_{mi}^{(1)} = 1 - \eta_1 n_{mi\uparrow} n_{mi\downarrow}$  leads to a reduction of the probability amplitude of finding two electrons at the orbital  $i$  and site  $m$ . Similarly,  $\sum_{\sigma\sigma'} n_{mi\sigma} n_{mj\sigma'}$  introduces density correlations, while  $\bar{S}_{mi} \cdot \bar{S}_{mj}$  introduces spin correlations between different orbitals. For convenience we define the  $O_n$  operators as describing only the respective two-particle excitations, so  $\langle O_n \rangle = 0$ . When taking into account equivalence of lattice sites, we have essentially only three different  $\eta_n$ 's in the variational ground state Eq. (2.10): one ( $\eta_1$ ) for correlations within the same orbitals, one ( $\eta_2$ ) for the density correlations  $n_{mi\sigma} n_{mj\sigma'}$ , and one ( $\eta_3$ ) for the spin

correlations  $\bar{S}_{mi} \cdot \bar{S}_{mj}$ .

In the calculation of the ground-state energy  $E_{GS}$  we take into account only such terms in Eq. (2.12) which contain the operators  $O_n$  acting at the same site. This approximation is consistent with the method discussed in the Appendix and used in determining the needed averages. In the resulting expression for  $E_{GS}$  we keep only the terms up to second order in  $\eta_n$ , what is justified for not too strong correlations. The result may be written as

$$E_{GS} = E_{HFA} + E_{corr} , \quad (2.13)$$

where  $E_{HFA}$  is the HFA ground-state energy

$$E_{HFA} = -\frac{1}{2} n (1 - \frac{1}{10} n) W + \frac{1}{20} n^2 (9U - 3J) - \frac{1}{20} (n_{\uparrow} - n_{\downarrow})^2 (U + 5J - W) , \quad (2.14)$$

with  $n_{\sigma} = \langle \sum_i n_{mi\sigma} \rangle$ , and

$$E_{corr} = - \frac{2 \sum_{k=1}^3 \eta_k \langle O_m^{(k)} \tilde{H} \rangle - \sum_{k,l=1}^3 \eta_k \eta_l (\langle O_m^{(k)} \tilde{H} O_m^{(l)} \rangle + \langle O_m^{(k)} O_m^{(l)} \tilde{H} \rangle')}{1 + \sum_{k,l=1}^3 \eta_k \eta_l \langle O_m^{(k)} O_m^{(l)} \rangle} , \quad (2.15)$$

where we have used  $O_m^{(l)} = \sum_i O_{mi}^{(l)}$  and  $O_m^{(k)} = \sum_{i < j} O_{mij}^{(k)}$  for  $k = 2, 3$ . The elements  $\langle O_m^{(k)} O_m^{(l)} \tilde{H} \rangle'$  do not contain such pairs of operators  $O_n$  where both operators describe correlations on the same orbitals. The correlation energy is calculated for an arbitrary site  $m$ , and  $\tilde{H} = H - \langle H \rangle$ . Final results for the matrix elements  $\langle O_m^{(k)} \tilde{H} \rangle$ ,  $\langle O_m^{(k)} \tilde{H} O_m^{(l)} \rangle$ ,  $\langle O_m^{(k)} O_m^{(l)} \tilde{H} \rangle'$ , and  $\langle O_m^{(k)} O_m^{(l)} \rangle$  are given in the Appendix. With these elements known we minimize the total energy  $E_{GS}$  with respect to  $\eta_k$

$$\frac{\partial E_{GS}}{\partial \eta_k} = 0, \quad \text{for } k = 1, 2, 3 , \quad (2.16)$$

what leads to a system of nonlinear equations for  $\eta_k$ , to be solved by iteration.

### III. COHESION ENERGY OF A PARAMAGNETIC METAL

The energy of cohesion  $E_{coh}$  is defined as the difference between the atomic-limit energy  $E_{AL}$  and the ground-state energy  $E_{GS}$ .<sup>17</sup> Up to now the few existing calculations of the cohesion energy in transition metals did not give a coherent picture as to

which correlation effects play a decisive role in the binding of these systems. It is well known that the transition metals show a remarkable minimum in cohesion energy near of the center of 3d and, but less distinctly, of 4d series.<sup>17</sup> Theoretical understanding of this fact is often based on the one-band Hubbard model (HM). For this model the cohesion energy, calculated with the model density of states Eq. (2.1) in the HFA, is just given by

$$E_{coh}^{HM} = \frac{1}{2} n (1 - \frac{1}{2} n) W - \frac{1}{4} n^2 U, \quad \text{for } n \leq 1 , \quad (3.1)$$

and has a maximum at  $n_0 = (1 + U/W)^{-1}$ , and local minimum at  $n = 1$ , due to the Coulomb energy  $U$ . The minimum at  $n = 1$  gets less distinct in the Gutzwiller approximation,<sup>18</sup> and the Green's-function approaches including correlation effects,<sup>19</sup> but qualitatively the cohesion energy preserves its HFA features. Local correlation at one orbital is, however, not the only mechanism present in real solids.

The present model Hamiltonian Eq. (2.2) gives in the HFA the cohesion energy

$$E_{coh}^{HFA} = E_{AL} - E_{HFA} , \quad (3.2)$$

with  $E_{AL}$  and  $E_{HFA}$  defined as in Eqs. (2.8) and

(2.14). This simplest approximation already shows the importance of the exchange interaction  $J$  in a transition metal. In a special case  $J=0$  the cohesion energy  $E_{\text{coh}}^{\text{HFA}}$  varies parabolically with increasing number of particles  $n$ , as was observed by Friedel and Sayers.<sup>10</sup> In the presence of the exchange interaction both the atomic energy  $E_{\text{AL}}$  and the HFA energy  $E_{\text{HFA}}$  are changed. The maxima of the cohesion energy appear then at

$$n_0 = 5[1 - 6J/(W - U + 7J)] ,$$

and  $10 - n_0$ , and show the strong influence of  $J$ . The resulting  $E_{\text{coh}}^{\text{HFA}}$  is strongly reduced in the middle of the band and is shown for  $U/W = 0.5$  and  $J/W = 0.1$  in Fig. 1.

With the variational ansatz Eq. (2.10) the cohesion energy is

$$E_{\text{coh}} = E_{\text{AL}} - E_{\text{GS}} = E_{\text{AL}} - E_{\text{HFA}} + |E_{\text{corr}}| . \quad (3.3)$$

The correlation energy  $E_{\text{corr}}$  depends on the parameters  $U$  and  $J$  in a complicated way and increases the cohesion energy  $E_{\text{coh}}$ . We present the numerical result in Fig. 1 for three representative values of the Coulomb energy  $U/W = 0.2, 0.3, \text{ and } 0.5$ , and for  $J/U = 0.2$ , which should be realistic for  $5d, 4d,$  and  $3d$  transition metals, respectively.<sup>10</sup> For each case there exists a local minimum in the cohesion energy, which gets deeper with increasing interaction energy. For  $U/W = 0.5$  we also show a comparison for the HFA result (dotted line). We would like to point out that, similar to the HFA, we obtain in the present scheme a parabolic dependence of  $E_{\text{coh}}$  on  $n$  in a special case when the exchange energy is neglected ( $J=0$ ).

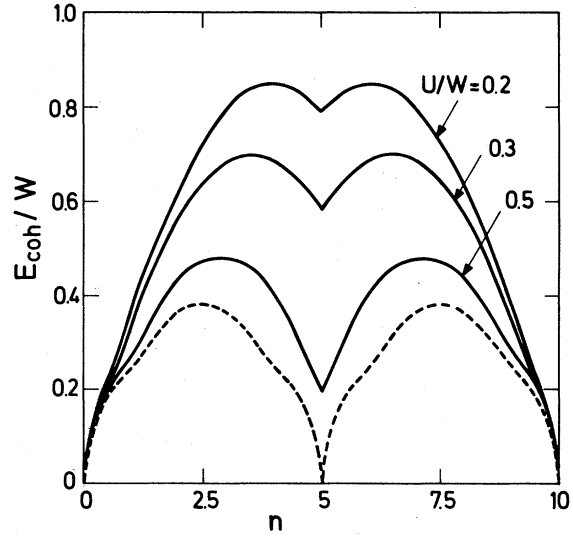


FIG. 1. Cohesion energy for transition metals as a function of band filling  $n$  for different values of the Coulomb energy  $U/W$ . Dotted lines show the HFA result for  $U/W = 0.5$ . The results are obtained for  $J/U = 0.2$ .

#### IV. ELECTRON LOCALIZATION AND THE STONER CRITERION

Perhaps the most intriguing and outstanding problem connected with magnetism of transition metals is the question about gradual localization of electrons. Such a localization, according to Hund's rule, is connected with building up of local moments, measured by

$$\langle S_m^2 \rangle = \frac{\langle \Psi_C | S_m^2 | \Psi_C \rangle}{\langle \Psi_C | \Psi_C \rangle} = \langle S_m^2 \rangle_{\text{HFA}} - \frac{2 \sum_{k=1}^3 \eta_k \langle O_m^{(k)} S_m^2 \rangle - \sum_{k,l=1}^3 \eta_k \eta_l (\langle O_m^{(k)} S_m^2 O_m^{(l)} \rangle + \langle O_m^{(k)} O_m^{(l)} S_m^2 \rangle')}{1 + \sum_{k,l=1}^3 \eta_k \eta_l \langle O_m^{(k)} O_m^{(l)} \rangle} . \quad (4.1)$$

The prime in  $\langle O_m^{(k)} O_m^{(l)} S_m^2 \rangle'$  has the same meaning as that in Eq. (2.15). The matrix elements needed to calculate the local moment  $\langle S_m^2 \rangle$  are found in a similar scheme to that reported in the Appendix for the correlation energy; the variational parameters  $\eta_k$  are known after the minimization procedure Eq. (2.16). The so calculated magnetic moment  $\langle S_m^2 \rangle$  indeed increases with increasing  $U/W$  from its HFA value to the maximal atomic limit value, which may be reached only in a completely localized state. Our

variational ground state  $|\Psi_C\rangle$  gives a strong enhancement of  $\langle S_m^2 \rangle$ , especially in the region near a half-filled band. The numerical result for  $U/W = 0.6$  and  $J/U = 0.2$  is presented in Fig. 2. We see that in this situation, being realistic for such transition metals as Fe, Co, and Ni, the local moment is already more close to being localized than itinerant.

A similar trend is seen in charge and spin fluctuations, defined as in Eqs. (2.3) and (2.4), with the averages now calculated over the correlated ground

state. They are

$$\sigma^2(n_m) = \sigma_{\text{HFA}}^2(n_m) - \frac{2 \sum_{k=1}^3 \eta_k \langle O_m^{(k)} \tilde{n}_m^2 \rangle - \sum_{k,l=1}^3 \eta_k \eta_l \left[ \langle O_m^{(k)} \left( \tilde{n}_m^2 - 2 \sum_{\sigma} n_{\sigma} \tilde{n}_{mi\sigma} \right) O_m^{(l)} \rangle + \langle O_m^{(k)} O_m^{(l)} \left( \tilde{n}_m^2 - 2 \sum_{\sigma} n_{\sigma} \tilde{n}_{mi\sigma} \right) \right]}{1 + \sum_{k,l=1}^3 \eta_k \eta_l \langle O_m^{(k)} O_m^{(l)} \rangle} \quad (4.2)$$

$$\sigma^2(S_m^z) = \sigma_{\text{HFA}}^2(S_m^z)$$

$$\frac{2 \sum_{k=1}^3 \eta_k \langle O_m^{(k)} (\tilde{S}_m^z)^2 \rangle - \sum_{k,l=1}^3 \eta_k \eta_l \left[ \langle O_m^{(k)} \left( (\tilde{S}_m^z)^2 - \frac{1}{2} \sum_{\sigma} n_{\sigma} \tilde{n}_{mi\sigma} \right) O_m^{(l)} \rangle + \langle O_m^{(k)} O_m^{(l)} \left( (\tilde{S}_m^z)^2 - \frac{1}{2} \sum_{\sigma} n_{\sigma} \tilde{n}_{mi\sigma} \right) \right]}{1 + \sum_{k,l=1}^3 \eta_k \eta_l \langle O_m^{(k)} O_m^{(l)} \rangle} \quad (4.3)$$

where  $\tilde{A} = A - \langle A \rangle_{\text{HFA}}$ , and  $n_{\sigma} = \langle \sum_i n_{mi\sigma} \rangle$ . The averages appearing in Eqs. (4.2) and (4.3) are calculated again within the same scheme as those given in the Appendix for the correlation energy.

For 3d metals, for which we put  $U/W = 0.6$  and  $J/U = 0.2$ , charge fluctuations are almost not reduced from their HFA values for low electron or hole concentrations in both paramagnetic and ferromagnetic states [see Fig. 3(a)]. The reduction of charge fluctuations is greater in the middle of the band for the paramagnetic state. It just corresponds to increasing correlation in hopping processes with increasing  $U/W$ , which eventually are of the nature of the kinetic exchange interaction. In this region the ground state is more close to the localized state, as

we have already seen from the cohesion energy (Fig. 1). At the same time spin fluctuations get strongly enhanced [see Fig. 3(b)]. For 3d metals their values become closer to the atomic-limit values than to the band limit, represented by the HFA result.

All these results for  $\langle S_m^z \rangle$ ,  $\sigma^2(n_m^z)$ , and  $\sigma^2(S_m^z)$  are in qualitative agreement with those of Stollhoff and Thalmeier<sup>20</sup> who have used the canonical bands for fcc and bcc transition metals instead of the constant density of states used here.

Comparing the HFA energy of a paramagnetic state ( $n_{\uparrow} = n_{\downarrow}$ ) and a completely ferromagnetic state ( $n_{\uparrow} = n$ ,  $n_{\downarrow} = 0$ ), one obtains the Stoner criterion for stability of ferromagnetism

$$U + 5J - W > 0, \quad (4.4)$$

applied to the present simplified band structure Eq. (2.1) [the factor 5 results from the orbital symmetry of the Hamiltonian Eq. (2.2)]. We notice that for that simple density of states there is no dependence of this condition on the actual filling of the band. On the other hand, it has been shown by Kanamori, that for a small band filling there should be no ferromagnetism possible.<sup>21</sup> So, one expects that the condition of ferromagnetism should be rather  $n$  dependent.

In the variational approximation we calculate the energy of the ground state  $E_{\text{GS}}$  according to Eq. (2.13), and find its minimum with respect to the value of the magnetic moment  $\langle S_m^z \rangle = \frac{1}{2}(n_{\uparrow} - n_{\downarrow})$ . That leads to the phase diagram presented in Fig. 4. The Stoner criterion is drastically changed if the correlation energy  $E_{\text{corr}}$  is taken into account, which also varies with the magnetic moment  $\langle S_m^z \rangle$ . From the physical point of view, the energy of the paramagnetic state may be reduced much more from its HFA value due to exclusion from the ground state

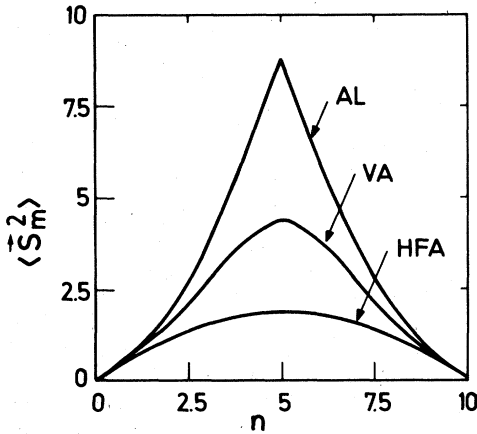


FIG. 2. Average local moment  $\langle S_m^z \rangle$  per site in the variational ground state (VA) for  $U/W = 0.6$  and  $J/U = 0.2$ . HFA and AL stand for the Hartree-Fock approximation and the atomic-limit result.

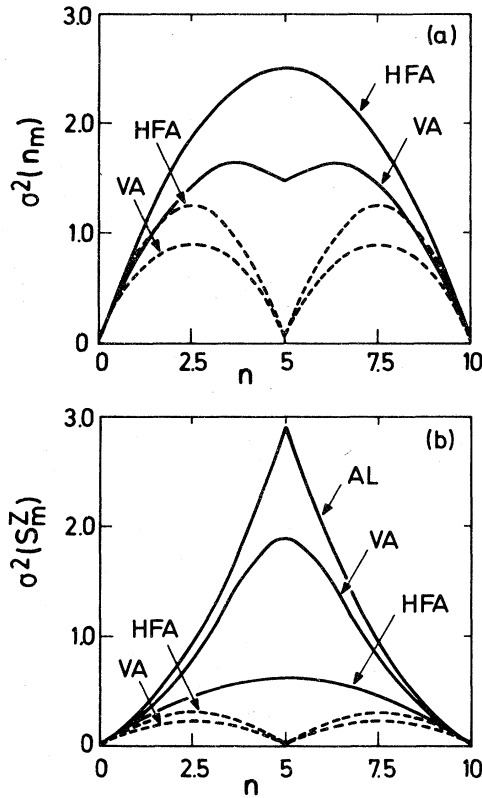


FIG. 3. Fluctuations in (a) charge and (b) spin in the correlated ground state Eq. (2.10) (VA) for  $U/W=0.6$  and  $J/U=0.2$ . Solid lines for the paramagnetic state and broken lines for the ferromagnetic state. HFA and AL have the same meaning as in Fig. 2.

of those atomic configurations, which have higher atomic energy. In the completely ferromagnetic state there is much less room for such reduction of the ground-state energy by the correlated hopping.

Figure 4 shows that ferromagnetism is not possible at very low filling of the  $d$  band (by electrons or holes), in agreement with the result of Kanamori.<sup>21</sup> The critical value of  $U/W$ , above which the ferromagnetic state is stable, changes slowly in the region  $1.5 < n < 8.5$  of band filling, and it is only by about 30% higher than that predicted by the HFA. This holds, however, only in presence of the exchange interaction  $J$ ; when  $J$  is set to zero the change in the Stoner criterion is more drastic.

In the present scheme we get a transition from paramagnetic to completely ferromagnetic phase for  $n < 3.6$  and  $n > 6.4$ , while for  $3.6 < n < 6.4$  the transition takes place first with a weakly ferromagnetic phase, where the moment increases gradually with increasing  $U/W$ , up to complete saturation. In reality, however, we expect that the antiferromagnetic phase will form near the half-filled band.

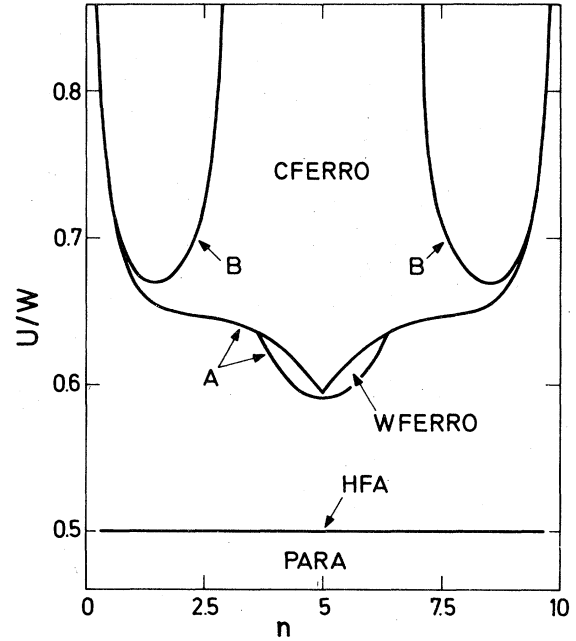


FIG. 4. Model phase diagram for transition metals for  $J/U=0.2$ : (A) present variational method, (B) expansion up to  $\eta_n^2$  terms of  $E_{\text{corr}}$ , (HFA) Stoner criterion, WFERRO and CFERRO denote weakly and completely ferromagnetic phases.

For a comparison, we also show the result obtained from the variational method, if the denominator in the correlation energy  $E_{\text{corr}}$  Eq. (2.15) is neglected (curves B in Fig. 4). Such an approximation overestimates the absolute value of the correlation energy for the paramagnetic state, so we may consider the curves B as giving the upper limit for the critical value of  $U/W$  with respect to the formation of the ferromagnetic state. This agrees with the present method (curves A in Fig. 4) very well for  $n < 2$  and  $n > 8$ , while indicating that a still more accurate treatment is needed in the center of the band.

## V. CONCLUSIONS AND FINAL REMARKS

In this paper we have discussed the cohesion energy of the ground state of transition metals, starting from a simple model of a  $d$  band, but with its degeneracy explicitly included. The model Hamiltonian Eq. (2.2) has full symmetry in both spin and orbital space. The variational solution constructed for this Hamiltonian shows that the cohesive energy is strongly reduced in the center of the band for moderate values of the interaction energies  $U/W$  and  $J/W$ . We find that the exchange energy  $J$  is responsible for the minimum in cohesion energy at  $n=5$ , which appears essentially for any  $U/W > 0$ , only if

$J > 0$ . Such a minimum, however, might not be present in the total cohesive energy, when the  $s$  electrons were also included (they give a parabolic contribution, characteristic of a free band), and if  $U/W$  were small. The spin-orbit coupling, being of greater importance for  $4d$  and  $5d$  metals, also reduces the minimum of the cohesion energy at  $n = 5$ .<sup>10</sup> For these reasons, we think, there is only a shallow minimum seen in the experimental data for  $4d$  metals and no minimum for  $5d$  metals.<sup>17</sup> Of course, for a quantitative comparison, a realistic density of states in the  $d$  band and the changes of  $U/W$  along the transition-metal series should be also included. But nevertheless, we may see already from the present model that the moderate values of the Coulomb and exchange integrals  $U/W$  and  $J/W$  give the cohesion energy in qualitative agreement with the experimental data.

Our analysis of the Stoner criterion also shows the importance of the exchange interaction in transition metals, as can be seen from the theory of Friedel and Sayers.<sup>10</sup> However, with the present approach one is able to go beyond lowest-order perturbation theory, and therefore reproduce correctly Kanamori's result in the limit of small electron and hole concentrations. The ferromagnetic ground state exists for any  $J/U > 0$ , while the lowest-order perturbation theory<sup>10</sup> gives ferromagnetism only if  $J/U > 0.25$  (of course, the Coulomb interaction  $U/W$  has to be large enough in both cases).

By means of the variational ansatz for the ground state we have shown that the local moments do build up in transition metals (if the Hund's-rule interaction is present, i.e., if  $J > 0$ ), and that ferromagnetism appears in the situation where the motion of electrons is already correlated and the local moments are formed. In such a situation new interactions of the kinetic exchange nature become important, and will further reduce the ground-state energy, stabilizing ferromagnetism away from and antiferromagnetism near to the half-filled band, as has been shown for the doubly-degenerate Hubbard model.<sup>22</sup> Inclusion of these interactions in the present variational scheme seems to be possible and will be reported in the future.

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#### APPENDIX: CALCULATION OF THE CORRELATION ENERGY EQ. (2.15)

As an illustrative example, we present here the results obtained for the expressions  $\langle O_n \tilde{H} \rangle$ ,  $\langle O_n \tilde{H} O_n' \rangle$ ,  $\langle O_n O_n' \tilde{H} \rangle$ , and  $\langle O_n O_n' \rangle$  needed to calculate the correlation energy  $E_{\text{corr}}$ . Thereby we make use of a method employed by Kajzar and Friedel<sup>19</sup> and Treglia *et al.*<sup>11</sup> in the perturbation expansion of the self-energy.

Any of the considered averages, written first in the real space, is Fourier transformed. An 8- or 12-operator expression so obtained then produces factors  $\bar{n}_{\vec{k}i\sigma}$  or  $(1 - \bar{n}_{\vec{k}i\sigma})$ , where  $\bar{n}_{\vec{k}i\sigma} = \langle a_{\vec{k}i\sigma}^\dagger a_{\vec{k}i\sigma} \rangle$  with  $a_{\vec{k}i\sigma}$  being the Fourier transform of  $a_{mi\sigma}$ , depending on the actual order of the contracted creation and annihilation operators. These factors are accompanied by exponential functions  $\exp(i\vec{k} \cdot \vec{R})$ , resulting from the Fourier transformation, and the whole expression is summed over the lattice vectors  $\vec{R}$ . For instance, for  $\langle O_m^{(1)} \tilde{H} \rangle$  we obtain

$$\langle O_m^{(1)} \tilde{H} \rangle = U \sum_R z_{i1}^R z_{i1}^R (1 - z_{i1})^{-R} (1 - z_{i1})^{-R}, \quad (\text{A1})$$

where

$$z_{i\sigma}^R = e^{i\vec{k} \cdot \vec{R}} \bar{n}_{\vec{k}i\sigma}, \quad (\text{A2})$$

$$(1 - z_{i\sigma})^{-R} = e^{i\vec{k} \cdot \vec{R}} (1 - \bar{n}_{\vec{k}i\sigma}). \quad (\text{A3})$$

The most important contribution to  $\langle O_m^{(1)} \tilde{H} \rangle$  in Eq. (A1) comes from the  $R = 0$  term. If we neglect the  $R \neq 0$  terms in Eq. (A1), the considered average may be expressed in terms of the average fillings of  $i$ th band by electrons with  $\sigma$  spin  $n_{i\sigma}$

$$\langle O^{(1)} \tilde{H} \rangle = U n_{i\uparrow} n_{i\downarrow} (1 - n_{i\uparrow}) (1 - n_{i\downarrow}). \quad (\text{A4})$$

Such an approximation we call the  $R = 0$  approximation. Then the couplings between different sites are neglected and the correlation energy  $E_{\text{corr}}$  may be written as Eq. (2.15). The  $R \neq 0$  terms give only about 10% of the  $R = 0$  term for the one-dimensional one-band Hubbard model, so we consider  $R = 0$  approximation as fully justified.

Let us define for convenience

$$a_0 = n_{i\uparrow} n_{i\downarrow} (1 - n_{i\uparrow}) (1 - n_{i\downarrow}), \quad (\text{A5})$$

$$a_1 = \sum_{\sigma} n_{i\sigma}^2 (1 - n_{i\sigma})^2, \quad (\text{A6})$$

$$b_0 = a_0 (1 - 2n_{i\uparrow}) (1 - 2n_{i\downarrow}), \quad (\text{A7})$$

$$b_1 = \sum_{\sigma} n_{i\sigma}^2 (1 - n_{i\sigma})^2 (1 - 2n_{i\sigma})^2, \quad (\text{A8})$$

$$b_2 = \sum_{\sigma} n_{i\sigma}^3 (1 - n_{i\sigma})^3, \quad (\text{A9})$$

$$b_3 = a_0 \sum_{\sigma} n_{i\sigma} (1 - n_{i\sigma}), \quad (\text{A10})$$

$$b_4 = a_0 [n_{i\uparrow} n_{i\downarrow} + (1 - n_{i\uparrow}) (1 - n_{i\downarrow})], \quad (\text{A11})$$

$$b_5 = a_0 [n_{i\uparrow} (1 - n_{i\downarrow}) + n_{i\downarrow} (1 - n_{i\uparrow})]. \quad (\text{A12})$$

Then the expressions which appear in Eq. (2.15) and depend on the operators  $O_m^{(k)}$  are

$$\langle O_m^{(1)} \tilde{H} \rangle = 5(U+J)a_0, \quad (\text{A13})$$

$$\langle O_m^{(2)} \tilde{H} \rangle = 20Ua_0 + 10(U-J)a_1, \quad (\text{A14})$$

$$\langle O_m^{(3)} \tilde{H} \rangle = -5(U+2J)a_0 + \frac{5}{2}(U-J)a_1, \quad (\text{A15})$$

$$\langle O_m^{(1)} \tilde{H} O_m^{(1)} \rangle = 5Wa_0 + 5(U+J)b_0, \quad (\text{A16})$$

$$\langle O_m^{(1)} \tilde{H} O_m^{(2)} \rangle = 20(2U-J)b_3, \quad (\text{A17})$$

$$\langle O_m^{(1)} \tilde{H} O_m^{(3)} \rangle = 5J(b_3+2b_5), \quad (\text{A18})$$

$$\begin{aligned} \langle O_m^{(2)} \tilde{H} O_m^{(2)} \rangle &= 10W(2a_0+a_1) + 20Ub_0 \\ &+ 10(U-J)b_1 + 40(U+J)b_3 \\ &+ 60(U-J)(b_2+b_3) + 120Ub_3, \end{aligned} \quad (\text{A19})$$

$$\begin{aligned} \langle O_m^{(2)} \tilde{H} O_m^{(3)} \rangle &= \frac{5}{2}W(a_1-2a_0) - 5Ub_0 + \frac{5}{2}(U-J)b_1 \\ &+ 10J(b_3-b_4) + 15(U-J)(b_2-b_3), \end{aligned} \quad (\text{A20})$$

$$\begin{aligned} \langle O_m^{(3)} \tilde{H} O_m^{(3)} \rangle &= \frac{25}{4}Wa_0 + \frac{5}{8}Wa_1 + \frac{5}{4}Ub_0 + \frac{5}{8}(U-J)b_1 \\ &- \frac{15}{2}Jb_3 - 5(U-\frac{1}{2}J)(b_3-b_4) + \frac{15}{4}Jb_4 \\ &+ \frac{15}{4}(U-J)(b_2+b_3) - \frac{15}{2}Ub_3 - 15Jb_5, \end{aligned} \quad (\text{A21})$$

$$\langle O_m^{(1)} O_m^{(1)} \tilde{H} \rangle' = 0, \quad (\text{A22})$$

$$\langle O_m^{(1)} O_m^{(2)} \tilde{H} \rangle' = 20(2U-J)b_3, \quad (\text{A23})$$

$$\langle O_m^{(1)} O_m^{(3)} \tilde{H} \rangle' = 5J(b_3+2b_5), \quad (\text{A24})$$

$$\langle O_m^{(2)} O_m^{(2)} \tilde{H} \rangle' = 60(U-J)(b_2+b_3) + 120Ub_3, \quad (\text{A25})$$

$$\langle O_m^{(2)} O_m^{(3)} \tilde{H} \rangle' = 15(U-J)(b_2-b_3), \quad (\text{A26})$$

$$\langle O_m^{(3)} O_m^{(3)} \tilde{H} \rangle' = \frac{15}{4}(U-J)(b_2-b_3) - \frac{15}{2}Ub_3 - 15Jb_5, \quad (\text{A27})$$

$$\langle O_m^{(1)} O_m^{(1)} \rangle = 5a_0, \quad (\text{A28})$$

$$\langle O_m^{(1)} O_m^{(2)} \rangle = \langle O_m^{(1)} O_m^{(3)} \rangle = 0, \quad (\text{A29})$$

$$\langle O_m^{(2)} O_m^{(2)} \rangle = 20a_0 + 10a_1, \quad (\text{A30})$$

$$\langle O_m^{(2)} O_m^{(3)} \rangle = -5a_0 + \frac{5}{2}a_1, \quad (\text{A31})$$

$$\langle O_m^{(3)} O_m^{(3)} \rangle = \frac{25}{2}a_0 + \frac{5}{4}a_1. \quad (\text{A32})$$

The matrices  $\langle O_m^{(k)} \tilde{H} O_m^{(l)} \rangle$ ,  $\langle O_m^{(k)} O_m^{(l)} \tilde{H} \rangle'$ , and  $\langle O_m^{(k)} O_m^{(l)} \rangle$  are symmetric.

In a similar way one may express in terms of the average fillings  $n_{i\sigma}$  the matrix elements needed to calculate the local moments  $\langle S_m^2 \rangle$  as well as the charge and spin fluctuations  $\sigma^2(n_m)$  and  $\sigma^2(S_m^z)$  [see Eqs. (4.1)–(4.3)].

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