Allowance for correlation effects in narrow energy bands

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The correlation energy in a certain model of the d-band of a transition metal is calculated in the first, second and third approximations in perturbation theory. The second-order correction is very small compared to the first-order energy, whereas the third-order correction is almost 40%. The calculations are such that they certainly overestimate this correction and hence it may be concluded that the random-phase approximation is satisfactory.

1. INTRODUCTION

Any attempt to explain some property of a metal, by starting from first principles, leads inevitably to the need for going outside the framework of the Hartree-Fock (HF) approximation. Bearing in mind that primarily a quantitative criterion of ferromagnetism[1], where correlation effects come particularly strongly into play (for example, vanadium has turned out to be ferromagnetic in the HF approximation), we consider here correlations of electrons of 3d-bands of transition metals. This portion was considered also by Kanamori[2] and by Hubbard[3,4]. Kanamori, using the Brueckner ladder approximation, considered the ferromagnetism of nickel, which apparently has few holes in the d-band. As to Co, Fe, V and the corresponding elements with unfilled 4d-bands, neither the number of holes nor the number of electrons is small in their case. Hubbard used the method of equal-time Green's functions, which is described in detail in Zubarev's review[5]. However, Hubbard's uncoupling of the coupled equations of motion for the Green's function[3,4] seems to us more or less arbitrary, since there is no intrinsic verification for this method.

In this connection, we attempt here to employ perturbation-theory methods, together with an integral equation of the type of Hubbard equation[6], for the summation of infinite sub-sequences of diagrams. This raises the question of the convergence of the series representing the kernel of the integral equation and of the series representing the solution, i.e., in fact the energy of the metal, and consequently the question of applicability of perturbation theory to a practical calculation of the correlations of the d-electrons in transition metals. Preliminary calculations have shown that in the series representing the nucleus it is necessary to sum beforehand diagrams of the self-energy and screening type, i.e., to consider a series of diagrams with modified interaction and the propagation functions. Otherwise it is impossible to obtain satisfactory convergence for the series representing the energy of the metal. Under any modification, the perturbation-theory series remains an expansion in powers of the ratio of the characteristic electron-interaction energy to a width of the d-band. This ratio is equal to approximately two. Wthi this value of the expansion parameter, the question of the convergence or divergence of the series can be solved only by numerical calculation, for which there would be no need if the parameter were small.

To investigate the convergence, we calculate in the present paper the energy in the first, second, and third orders for only one typical transition metal, vanadium. In the first (random phase approximation—RPA) and second orders there is only one diagram each, while in third order there are six diagrams (see formula (5)). The second- and third-order energy corrections were calculated in fact without modifying the interaction and the propagation functions. Introduction of the modified interaction obviously only decreases the contribution of these corrections. The calculations, which are too cumbersome to present here, have shown that the modification of the interaction in second order (in the RPA approximation) decreases the contribution of the diagram to the kernel by a factor of 1.5. In the third order, this decrease is stronger, since there are here two internal interaction lines as against one in second order. As to the modification of the self energy, it apparently produces a small change in the initial width of the d-band.

Since the calculations, particularly in third order, are very cumbersome, they are performed in fact using the degenerate d-band model, first used by Hubbard[4]. The contribution of second-order corrections to the energy turns out to be quite small in comparison with the first order, and the contribution of the third-order correction amount to approximately 40% of the first order. Recognizing that replacement of the initial interaction by a modified one is likely to decrease the contribution of the third-order correction by a factor of more than two, we can assume that the RPA is sufficiently accurate for d-bands of transition metals. It should be noted, however, that the contribution of the higher-order corrections to the kernel of the integral equation is much larger than the contribution to the energy (see the table). Regardless of the numerical results, we consider the useful result of the paper to be the fact that we have demonstrated the possibility of performing the calculations up to third order, even though the number of diagrams is quite large.

2. THE HAMILTONIAN

In the assumed model, the motion of the d-electrons is determined by the Hubbard Hamiltonians[3,4]

$$H=\sum \varepsilon_{\mathbf{k}} a_{\mathbf{k}\nu}{}^{+} a_{\mathbf{k}\nu}+\frac{B}{2\mathscr{K}}\sum a^{\pm}_{\mathbf{k}_2'\nu_2} a_{\mathbf{k}_1'\nu_1} a_{\mathbf{k}_1\nu_1} a_{\mathbf{k}_2\nu_2} \delta_{\mathbf{k}_1+\mathbf{k}_2\mathbf{k}_1'+\mathbf{k}_2'}, \qquad (1)$$

where $\nu \equiv m\alpha$, m is the magnetic quantum number, α is the spin index, B is the interaction energy of two 3d-electrons of one atom in atomic energy units (a.e.u.), and $\mathscr{K}$ is the total number of cells of the metal. The conservation of the quasimomentum of the electron, expressed by the δ-function, is understood with accuracy to within an arbitrary reciprocal-lattice vector **K**. The single-particle energy is taken in the form $\epsilon_k = a(k/k_0)^2$, where k_0 is the radius of a sphere having the same volume as the first Brillouin zone, and a is the width of the 3d band in the spherical approximation[1].

The interaction term in (1) can be expressed in the form of a sum over the lattice points $B\Sigma N_i(N_i - 1)/2$, $0 \le N_i \le 10$ is the number of 3d electrons of the i-th point, i.e., the interaction between different cells and between electrons of different bands is neglected. The energy of the true ground state of the metal is determined as the sum of the Hartree-Fock part and the correlation part. The Hartree-Fock part is in this case

$$E_{HF} = \sum_{\nu k} \varepsilon_k + \frac{B}{2\mathscr{K}}\left(N^2 - \sum_{\nu} N_\nu^2\right), \tag{2}$$

where the summation in first term proceeds only over $\epsilon_k < \epsilon_\alpha^F$.

3. CORRELATION ENERGY

The correlation part, according to Goldstone[7], is equal to the sum of all possible connected diagrams, starting with second order. If we separate from H the interaction terms with zero quasimomentum transfer $\mathbf{k}_{1'} - \mathbf{k}_1 = \mathbf{Q} = \mathbf{k}_2 - \mathbf{k}_{2'}$, and if we include them in the unperturbed part of the interaction, then the diagrams that break up into two individual parts when one of the interaction lines is broken drop out from E_{corr}. For the assumed model, the two-particle matrix elements depend only on Q, so that the Hubbard theory for a homogeneous gas is fully applicable[6]. Since, however, the homogeneity takes place here only in the sense of displacement by an arbitrary lattice vector, the region of variation of Q is the reciprocal-lattice cell.

Following his reasoning, we can obtain the following expression for the correlation energy of the metal per cell

$$E_{corr} = -\frac{a}{2}\int\frac{dQ}{|\omega_Q|}\int_0^1\frac{d\lambda}{\lambda}\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\frac{F_0}{1-F_0} - \frac{BN_d}{2} - E_{ex}. \tag{3}$$

Here $F_0(i\omega, \mathbf{Q}, \lambda)$ is the kernel of the integral equation and is the sum of the open (with one interaction line broken) irreducible diagrams, and N_D is the number of 3d electrons of the cell. The last term in (3) is the usual exchange energy

$$E_{ex} = -{}^5/_2 B[(N_d^+/5)^2 + (N_d^-/5)^2].$$

Formula (3) coincides with formula (12) from Hubbard's paper[8], if ω in (3) is measured in units of a and if it is recognized that the Coulomb interaction is replaced here by the intracell interaction in accordance with the Hamiltonian (1).

The constant terms in the right-hand side of (3) do not influence the convergence of the series, and are therefore omitted from now on; the remaining part is designated $\overline{E}_{corr}$. We can also show that $F_0(i\omega, \mathbf{Q}, \lambda)$ on the imaginary axis is a real and even function of $i\omega \equiv \xi$. Then the final formula for $\overline{E}_{corr}$ becomes

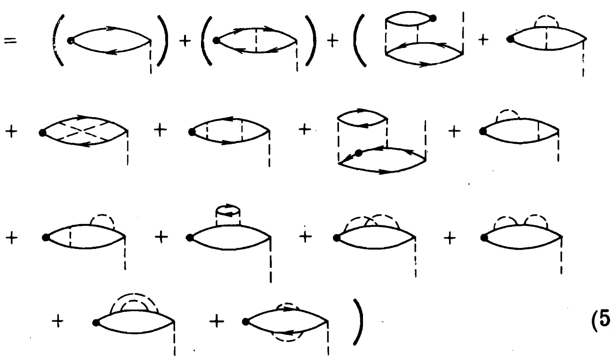
$$\overline{E}_{corr}(|\mu|) = -\frac{a}{2}\int\frac{dQ}{|\omega_Q|}\int_0^1\frac{d\lambda}{\lambda}\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\frac{\mathrm{Re}\,F_0}{1-\mathrm{Re}\,F_0}. \tag{4}$$

Here μ is the magnetic moment of the cell in Bohr magnetons.

4. CALCULATION OF THE CORRELATION ENERGY

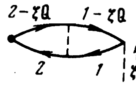
The kernel F_0 of the integral equation is given in third order by a sum of 22 diagrams:

$$F_0^{III} = (F_0^I) + (\Delta F_0^{II}) + (\Delta F_0^{III})$$



(5)

where the loops without the arrows are circuited in the two possible directions. If we modify the interaction and the propagation functions, then the fifth, sixth, and seventh structures in ΔF_0^{III} are included in the second-order diagram, and all the succeeding structures of ΔF_0^{III} are included in the first-order diagram. We shall henceforth assume for the kernel F_0^{III} the contribution of only the first six structures of (5), i.e., we take only eight diagrams into account. By way of example, we write down the contribution of the second order diagram $\Delta F_0^{II}(\xi, \mathbf{Q}, \lambda)$:



$$= -\left(\frac{\lambda B}{a\mathscr{K}}\right)^2\sum_{12}\delta_{\nu_1\nu_2}\left(\frac{1}{2\pi i}\right)^2\iint_{-i\infty}^{+i\infty}\frac{d\xi_1\,d\xi_2}{(\varepsilon_1-\xi_1)(\varepsilon_2-\xi_2)(\varepsilon_{1'}+\xi-\xi_1)(\varepsilon_{2'}+\xi-\xi_2)}.$$

We consider first the kernel in first order—the first term of (5). Its real part is

$$\mathrm{Re}\,F_0^{I} = \lambda A\sum_\alpha\iint\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|}\frac{\theta(1-F)-\theta(2-F)}{(\varepsilon_2-\varepsilon_1)^2+\omega^2}(\varepsilon_2-\varepsilon_1)\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q})$$

$$= -\lambda A\sum_\alpha f_\alpha^{I}(\omega, \mathrm{Q}) \equiv -\lambda D_1(\omega, \mathrm{Q}). \tag{6}$$

Here $\theta(1 - F) \equiv \theta(\epsilon_1 - \epsilon_F)$, $A = 5B/a$, and the factor 5 is obtained from summing over m;

$$\theta(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0. \end{cases}$$

The numerical calculation was carried out for a face-centered reciprocal lattice with large cube edge equal to 2. If ω_k is the cell proper (the first Brillouin zone), described by the conditions

$$|k_x| + |k_y| \leqslant 1, \quad |k_x| + |k_z| \leqslant 1, \quad |k_y| + |k_z| \leqslant 1,$$

then $|\omega_k| = 2$ and $k_0 = (3/2\pi)^{1/3} \approx 0.781$. The following vectors K of the reciprocal lattice participate in the umklapp processes:

$$\mathbf{K}_1 = (0, \pm1, \pm1), \quad (\pm1, 0, \pm1), \quad (\pm1, \pm1, 0), \quad |\mathbf{K}_1| = 2^{1/2};$$

$$\mathbf{K}_2 = (0, 0, \pm2), \quad (0, \pm2, 0), \quad (\pm2, 0, 0), \quad |\mathbf{K}_2| = 4^{1/2};$$

$$\mathbf{K}_3 = (\pm1, \pm1, \pm2), \quad (\pm1, \pm2, \pm1), \quad (\pm2, \pm1, \pm1), \quad |\mathbf{K}_3| = 6^{1/2}.$$

The fraction of the vectors $\mathbf{K}_3$ (they appear only in third order) amounted to about 1% and therefore umklapp processes with $\mathbf{K}_3$ were completely disregarded. The function D_1 was calculated by the Monte Carlo method with a calculation error ≤5%. Three directions were considered for the parameter Q: (1, 0, 0), $(2^{-1/2}, 2^{-1/2}, 0)$ and $(3^{-1/2}, 3^{-1/2}, 3^{-1/2})$. It turned out that D_1 depends very little on the direction of Q.

The subsequent calculations were performed only for the last direction. The integration with respect to Q

ω	D_1	D_2	D_3
0.1	25.0	2.50	44.5
1	3.26	0.326	5.35
100	$0.44\cdot10^{-3}$	$0.44\cdot10^{-4}$	0 0011

$\mu = 0$; $D_2 = 0.1\cdot D_1$; $Q = 0.6$.

was carried out within the limits of a sphere of radius $k_0 \approx 0.781$. The final calculated formula in first order is

$$\bar{E}^{\,\mathrm{I}}_{corr} = a\int_0^{k_0} Q^2\,dQ\int_0^\infty d\omega\int_0^1 d\lambda\frac{D_1}{1+\lambda D_1}. \tag{7}$$

Since vanadium has only three 3d electrons, we have for the nonmagnetic state $(k_F/k_0)^3 = 3/10$, and for the maximal magnetic state $(k_F/k_0)^3 = 3/5$. For these states, formula (7) yields respectively 0.231 and 0.149 a.e.u. The differences are

$$\Delta\bar{E}^{\,\mathrm{I}}_{corr}(\mu=3) = \bar{E}^{\,\mathrm{I}}_{corr}(3) - \bar{E}^{\,\mathrm{I}}_{corr}(0) = -0.082 \text{ a.e.u.},$$

$$\Delta E_{\mathrm{Hart}}(3) = 0.1225 \text{ a.e.u. } [^1]$$

and consequently the ferromagnetism previously obtained[1] for vanadium disappears. The behavior of D_1 can be judged from the table.

The real part of the second-order correction (the second term in (5) is given by

$$\mathrm{Re}\,\Delta F_0^{\mathrm{II}} = -\frac{\lambda^2}{5}A^2\sum_\alpha [f_\alpha^1(\omega,Q)]^2 \equiv -\lambda D_2(\omega,Q). \tag{8}$$

For the correlation energy in second order we obtain

$$\bar{E}^{\,\mathrm{II}}_{corr} = a\int_0^{k_0} Q^2\,dQ\int_0^\infty d\omega\int_0^1 d\lambda\frac{D_1+\lambda D_2}{1+\lambda D_1+\lambda^2 D_2}. \tag{9}$$

Calculations by means of this formula yielded

$$\bar{E}^{\,\mathrm{II}}_{corr}(0) = 0.237,\quad \bar{E}^{\,\mathrm{II}}_{corr}(3) = 0.175,\quad \Delta\bar{E}^{\,\mathrm{II}}_{corr}(3) = -0.080 \text{ a.e.u.}$$

The third-order correction, which takes into account the contributions of only the six diagrams indicated above (the third term of (5)), is

$$\Delta F_0^{\mathrm{III}} = -\lambda^3\frac{A^3}{5}\sum_{\alpha\beta}\int_\alpha\frac{d\mathbf{k}_1}{|\omega_k|}\int_\beta\frac{d\mathbf{k}_2}{|\omega_k|}\int_\alpha\frac{d\mathbf{k}_3}{|\omega_k|}\int_\beta d\mathbf{k}_4$$
$$\times\left(\frac{1}{2\pi i}\right)^3\int_{-i\infty}^{+i\infty}\!\!\int\!\!\int\prod_{j=1}^{3}\frac{d\xi_j}{(\varepsilon_j-\xi_j)}\Big[\frac{\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3+\mathbf{k}_4)}{(\varepsilon_4+\xi_1-\xi_2-\xi_3)(\varepsilon_{1'}-\xi-\xi_1)(\varepsilon_{2'}-\xi-\xi_2)}$$
$$+\frac{\delta(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3-\mathbf{k}_4)}{(\varepsilon_4-\xi_1-\xi_2+\xi_3)(\varepsilon_{1'}-\xi-\xi_1)(\varepsilon_{2'}+\xi-\xi_2)}\Big]$$
$$+\lambda^3\frac{A^3}{25}\sum_\alpha\prod_{i'=1}^{4}\int_{k_i^\alpha}\frac{d\mathbf{k}_i}{|\omega_k|}\left(\frac{1}{2\pi i}\right)^3\iiint_{-i\infty}^{+i\infty}\prod_{j=1}^{3}\frac{d\xi_j}{(\varepsilon_j-\xi_j)}$$
$$\times\Big[\frac{\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3+\mathbf{k}_4)}{(\varepsilon_4+\xi_1-\xi_2-\xi_3)}\Big(\frac{1}{(\varepsilon_{1'}-\xi-\xi_1)(\varepsilon_{3'}-\xi-\xi_3)}$$
$$+\frac{1}{(\varepsilon_{1'}+\xi-\xi_1)(\varepsilon_{3'}+\xi-\xi_3)}\Big)+\frac{\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3+\mathbf{k}_4)}{(\varepsilon_4+\xi_1-\xi_2-\xi_3)(\varepsilon_{2'}-\xi-\xi_2)(\varepsilon_{3'}-\xi-\xi_3)}$$
$$+\frac{\delta(\mathbf{k}_2-\mathbf{k}_4+\mathbf{Q})}{(\varepsilon_4-\xi-\xi_2)(\varepsilon_{1'}-\xi-\xi_1)(\varepsilon_{3'}-\xi-\xi_3)}\Big]. \tag{10}$$

The contributions from the six diagrams are separated here as individual terms.

The real part of this expression can be transformed into

$$\mathrm{Re}\,\Delta F_0^{\mathrm{III}} \equiv -\lambda^3 D_3(\omega,Q),$$

$$D_3 = \frac{A^3}{5}\int\prod_{j=1}^{4}\frac{d\mathbf{k}_j}{|\omega_k|^3}\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3+\mathbf{k}_4)\Big\{\left(\frac{12}{34}-\frac{34}{12}\right)\frac{1}{\mathscr{E}_1}\Big[\frac{2\theta_1}{\varkappa_1\varkappa_2}(\bar\varepsilon_1\bar\varepsilon_2+\omega^2)$$
$$+\frac{4\theta}{\varkappa_1\varkappa_4}(\bar\varepsilon_1\bar\varepsilon_4-\omega^2)-\frac{2\theta_2}{5\varkappa_3\varkappa_4}(\bar\varepsilon_3\bar\varepsilon_4+\omega^2)\Big]-\left(\frac{1'2}{34}-\frac{34}{1'2}\right)$$
$$\times\frac{1}{\bar\varkappa_{1'}}\Big[\frac{2\theta_1}{\varkappa_1\varkappa_2}(\bar\varepsilon_1\bar\varepsilon_2\mathscr{E}_{1'}+\omega^2(-\bar\varepsilon_1+\bar\varepsilon_2+\mathscr{E}_{1'}))+\frac{4\theta}{\varkappa_1\varkappa_4}(\bar\varepsilon_1\bar\varepsilon_4\mathscr{E}_{1'}$$
$$+\omega^2(\bar\varepsilon_1+\bar\varepsilon_4-\mathscr{E}_{1'}))+\frac{2\theta_2}{5\varkappa_3\varkappa_4}(\bar\varepsilon_3\bar\varepsilon_4\mathscr{E}_{1'}+\omega^2(\bar\varepsilon_3+\bar\varepsilon_4-\mathscr{E}_{1'}))\Big];$$

$$\left(\frac{12}{34}-\frac{34}{12}\right) \equiv \theta(1-F)\theta(2-F)\theta(F-3)\theta(F-4) \tag{11}$$
$$-\theta(3-F)\theta(4-F)\theta(F-1)\theta(F-2),$$
$$\theta = {}^1/_2\theta_1 - {}^1/_5\theta_2,$$
$$\theta_1 = \begin{cases}4, & \mu=0\\ 1, & \mu=3\end{cases},\qquad \theta_2 = \begin{cases}2, & \mu=0\\ 1, & \mu=3\end{cases},$$
$$\bar\varepsilon_i = \varepsilon_i - \varepsilon_{i'},\qquad \varkappa_i = \bar\varepsilon_i^{\,2}+\omega^2,$$
$$\mathscr{E}_1 = \varepsilon_1+\varepsilon_2-\varepsilon_3-\varepsilon_4,\qquad \mathscr{E}_{1'} = \varepsilon_{1'}+\varepsilon_2-\varepsilon_3-\varepsilon_4,$$
$$\bar\varkappa_{1'} = \mathscr{E}_{1'}^{\,2}+\omega^2,$$
$$\varepsilon_i = (k_i/k_0)^2,\qquad \varepsilon_{i'} = (\mathbf{k}_i+\mathbf{Q})^2/\mathbf{k}_0^2\qquad (i=1,2,3,4).$$

If $\mathbf{k}_i + \mathbf{Q}$ goes beyond the limits of the first zone, then it can be returned by subtracting the corresponding reciprocal-lattice vector. The function $D_3(\omega, Q)$ was calculated by the Monte Carlo method. The error was of the order of 15%. The behavior of D_3 can be assessed from the table.

The expression third-order for the correlation energy is

$$\bar{E}^{\,\mathrm{III}}_{corr} = a\int_0^{k_0} Q^2\,dQ\int_0^\infty d\omega\int_0^1 d\lambda\frac{D_1+\lambda D_2+\lambda^2 D_3}{1+\lambda D_1+\lambda^2 D_2+\lambda^3 D_3}. \tag{12}$$

Calculations by means of this formula yielded

$$\bar{E}^{\,\mathrm{III}}_{corr}(0) = 0.320,\quad \bar{E}^{\,\mathrm{III}}_{corr}(3) = 0.228,\quad \Delta\bar{E}^{\,\mathrm{III}}_{corr}(3) = -0.092 \text{ a.e.u.}$$

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