The role of correlation effects in the equation of state of a metal at zero temperature

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The correlation correction to the pressure in a transition metal at zero temperature is estimated in the random-phase approximation (RPA). With the example of vanadium it is shown that when correlation is taken into account the part of the pressure associated with the Coulomb interaction of the *d*-electrons is several times smaller than in the Hartree–Fock approximation.

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1. INTRODUCTION

The purpose of the present paper is to elucidate the possibility of using the Hartree-Fock approximation to calculate the equation of state of transition metals. In[1, 2], calculations of the pressure and compressibility in the primitive cell were carried out in the Hartree-Fock (HF) approximation for diamond and aluminum respectively. In the case of diamond the results indicate that the correlations play an unimportant role, while the calculations on aluminum gave no definite results on this question. As regards the role of the d-electrons, it is found that the HF approximation is unsatisfactory. Here we shall use the random-phase approximation (RPA). Although, as shown in[3], the perturbation-theory series evidently does not converge for this case, the RPA appears, nevertheless, to be reasonable for qualitative estimates.

The pressure of a metal at zero temperature, which is equal to the volume derivative of the ground-state energy, can be represented in the form of a sum of two terms[4, 5]—a term which may be called the kinetic pressure, which is expressed in terms of derivatives of the one-electron density matrix at the boundaries of the crystal cell, and a term which may be called the Coulomb part of the pressure, which is expressed in terms of the Coulomb interaction between the cells, so that the strong intra-cell interaction is completely excluded. The Coulomb interaction between cells is principally determined by the quantum oscillations of their charge density, inasmuch as the interaction of the neutral cells is small. In essence, the interaction associated with fluctuation of the charge of the cells determines the cohesion of the metal. It may be thought that the conduction electrons, and the oscillations of their density, are satisfactorily described by the HF approximation, although there is doubt about the applicability of this approximation for an unfilled d-shell. It is known[6] that, as the density of a metal is reduced to zero, in the presence of unfilled bands the Hartree-Fock description of the metal does not go over to a state of neutral atoms but preserves finite fluctuations of charge between them. Of course, on decrease of the density the metal ceases to exist; however, the d-electrons are in an analogous state even at normal density. Therefore, if they do give a contribution to the electrical conductivity and specific heat, the HF approximation should give a considerable error for them. An investigation of this question by perturbation theory was carried out in[3]. There it was shown that the state of the d-electrons is considerably closer to the limiting case of electrons localized at the atoms than to the Hartree-Fock limit. Therefore, the fluctuations of the charges at neighboring atoms should be considerably smaller. Consequently, the Coulomb pressure for the d-electrons will be considerably smaller than in the HF approximation. In the present paper we calculate this pressure directly in the approximations that were used in[3]. We confine ourselves to the RPA, i.e., effectively, to first order of the modified perturbation theory. This appears reasonable, since the passage to the limit of isolated atoms already goes through in this approximation (see below). The calculation for vanadium in this approximation gives a decrease of the Coulomb pressure of the d-electrons by a factor of seven compared with the HF approximation, i.e., correlation effects are extremely important.

2. COULOMB PRESSURE OF THE d-ELECTRONS

From formulas (5) and (6) of the paper[4], for the Coulomb part of the pressure in a metal we can obtain

$$P_{\text{Coul}}=\frac{1}{6|\omega|}\sum_{\mathbf{R}\neq 0}\int_{\omega}d\mathbf{r}_1\int_{\omega}d\mathbf{r}_2\rho(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})\frac{d}{d\lambda}\frac{\lambda}{|\mathbf{R}+\lambda(\mathbf{r}_2-\mathbf{r}_1)|}\Bigg| \qquad (1)$$

Here ω is the crystal cell, $|\omega|$ is its volume, $\mathbf{R}$ has its origin at the center of the cell ω and runs over the centers of all the other cells in the metal, and

$$\rho(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})=2\Gamma(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})-z\gamma(\mathbf{r}_1)\delta(\mathbf{r}_2)-z\gamma(\mathbf{r}_2+\mathbf{R})\delta(\mathbf{r}_1)+z^2\delta(\mathbf{r}_1)\delta(\mathbf{r}_2).$$

Here γ and Γ are the one- and two-electron matrices[4]; the first term describes the interaction of two electrons situated at the points $\mathbf{r}_1$ and $\mathbf{r}_2+\mathbf{R}$, the second and third describe the interaction of the electrons of a cell with a nucleus from another cell, and the fourth describes the interaction of the nuclei.

The function $\rho(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})$ can be represented in a more convenient form:

$$\rho(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})=[2\Gamma(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})-\gamma(\mathbf{r}_1)\gamma(\mathbf{r}_2+\mathbf{R})]+[\gamma(\mathbf{r}_1)-z\delta(\mathbf{r}_1)][\gamma(\mathbf{r}_2+\mathbf{R})-z\delta(\mathbf{r}_2)]. \qquad (2)$$

In the first term, which is in essence the two-electron correlation function, we shall be interested in the contributions pertaining only to the mutual interaction of the d-electrons. Inasmuch as their density is principally concentrated near the nuclei, it seems reasonable to neglect the multipole interaction of the cells, i.e., to put $\mathbf{r}_1=\mathbf{r}_2=0$ in the kernel of the integral (1). Then it is all the more necessary to neglect the second term in the expression (2), as it corresponds to the interaction of neutral cells having an almost spherically symmetric charge distribution. Finally, the expression (1) takes the form

$$P_{\text{Coul}}^{dd}=\frac{1}{6|\omega|}\sum_{\mathbf{R}\neq 0}\frac{1}{R}\left[\int_{\omega}d\mathbf{r}_1\,d\mathbf{r}_2 2\Gamma_{dd}(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R})-n_d^2\right]. \qquad (3)$$

Here n_d is the mean number of d-electrons per cell. It can be seen from the expression (3) that if the two-electron part of the Hamiltonian of the metal is defined in the form

$$H_{dd}(\delta)=\frac{1}{2}\sum_{i,j}{}'\left[\frac{1-\theta_{ij}}{|\mathbf{r}_i-\mathbf{r}_j|}+\delta\frac{\theta_{ij}}{R_{ij}}\right],$$

(θ_{ij} = 1 if the i-th and j-th electrons belong to different cells with distance R_{ij} between the centers, and θ_{ij} = 0 if the electrons belong to the same cell), then the expression (3) can be represented as

$$P^{dd}_{\mathrm{Coul}}=\frac{1}{3|\omega|K}\frac{\partial}{\partial\delta}E(\delta) \tag{4}$$

(K is the total number of cells in the metal).

In fact, if H(δ) is the total Hamiltonian, we have

$$\frac{\partial}{\partial\delta}E(\delta)=\frac{\partial}{\partial\delta}\langle|H(\delta)|\rangle=\left\langle\left|\frac{\partial H_{dd}}{\partial\delta}\right|\right\rangle=\frac{K}{2}\sum_{\mathbf{R}\neq0}\frac{1}{R}\int_{\omega}d\mathbf{r}_1\,d\mathbf{r}_2\,2\Gamma(\mathbf{r}_1|\mathbf{r}_2+\mathbf{R}),$$

since the exact, δ-dependent function $|\rangle$ of the ground state of the electron system of the metal is normalized to unity. This expression coincides with (3) to within a term related to n_d^2. This fact will be taken into account when we write down the perturbing part of the Hamiltonian in the next Section.

3. APPROXIMATION OF A COMPLETELY DEGENERATE d-BAND

For a qualitative estimate of P^{dd}_{Coul} we shall take the model of a completely degenerate d-band, introduced by Hubbard[7] and already used by us[3]. Thus, we assume that the motion of the d-electrons within one cell of the metal is determined by the Hamiltonian[3]

$$H_0^{dd}=\sum\varepsilon_k a_{\mathbf{k}\nu}{}^{+}a_{\mathbf{k}\nu}+\frac{B}{2K}\sum a^{+}_{\mathbf{k}_2{}',\nu_2}a^{+}_{\mathbf{k}_1{}',\nu_1}a_{\mathbf{k}_1\nu_1}a_{\mathbf{k}_2\nu_2}\delta_{\mathbf{k}_1+\mathbf{k}_2\mathbf{k}_1{}'+\mathbf{k}_2{}'}. \tag{5}$$

Here $\nu \equiv m\alpha$ takes ten values, m is the magnetic quantum number, α is the spin index, B is the interaction energy of two d-electrons of the same cell, and K is the total number of cells in the metal. The one-particle energy is taken in the form $\epsilon_k = a(k/k_0)^2$, where k_0 is the radius of the sphere with the volume of the first Brillouin zone and a is the width of the d-band in the spherical approximation[8]. Conservation of the total quasi-momentum holds to within an arbitrary reciprocal-lattice vector. The perturbation of the two-electron part of the Hamiltonian, in terms of which, according to (4), P^{dd}_{Coul} is expressed, has the form

$$H_{dd}'(\delta)=\frac{\delta}{2K}\sum_{\mathbf{R}\neq0}\frac{1}{R}\sum\exp[-i(\mathbf{k}_{2'}-\mathbf{k}_2)\mathbf{R}]a^{+}_{\mathbf{k}_2{}',\nu_2}a^{+}_{\mathbf{k}_1{}',\nu_1}a_{\mathbf{k}_1\nu_1}a_{\mathbf{k}_2\nu_2}\delta_{\mathbf{k}_1+\mathbf{k}_2\mathbf{k}_1{}'+\mathbf{k}_2{}'}. \tag{6}$$

If here we throw away the term with $\mathbf{k}_2 = \mathbf{k}_{2'}$, formula (4) will then give the expression (3) exactly, i.e., this is equivalent to subtracting n_d^2.

4. COULOMB PRESSURE IN THE HARTREE-FOCK APPROXIMATION

The HF approximation is, as usual, the first approximation of perturbation theory, i.e., the energy perturbation is equal to the trace of the perturbation over the unperturbed ground state. Inasmuch as the term corresponding to the perturbation with $\mathbf{k}_2 = \mathbf{k}_{2'}$ and, consequently, the term with $\mathbf{k}_1 = \mathbf{k}_{1'}$ have been discarded, there remains only the exchange part of the trace of the perturbation:

$$\langle0|H'(\delta)|0\rangle=-\frac{\delta}{2K}\sum\frac{1}{R}\exp[-i(\mathbf{k}_1-\mathbf{k}_2)\mathbf{R}]\langle0|a^{+}_{\mathbf{k}_1\nu_1}a_{\mathbf{k}_1\nu_1}a_{\mathbf{k}_2\nu_1}a^{+}_{\mathbf{k}_2\nu_1}|0\rangle$$
$$=-\frac{\delta}{2K}\sum_{\mathbf{k}_1,\mathbf{k}_2,\nu,\mathbf{R}\neq0}\frac{1}{R}\exp[-i(\mathbf{k}_1-\mathbf{k}_2)\mathbf{R}]\theta(k_F-k_1)\theta(k_F-k_2),$$

where, by definition of the unperturbed ground state $|0\rangle$ we have $a_{\mathbf{k}\nu}|0\rangle = 0$ if $k > k_F$ and $a^{+}_{\mathbf{k}\nu}|0\rangle = 0$ if $k < k_F$. Then, for the pressure of the d-electrons in the HF approximation we obtain, from (4),

$$P^{dd}_{\mathrm{Coul}}(\mathrm{HF})=\frac{-1}{6|\omega!}\frac{1}{K^2}\sum_{\mathbf{k}_1\neq\mathbf{k}_2}\frac{1}{R}\exp[-i(\mathbf{k}_1-\mathbf{k}_2)\mathbf{R}]\theta(k_F-k_1)\theta(k_F-k_2)$$
$$=-\frac{1}{6|\omega|}\sum_{\nu}\int_{\substack{\omega_k\\ \mathbf{k}_1\neq\mathbf{k}_2}}\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|^2}\sum_{\mathbf{R}\neq0}\frac{1}{R}\exp[-i(\mathbf{k}_1-\mathbf{k}_2)\mathbf{R}]\theta(k_F-k_1)\theta(k_F-k_2). \tag{7}$$

We introduce the notation

$$\sum_{\mathbf{R}\neq0}e^{-i\mathbf{QR}}/R\equiv F(Qr_0)/r_0, \tag{8}$$

where r_0 is the radius of the spherical cell of the metal. The function $F(Qr_0)$ has been tabulated by A. I. Voropinov by Ewald's method[9]. Then the final formula for the pressure in this approximation is

$$P^{dd}_{\mathrm{Coul}}(\mathrm{HF})$$
$$=\frac{-1}{6|\omega|r_0}\sum_{\nu}\int_{\omega_K}d\mathbf{Q}\int_{\omega_K}\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|^2}F(Qr_0)\theta(k_F-k_1)\theta(k_F-k_2)\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q}). \tag{9}$$

Here the pressure is obtained in atomic units of pressure (1 a.u.p. ≈ 293 × 10^6 atm) if the lengths are expressed in Bohr radii.

5. CORRELATION CORRECTION TO THE PRESSURE

The correlation correction to the energy is represented as the sum of all possible connected closed diagrams of second order and higher. This sum of diagrams can be obtained, e.g., as was done in[3], i.e., by detaching one of the ends of an interaction line and summing the diagrams already broken. In the given case we need to know only the small change, induced by the perturbation (6), in the intra-cell part of the correlation energy. It is equal to the same sum of diagrams, in which, however, one of the interaction lines is replaced by a line corresponding to this perturbation and all the other interaction lines in the diagram correspond to the operator (5). It is simpler to obtain the sum of such diagrams, inasmuch as we must now detach only the line corresponding to the perturbation. Therefore, each diagram appears only twice in the sum, instead of the 2n times for an n-th order diagram in the calculation of the energy itself. Therefore, the factor 1/n hindering the summation of the diagrams (a further integration is required to eliminate it[3]) is absent here. Taking into account these differences between the desired sum of diagrams and that found in[3] and the difference between the metric element in (5) and that in (6), we can immediately write down the answer on the basis of formula (3) of the paper[3]:

$$E_{\mathrm{RPA}}(\delta)=-\delta\frac{K}{2B}\int_{\omega_k}\frac{d\mathbf{Q}}{|\omega_k|}\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}d\xi\frac{X^2(\xi\mathbf{Q})}{1-X}\sum_{\mathbf{R}\neq0}\frac{1}{R}e^{i\mathbf{QR}}. \tag{10}$$

The function $X(\xi\mathbf{Q})$ in the random phase approximation has the form

$$X(\xi Q)=B\sum_{\nu}\int_{\omega_k}\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|}\frac{\theta(k_2-k_F)-\theta(k_1-k_F)}{\varepsilon_1-\varepsilon_2-\xi}\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q}). \tag{11}$$

Now formula (4) leads to the following correlation correction to the pressure:

$$P^{dd}_{\mathrm{Coul}}(\mathrm{RPA})=-\frac{1}{6|\omega|Br_0}\int_{\omega_K}\frac{d\mathbf{Q}}{|\omega_k|}F(Qr_0)\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}d\xi\frac{X^2(\xi Q)}{1-X}. \tag{12}$$

To conclude this Section we shall show that as B → ∞ the transition to isolated atoms occurs, and the Coulomb pressure vanishes as it should.

We note here that $P^{dd}_{\text{Coul}}(\text{HF})$ does not depend at all on the parameter B—the strength of the intra-cell interaction, since this pressure corresponds to taking into account only one ordinary exchange diagram, the interaction line of which is given by the operator (6).

From the expression (12), for B →∞, taking (11) into account, we obtain

$$\lim_{B\to\infty} P^{dd}_{\text{Coul}}(\text{RPA})=\lim_{B\to\infty}\frac{1}{6|\omega|r_0}\int\frac{dQ}{|\omega_k|}F\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}d\xi\,\frac{X(\xi Q)}{B}$$

$$=\frac{1}{6|\omega|r_0}\int\frac{dQ}{|\omega_k|}F\sum_{\nu}\int\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|}$$

$$\times\,[\theta(k_2-k_F)-\theta(k_1-k_F)]\,\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q})\frac{1}{2}\frac{\varepsilon_1-\varepsilon_2}{|\varepsilon_1-\varepsilon_2|} \tag{13}$$

$$=-\frac{1}{6|\omega|r_0}\int_{\omega_k}\frac{dQ}{|\omega_k|}F\sum_{\nu}\int_{\omega_k}\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|}\theta(k_F-k_1)\,\theta(k_2-k_F)\,\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q}).$$

Now, combining (9) and (13), we obtain

$$P^{dd}_{\text{Coul}}(\text{HF})+\lim_{B\to\infty}P^{dd}_{\text{Coul}}(\text{RPA})$$

$$=-\frac{1}{6|\omega|r_0}\int\frac{dQ}{|\omega_k|}F\int\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|}\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q})\,\theta(k_F-k_1)$$

$$=-\frac{1}{6|\omega|r_0}\int_{\omega_k}\frac{d\mathbf{k}_1}{|\omega_k|}\theta(k_F-k_1)\int_{\omega_k}\frac{dQ}{|\omega_k|}F(Qr_0)=0 \tag{14}$$

according to the expression (8).

6. NUMERICAL CALCULATION

It can be seen from the expression (11) for the function $X(\xi\mathbf{Q})$ that it is real and even on the imaginary axis. Therefore, the expression (12) for the correlation correction to the pressure can be rewritten in final form as:

$$P^{dd}_{\text{Coul}}(\text{RPA})=-\frac{a}{6|\omega|Br_0}\int\frac{dQ}{|\omega_k|}\frac{1}{\pi}\int_0^{\infty}d\bar{\omega}\,\frac{[\operatorname{Re}X(i\bar{\omega}\mathrm{Q})]^2}{1-\operatorname{Re}X}F(Qr_0), \tag{15}$$

where $\overline{\omega}=\omega/a$. Here the real part of the function X is

$$\operatorname{Re}X(i\bar{\omega}\mathrm{Q})=\frac{B}{a}\sum_{\nu}\int_{\omega_k}\frac{d\mathbf{k}_1\,d\mathbf{k}_2}{|\omega_k|}\frac{\theta(\bar{\varepsilon}_1-\bar{\varepsilon}_F)-\theta(\bar{\varepsilon}_2-\bar{\varepsilon}_F)}{(\bar{\varepsilon}_1-\bar{\varepsilon}_2)^2+\bar{\omega}_2}(\bar{\varepsilon}_2-\bar{\varepsilon}_1)\,\delta(\mathbf{k}_1-\mathbf{k}_2-\mathbf{Q}), \tag{16}$$

where $\bar{\epsilon}=\epsilon_i/a$. It can be seen from this expression that $\operatorname{Re}X \le 0$, and therefore (15) has no singularities.

The relation $B/a \approx 0.6/0.3 = 2$ holds for a whole series of transition metals: V, Fe, Ni, Ru, Pd, Nb[8]. The function defined by the expression (16) coincides exactly with $(-D_1)$ from[3], and has been computed in exactly the same way, but with ten points in Q instead of the previous three. All the details of the numerical calculation from this formula are described in[3]. The numerical calculation of the correlation correction to the pressure was performed only for vanadium in a nonmagnetic state, corresponding to $(k_F/k_0)^3 = 3/10$. Furthermore, since $|\omega_k||\omega| = (2\pi)^3$, $r_0 = 3.090$ and does not depend on the metal. We now note the following. According to (8), the function F integrated over the whole volume of the cell ω_k should give zero. In practice, we have

$$\int_0^{2{,}42}x^2F(x)\,dx=0.095.$$

The effect of this error can lead to a minimum only in the total pressure, consisting of exchange and correlation parts with opposite signs. For this it is necessary that the regions of integration in k-space in the expressions (9) and (16) be the same. Here, the region of integration in (9) has reduced to the region in (16). The results of the numerical calculation are the following:

$$P^{dd}_{\text{Coul}}(\text{HF})=-0.376\cdot10^{-3}\ \text{a.u.p.}\approx-0.110\cdot10^{6}\ \text{atm}$$

$$P^{dd}_{\text{Coul}}(\text{RPA})=0.323\cdot10^{-3}\ \text{a.u.p.}\approx0.0947\cdot10^{6}\ \text{atm}$$

$$P^{dd}_{\text{Coul}}(\text{HF})+P^{dd}_{\text{Coul}}(\text{RPA})=-0.535\cdot10^{-4}\ \text{a.u.p.}\approx-0.157\cdot10^{5}\ \text{atm}$$

Thus, it can be seen that correlation effects in the d-bands are very important.

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