On the Interaction of Electrons in Metals

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The energy of interaction between free electrons in an electron gas is considered. The interaction energy of electrons with parallel spin is known to be that of the space charges plus the exchange integrals, and these terms modify the shape of the wave functions but slightly. The interaction of the electrons with antiparallel spin, contains, in addition to the interaction of uniformly distributed space charges, another term. This term is due to the fact that the electrons repell each other and try to keep as far apart as possible. The total energy of the system will be decreased through the corresponding modification of the wave function. In the present paper it is attempted to calculate this "correlation energy" by an approximation method which is, essentially, a development of the energy by means of the Rayleigh-Schrödinger perturbation theory in a power series of e^2.

1.

THE attempt has been made in previous work[1] to give a more general expression for the wave function of free electrons in metals than that provided by Hartree's method of the self-consistent field[2, 3] or Fock's equations. The form of the wave function assumed in Fock's equations for a system of $2n$ electrons, occupying n doubly-degenerate states is

$$\frac{1}{n!}\begin{vmatrix} \psi_1(x_1) & \cdots & \psi_1(x_n) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \psi_n(x_1) & \cdots & \psi_n(x_n) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(y_1) & \cdots & \psi_1(y_n) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \psi_n(y_1) & \cdots & \psi_n(y_n) \end{vmatrix}, (1)$$

where x stands for three Cartesian coordinates of electrons with upward spin, and y for those of electrons with downward spin. The ψ_ν are the solutions of a Schrödinger equation in which the potential of the charge distribution of the other electrons enters as well as the potential arising from the ions.

In a metal the charge distribution of all electrons is practically unaltered by removing one so that the second quantity may be replaced by the former and the potential for a given

electron at the point u is given by adding to the Coulomb field of the ions the fields of all electrons with parallel and with antiparallel spin. The former distribution may be obtained by inserting u for x_n in (1) and integrating over all coordinates except x_1 and u, while the latter is obtained by a similar operation with the exception that the integration should be carried out over all coordinates except y_1 and u.

Actually, it had been shown in[1, 4] that the wave functions ψ_ν of the free electrons in a Na-lattice are very nearly plane waves $e^{2\pi i\nu \cdot x/L}$ where L is the cube edge of the crystal and ν stands for a set of three integers, $\nu \cdot x$ denotes the scalar product of ν and x. Hence the charge distribution of the electrons with opposite spin is practically uniform, that of the electrons with parallel spin uniform with a "hole" around u.[5]

In no wave function of the type (1) is there a statistical correlation between the positions of electrons with antiparallel spin. The purpose of the aforementioned generalization of (1) is to allow for such correlations. This will lead to an improvement of the wave function and, therefore, to a lowering of the energy value. This energy gain will be called "correlation energy."

2.

The new form of the wave function, assumed in[1] was

$$\frac{1}{n!}\begin{vmatrix} \psi_1(y_1\cdots y_n; x_1) & \cdots & \psi_1(y_1\cdots y_n; x_n) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \psi_n(y_1\cdots y_n; x_1) & \cdots & \psi_n(y_1\cdots y_n; x_n) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(y_1) & \cdots & \psi_1(y_n) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \psi_n(y_1) & \cdots & \psi_n(y_n) \end{vmatrix}, (2)$$

[1] E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1934).
[2] D. R. Hartree, Proc. Camb. Phil. Soc. 24, 89 (1928).
[3] J. C. Slater, Phys. Rev. 35, 210, 1930; V. Fock, Zeits. f. Physik 61, 126 (1930).

[4] J. C. Slater, Phys. Rev. 45, 794 (1934); A. Sommerfeld and H. Bethe, Geiger-Scheel's Handbuch der Physik, Vol. 24, 2nd part, 2nd edition, p. 406.
[5] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).

which contains the functions $\psi_\nu(y_1 \cdots y_n; x)$ which are different functions of x for different configurations $y_1, \cdots, y_n$ of the electrons with opposite spin, instead of the $\psi_\nu(x)$. It is proposed to find the best wave function, i.e., that with the lowest total energy of the form[6] (2). The $y_1, \cdots, y_n$ in $\psi_\nu(y_1 \cdots y_n; x)$ are to be viewed merely as parameters. (Cf. Eq. (23) ref. 1.) The total energy of the wave function (2) was previously calculated and relative to the solution of Fock's equations yielded the following energy

$$E_1 = \frac{1}{n!} \int dy\, |y|^2 \left\{ \sum_\nu \epsilon_\nu - \frac{h^2}{2m} \sum_{\nu\nu'} \sum_\kappa \left| \int \psi_{\nu'}(y; x_1)^* \frac{\partial \psi_\nu(y; x_1)}{\partial y_\kappa} dx_1 \right|^2 \right\}, \tag{3}$$

where $|y|$ denotes the second determinant of (1), the summation κ runs over all $3n$ coordinates y and that over ν and ν' over all occupied states, i.e., over all indices occurring in the wave functions in (1) or (2); $\psi_\nu(y; x)$ stands for $\psi_\nu(y_1 \cdots y_n; x)$ and dy for $dy_1 \cdots dy_n$. The quantities ϵ_ν are the integrals

$$\epsilon_\nu(y_1 \cdots y_n) = \int \psi_\nu(y; x_1)^* \{ V - (h^2/2m)(\Delta_{x_1} + \Delta_{y_1} + \cdots + \Delta_{y_n}) \} \psi_\nu(y; x_1) dx_1$$

$$+ \int \psi_\nu(x_1)^* (h^2/2m) \Delta_{x_1} \psi_\nu(x_1) dx_1, \tag{3a}$$

where again $V(y_1 \cdots y_n; x)$ is the difference between the potentials at the point x of a charge distribution corresponding to $\psi_1(y), \psi_2(y), \cdots, \psi_n(y)$, on the one hand, and point charges at $y_1, \cdots, y_n$, on the other.

It is necessary now to assume for $\psi_\nu(y_1, \cdots, y_n; x)$ the form

$$\psi_\nu(y; x) = \psi_\nu(x) \{ 1 + f_\nu(y_1 - x) + f_\nu(y_2 - x) + \cdots + f_\nu(y_n - x) \} \tag{4}$$

and that if ν and ν' are both occupied states

$$\int \psi_{\nu'}(y; x_1)^* (\partial \psi_\nu(y; x_1)/\partial y_\kappa) dx_1 = 0 \tag{4a}$$

so that the second term in (3) vanishes. Both (4) and (4a) will turn out to be correct in the approximation to be used. By means of (4) it is possible to transform (3a) so as to get rid of all derivatives with respect to the y, after which one may minimize (3) by minimizing $\epsilon_\nu(y_1, \cdots, y_n)$ for every combination of the y. This would lead to a differential equation for the $\psi_\nu(y_1 \cdots y_n; x)$ in which the y would be merely parameters. (The solutions $\psi_\nu(x)$ of Fock's equations which also enter into this equation are supposed to be known.) The result of the transformation is especially simple if one uses for $\psi_\nu(x) = \epsilon^{2\pi i\nu \cdot x/L}$, namely,

$$\epsilon_\nu(y_1 \cdots y_n) = \int \psi_\nu(y; x)^* \{ V - (h^2/m)(\Delta_x - (2\pi i\nu/L)\, \mathrm{grad}_x) \} \psi_\nu(y; x) dx. \tag{3b}$$

In addition to the energy contribution (3) which is negative and was calculated in[1] there is a further one which is generally positive. This arises from the fact that the probabilities of the relative distances of electrons with upward spin are changed by the transition from the $\psi_\nu(x)$ to the $\psi_\nu(y_1, \cdots, y_n; x)$. Since the latter will be large for x's, which lie in regions comparatively free from y's, the distribution of the x's will not be uniform throughout space and they will be nearer together than they were under the previous assumption.

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[6] The form (2) of the wave function is certainly not the correct one. It does not belong even to one single multiplicity but is a linear combination of functions of different "multiplicities" (belonging to different representations of the symmetric group). If, however, the functions $\psi_\nu(y_1 \cdots y_n; x)$ are not too different from the functions $\psi_\nu(x)$, they all belong to very low multiplicities. This is the only case, anyway, in which the present approximation is good and it can be expected that the real wave function is in this case near to (2).

In order to evaluate this energy change, one may first calculate the probability of two electrons with parallel spin being at the points x_1 and x_2, respectively, if the complete wave function is given by (1). Under the approximate assumption that $\psi_\nu(x) = \psi_0(x)e^{2\pi i \nu \cdot x/L}$ one obtains for this in the way given in reference 5,

$$|\psi_0(x_1)\psi_0(x_2)|^2 g(|x_1 - x_2|),\tag{5}$$

where

$$g(r) = 1 - 9\left(\frac{\sin (r/d) - (r/d)\cos (r/d)}{(r/d)^3}\right)^2\tag{5a}$$

is the probability of the distance $|x_1 - x_2| = r$ for free electrons with parallel spin,

$$d = (v_0/3\pi^2)^{\frac{1}{3}} = (4/9\pi)^{\frac{1}{3}}r_s = 0.521 r_s\tag{6}$$

is $1/(2\pi)$ times the wave-length of the fastest electron, v_0 is the atomic volume and r_s the radius of the sphere with this volume. If we make the assumption $\psi_\mu(y, x) = \psi_\nu(y, x)e^{2\pi i(\mu - \nu)\cdot x/L}$, an expression of the form (5) is valid for the wave function (2) as well as for (1) and the change of mutual potential energy of the electrons with upward spin arising from the transition from (1) to (2) is

$$E_2 = \frac{1}{n!}\int dy\,|y|^2 \sum_\nu \epsilon_\nu'(y_1 \cdots y_n),\tag{7}$$

where

$$\epsilon_\nu'(y_1 \cdots y_n) = \int dx_1 dx_2 (ne^2/2r)\{|\psi_\nu(y; x_1)\psi_\nu(y; x_2)|^2 - |\psi_\nu(x_1)\psi_\nu(x_2)|^2\}g(r).\tag{7a}$$

The $\frac{1}{2}$ enters once again because the interaction of a pair of electrons should be counted once only. In order to be able to evaluate the integral (7a), $g(r)$ has been replaced by

$$1 - e^{-1.6r/d}(1 + 1.6r/d + 1.2(r/d)^2),\tag{8}$$

which, as is shown in Fig. 1, runs rather near to $g(r)$.

3.

The task of Section 4 will be to calculate the wave functions $\psi_\nu(y_1 \cdots y_n; x)$ which minimize the sum of expressions (3b) and (7a) and to calculate $E_1 + E_2$ corresponding to these wave functions. Before doing this, however, an estimate of the order of magnitude of the effect to be expected should be given. This can be taken from calculations of atomic spectra by the method of Fock's equation or Hartree's field, and their comparison with experimental results. The best result in this connection seems to be that on the normal state of He, where Fock's equation is identical with Hartree's. The discrepancy here is[7] $0.077Ry$ (Rydberg units) for both electrons, or 12 Cal. per electron. This must be the amount of correlation energy in He.

The situation is somewhat more complicated in the calculation of the terms of O^{++}, O^+, and O by Hartree and Black,[8] since Hartree's method has been used instead of Fock's, and also because in the latter cases more than two electrons play important rôles. For O^{++} the differences between observed values (in brackets) and theory are

$$^3P(4.050)0.074; \quad ^1D(3.868)0.090;$$
$$^1S(3.658)0.176.$$

If we denote the radial wave function for the electrons by $P(r)$, these terms correspond to the linear combinations $P(r)P(r')$ multiplied by

$$xy' - yx'; \quad (x+iy)(x'+iy'); \quad xx' + yy' + zz'.$$

In the first case the correlation energy is very small, since the electrons are probably far away

[7] Cf. D. R. Hartree and A. L. Ingman, Mem. of the Manchester Lit. and Phil. Soc. **77**, 69, 87 (1933).

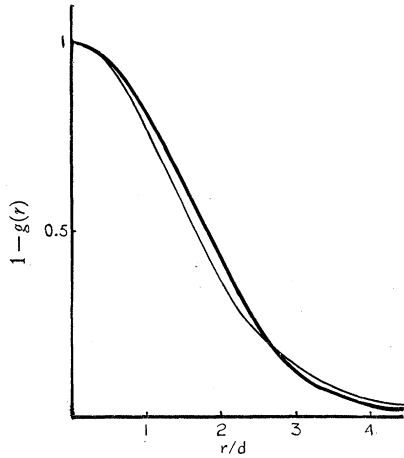[8] D. R. Hartree and M. M. Black, Proc. Roy. Soc. **A139**, 311 (1933).

FIG. 1.

from each other anyway, because their spins are parallel. In such cases in the theory of metals we do not take into account any correlation energy at all. The discrepancy in this case may, to a considerable extent, be due to the use of Hartree's instead of Fock's method, and certainly would be further diminished by the use of the latter. On the other hand, in the case of singlet's, Hartree's equations correspond much more closely to Fock's equation and the increased discrepancy of about $0 \cdot 050Ry$ is probably due to the neglect of the correlation energy. It is not quite clear, however, why it is so much greater in the ^1S than in the ^1D term.

A comparison of experimental and theoretical values in O^+ and O points in a similar direction, the correlation energy is smaller though in these cases by a factor of the order 2. It is evident that it must diminish eventually if one goes over to more and more loosely bound electrons, since because of the lower electron densities the total interaction energy diminishes and the correlation energy is only the non-appearance of part of this.

If one goes over to a metal like Na, on first sight the effect could be expected (because of the low electron density) to be much smaller than in He, about as great as in O. This will not be quite so, however, because the fluctuations in the potential of the electrons with downward spin will be greatly increased by their great number. The effect to be calculated in the next section will be about equal, therefore, to the effect per electron in He.

4.

Although the actual wave functions $\psi_\nu(x)$ in the Na lattice are actually different from plane waves $e^{2\pi i \nu \cdot x/L}$ in the Hartree-Fock approximation, we shall use plane waves for $\psi_\nu(x)$ in the subsequent calculation. Since only integrals over the unperturbed functions occur in the perturbation calculation, this will not introduce a great error, because the $\psi_\nu(x)$ are extremely near to plane waves in much the greatest part of the volume.

The whole following calculation will be performed in the approximation which corresponds to the second approximation in the Rayleigh-Schrödinger perturbation theory. The wave functions will be developed into a Fourier series

$$\psi_\nu(y; x) = L^{-\frac{3}{2}}(e^{2\pi i \nu \cdot x/L} + \sum_\mu \alpha_{\nu\mu} e^{2\pi i \mu \cdot x/L}), \quad (9)$$

$e^{2\pi i \nu \cdot x/L}$ being taken as unperturbed function and $V(y_1, \cdots, y_n; x)$ the perturbation. The $\alpha_{\nu\mu}$, which are functions of the y, are supposed to be small, so that third order terms of α and V will be neglected for the energy, and second order terms for the wave function.

For the actual calculation it can be seen, first of all, that one can replace a set of $\psi_\nu(y; x)$ by any orthogonal linear combination of them without affecting the final result. The orthogonality condition between $\psi_\nu(y; x)$ and $\psi_{\nu'}(y; x)$ gives

$$\alpha_{\nu\nu'} + \alpha_{\nu'\nu}{}^* + \sum_\mu \alpha_{\nu\mu} \alpha_{\nu'\mu}{}^* = 0. \quad (10)$$

By Schmidt's method one can build a set of orthogonal $\psi_\nu(y; x)$ such that $\alpha_{\nu\nu'} = 0$ for $\nu < \nu'$
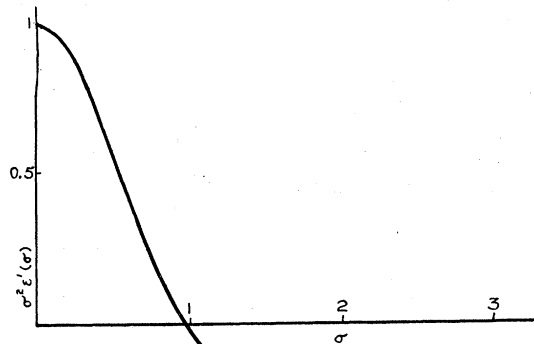

FIG. 2.

if ν' is occupied. It then follows under omission of the last term in (10) that $\alpha_{\nu\nu'}=0$ if ν and ν' are both occupied states, whence the summation over μ in (9) must be extended only over the unoccupied states. It is then seen at once that (4a) is satisfied in our approximation.

In order to calculate $\epsilon_\nu(y_1\cdots y_n)$ one must first calculate the matrix elements of $V(y_1,\cdots,y_n;x)$. The matrix elements $V_{\nu\nu}(y_1,\cdots,y_n;x)=V_{00}$ will

not be zero for all values of the y, but they evidently will not change the wave functions and merely give a contribution to the energy. The average value over all configurations of this contribution is zero, however, since the mean value of the potential of different configurations of charges is equal to the potential of the mean charges. Therefore, we shall set $V_{\nu\nu}(y_1,\cdots,y_n;x)=0$. For $\mu\neq\nu$ we have

$$
\begin{aligned}
V_{\nu\mu}(y_1\cdots y_n;x) &= L^{-3}\int e^{2\pi i(\mu-\nu)\cdot x/L}V(y;x)dx \\
&= -(1/4\pi^2(\mu-\nu)^2L)\int e^{2\pi i(\mu-\nu)\cdot x/L}\Delta V(y;x)dx \\
&= (e^2/\pi(\mu-\nu)^2L)\sum_{\kappa=1}^{n}e^{2\pi i(\mu-\nu)\cdot y_\kappa/L}
\end{aligned}
\tag{11}
$$

because of Poisson's equation.

For ϵ_ν, (3b) yields

$$
\epsilon_\nu(y_1\cdots y_n)=\sum_\mu(\alpha_{\nu\mu}V_{\nu\mu}+\alpha_{\nu\mu}{}^*V_{\nu\mu}{}^*)+\sum_{\mu\mu'}\alpha_{\nu\mu}{}^*\alpha_{\nu\mu'}V_{\mu\mu'}+\sum_\mu\frac{4\pi^2\hbar^2}{mL^2}(\mu^2-\mu\cdot\nu)\,|\,\alpha_{\nu\mu}\,|^2,
\tag{12}
$$

In order to calculate the $\epsilon_\nu'(y_1\cdots y_n)$ by means of (7a), the charge distribution for $\psi_\nu(y;x)$ will first be found:

$$
|\,\psi_\nu(y;x)\,|^2=L^{-3}+L^{-3}\sum_\mu(\alpha_{\nu\mu}e^{2\pi i(\mu-\nu)\cdot x/L}+\alpha_{\nu\mu}{}^*e^{2\pi i(\nu-\mu)\cdot x/L})+L^{-3}\sum_{\mu\mu'}\alpha_{\nu\mu}{}^*\alpha_{\nu\mu'}e^{2\pi i(\mu-\mu')\cdot x/L}.
\tag{13}
$$

Now $g(r)$ is 1 minus the function of the "hole," which decreases rapidly with increasing r. The 1, inserted into (7a), simply gives the energy difference of a uniform charge distribution and that corresponding to $\psi_\nu(y;x)$, namely,

$$
4\pi ne^2L^{-3}\left\{\sum_\mu\frac{|\,\alpha_{\nu\mu}\,|^2}{4\pi^2(\mu-\nu)^2/L^2}+R\sum_{\substack{2\nu-\mu\\ \text{unocc.}}}\frac{\alpha_{\nu\mu}\alpha_{\nu 2\nu-\mu}}{4\pi^2(\mu-\nu)^2/L^2}\right\},
\tag{14a}
$$

in which the terms higher than the second order in α are omitted, and R means that the real part of the following expression is to be taken. The second sum must be taken only over those μ's for which $2\nu-\mu$ is unoccupied, while μ itself is an unoccupied state in all summations. For the calculation of the other part of (7a), arising from the function of the hole, one sets x_1+r for x_2 in (7a), introduces (13), and performs the integration over x_1. The result

$$
2L^{-3}R\left\{\sum_\mu|\,\alpha_{\nu\mu}\,|^2+\sum_{\substack{2\nu-\mu\\ \text{unocc.}}}\alpha_{\nu\mu}\alpha_{\nu 2\nu-\mu}\right\}e^{2\pi i(\nu-\mu)\cdot r/L}
$$

must be multiplied with $ne^2/2r$ and the function of the hole $g(r)-1$, which must be taken from (8), and integrated over r. Setting $\sigma=2\pi(\mu-\nu)d/L$, this yields

$$
-\frac{4\pi d^2ne^2}{2.56L^3}R\left(\sum_\mu|\,\alpha_{\nu\mu}\,|^2+\sum_{\substack{2\nu-\mu\\ \text{unocc.}}}\alpha_{\nu\mu}\alpha_{\nu 2\nu-\mu}\right)\cdot\left(\frac{1}{1+\sigma^2/2.56}+\frac{1.063}{(1+\sigma^2/2.56)^2}+\frac{3.75}{(1+\sigma^2/2.56)^3}\right).
\tag{14b}
$$

Added to (14a) this gives with help of the relation $4\pi r_s^3/3=v_0$

$$\epsilon_\nu'(y_1\cdots y_n)=\frac{2^{\frac{1}{3}}}{3^{\frac{1}{3}}\pi^{\frac{3}{3}}}\frac{e^2}{r_s}R\left(\sum_\mu|\alpha_{\nu\mu}|^2+\sum_{\substack{2\nu-\mu\\ \text{unocc.}}}\alpha_{\nu\mu}\alpha_{\nu2\nu-\mu}\right)\epsilon'(\sigma),$$

$$\epsilon'(\sigma)=\frac{1}{\sigma^2(1+\sigma^2/2.56)}-\frac{0.415}{(1+\sigma^2/2.56)^2}-\frac{1.465}{(1+\sigma^2/2.56)^3}.$$

(14)

$\sigma^2\epsilon'(\sigma)$ is given graphically in Fig. 2.

This formula for the increase of potential energy between electrons with upward spin is not exact and may be viewed as containing two parts: First (14a), the increase of the potential of the space charges, due to the less even charge distribution for $\psi_\nu(y;x)$ than for $\psi_\nu(x)$. This increase is lowered by the second part (14b), caused by the greater efficiency of the Fermi hole in a non-uniform charge distribution. The first neglection was made in setting $\psi_\mu(y;x)=e^{2\pi i(\mu-\nu)\cdot x/L}\psi_\nu(y;x)$ when calculating ϵ_ν'. This tends to increase the ϵ_ν' especially for those ν, for which it is large anyway, because it overemphasizes the unevenness in the charge distribution. The second neglection was to keep no terms higher than the second order terms in α. This certainly decreases ϵ_ν', because part of the uneveness in the charge density is due to the higher terms, especially to those of the fourth order. Finally, the normalization constant, which is smaller than 1, enters in the second power in (14) and only in the first in (12). Its omission again increases (14). In the whole these errors will about compensate.

The final quantity to be minimized is, after omission of the higher order terms,

$$\epsilon_\nu+\epsilon_\nu'=R\sum_\mu\{2\alpha_{\nu\mu}V_{\nu\mu}+(t_{\nu\mu}+t_{\nu\mu}')|\alpha_{\nu\mu}|^2+t_{\nu\mu}'\alpha_{\nu\mu}\alpha_{\nu2\nu-\mu}\},$$

(15)

where

$$t_{\nu\mu}=\frac{4\pi^2h^2}{mL^2}(\mu^2-\mu\cdot\nu),\qquad t_{\nu\mu}'=\frac{2^{\frac{1}{3}}}{3^{\frac{1}{3}}\pi^{\frac{3}{3}}}\frac{e^2}{r_s}\epsilon'\left(\frac{2\pi(\mu-\nu)d}{L}\right).$$

(15a)

$V_{\nu\mu}$ is given in (11), $\epsilon'(\sigma)$ in (14), ν is an occupied state, the last term in (15) should be taken only if $2\nu-\mu$ is an unoccupied state. By setting the derivative of (15) with respect to $\alpha_{\nu\mu}^*$ equal to zero, one obtains

$$V_{\nu\mu}^*+(t_{\nu\mu}+t_{\nu\mu}')\alpha_{\nu\mu}=0$$

(16a)

if $2\nu-\mu$ is occupied. If it is unoccupied

$$V_{\nu\mu}^*+(t_{\nu\mu}+t_{\nu\mu}')\alpha_{\nu\mu}+t_{\nu\mu}'\alpha_{\nu2\nu-\mu}=0,\qquad V_{\nu\mu}^*+(t_{\nu2\nu-\mu}+t_{\nu\mu}')\alpha_{\nu2\nu-\mu}^*+t_{\nu\mu}'\alpha_{\nu\mu}=0.$$

(16b)

The last equation is obtained by differentiating (15) with respect to $\alpha_{\nu2\nu-\mu}$ and considering that $V_{\nu2\nu-\mu}=V_{\nu\mu}^*$ and $t_{\nu2\nu-\mu}'=t_{\nu\mu}'$. Solving (16), one finds if $2\nu-\mu$ is occupied

$$\alpha_{\nu\mu}=-V_{\nu\mu}^*/(t_{\nu\mu}+t_{\nu\mu}')$$

(17a)

and

$$\alpha_{\nu\mu}=-V_{\nu\mu}^*t_{\nu2\nu-\mu}/[(t_{\nu\mu}+t_{\nu\mu}')t_{\nu2\nu-\mu}+t_{\nu\mu}t_{\nu\mu}']$$

(17b)

if $2\nu-\mu$ is unoccupied, while μ is, of course, always unoccupied. These formulas show that the $\psi_\nu(y_1,\cdots,y_n;x)$ do have the form (4) with

$$f_\nu(y-x)=-\frac{e^2}{\pi L}\left(\sum_{\substack{2\nu-\mu\\ \text{occ.}}}\frac{e^{2\pi i(\nu-\mu)\cdot(y-x)/L}}{(\mu-\nu)^2(t_{\nu\mu}+t_{\nu\mu}')}+\sum_{\substack{2\nu-\mu\\ \text{unocc.}}}\frac{e^{2\pi i(\nu-\mu)\cdot(y-x)/L}}{(\mu-\nu)^2(t_{\nu\mu}+t_{\nu\mu}'+t_{\nu\mu}t_{\nu\mu}'/t_{\nu2\nu-\mu})}\right).$$

(18)

Inserting (17) into (15) one obtains for the total energy

$$\epsilon_\nu+\epsilon_\nu'=-\sum_{\substack{2\nu-\mu\\ \text{occ.}}}\frac{|V_{\nu\mu}|^2}{t_{\nu\mu}+t_{\nu\mu}'}-\sum_{\substack{2\nu-\mu\\ \text{unocc.}}}\frac{|V_{\nu\mu}|^2t_{\nu2\nu-\mu}}{(t_{\nu\mu}+t_{\nu\mu}')t_{\nu2\nu-\mu}+t_{\nu\mu}t_{\nu\mu}'}.$$

(19)

Instead of the second term one could write half of the sum of the terms for μ and $2\nu - \mu$, which makes it somewhat more symmetric.

5.

It would be rather difficult to perform the summation over μ in (19) for an arbitrary set of y_1, $\cdots$, y_n. Fortunately only the mean value of (19) with the weight $|y|^2/n!$ is needed and this can be computed quite easily. Since the t do not depend on the y, one finds

$$\frac{1}{n!}\int |V_{\nu\mu}|^2|y|^2 dy = \frac{e^4}{\pi^2(\mu-\nu)^4 L^2}\sum_{\kappa,\lambda=1}^{n}\int e^{2\pi i(\mu-\nu)\cdot(y_\kappa-y)/L}|y|e^{2\pi i(\nu_1 y_1 + \cdots + \nu_n y_n)/L}dy$$

$$= \frac{e^4}{\pi^2(\mu-\nu)^4 L^2}\left(\sum_{\kappa=1}^{n}1 - \sum_{\kappa\neq\lambda}\delta(\nu-\mu+\nu_\kappa-\nu_\lambda)\right).$$

(20)

The first term comes from $\kappa=\lambda$, the second from $\kappa\neq\lambda$. In the second, the summation over λ can be carried out, and it yields 1 if $\nu-\mu+\nu_\kappa$ is an occupied state, zero otherwise. The whole bracket is, therefore, equal to the number of occupied states ν', for which $\nu+\nu'-\mu$ is not occupied. Fig. 3 shows a cross section of the ν'-space through the origin and the point $\nu-\mu$. The radius of the circles is $(3n/4\pi)^{\frac{1}{3}}=L/2\pi d$. The sphere through the weak circle contains the points $\nu-\mu+\nu'$ and the hatched part is unoccupied. As a consequence, it is

$$\frac{1}{n!}\int |V_{\nu\mu}|^2|y|^2 dy = \frac{e^4 n}{\pi^2(\mu-\nu)L^2}\eta(2\pi(\mu-\nu)d/L), \qquad \eta(\sigma)= \begin{cases} 1 & \text{for } |\sigma|>2 \\[2mm] \dfrac{3|\sigma|}{4}-\dfrac{|\sigma|^3}{16} & \text{for } |\sigma|<2 \end{cases}$$

(21)

and hence

$$F_\nu = \frac{1}{n!}\int (\epsilon_\nu+\epsilon_\nu')|y|^2 dy = -\frac{2Ry}{3\pi^3}\int\limits_{\substack{|\sigma+\rho|>1 \\ |\sigma-\rho|<1}}\frac{\eta(\sigma)d\sigma}{\sigma^4[\sigma^2+\sigma\cdot\rho+c\epsilon'(\sigma)]} - \frac{2Ry}{3\pi^3}\int\limits_{\substack{|\sigma+\rho|>1 \\ |\sigma-\rho|>1}}\frac{\eta(\sigma)d\sigma}{\sigma^2[\sigma^4-(\sigma\cdot\rho)^2+2c\sigma^2\epsilon'(\sigma)]}.$$

(22)

Here $\rho=2\pi\nu d/L$, $\sigma=2\pi(\mu-\nu)d/L$ and the summation over μ has been replaced by an integration over σ. The total energy is expressed in Rydberg units. The constant c is

$$c=(2^{\frac{1}{3}}/3^{\frac{1}{3}}\pi^{\frac{2}{3}})(e^2 m d^2/h^2 r_s)=0.1106 r_s/a_0$$

(22a)

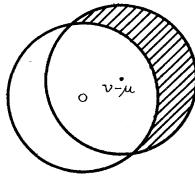when expressed as function of the radius of the "s-sphere" in Bohr units a_0.
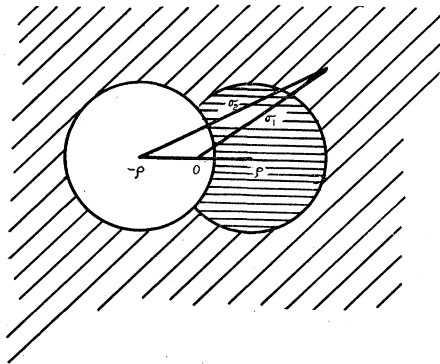

FIG. 3. Cross section of ν' space.
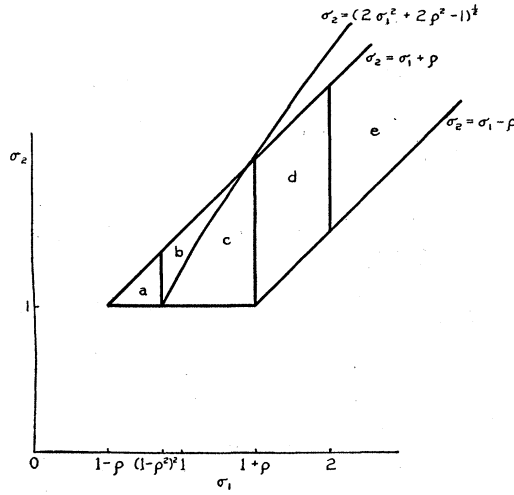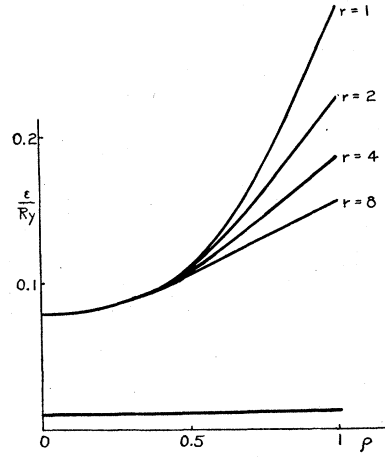

FIG. 4. Section of σ space.

FIG. 5. *Note:* $(1-\rho^2)^2$ should read $(1-\rho^2)^{\frac{1}{2}}$.

FIG. 6.

In order to perform the integration of (22), one may first introduce elliptic coordinates $\sigma_1 = |\sigma|$, $\sigma_2 = |\sigma+\rho| = |2\pi\mu d/L|$ in the σ-space, using as centers the origin and the point $-\rho$ (cf. Fig. 4). The first integral is to be extended over the horizontally, the second over the obliquely hatched region. The first will be a sum of two integrals (a) and (b) in Fig. 5, in both of which $\eta(\sigma) = 3\sigma_1/4 - \sigma_1^3/16$. The second integral is a sum of three integrals (c), (d) and (e), and in the first two of them the same expression is valid for $\eta(\sigma)$ while $\eta(\sigma) = 1$ in the last. For $d\sigma$ one writes $2\pi\sigma_1 d\sigma_1\sigma_2 d\sigma_2/\rho$, σ_1^2 for σ^2, and $\sigma \cdot \rho = \frac{1}{2}(\sigma_2^2 - \sigma_1^2 - \rho^2)$. The integration over σ_2 can be carried out simply and gives the five integrals

$$
\begin{aligned}
-F_\rho = {} & \frac{4Ry}{3\pi^2\rho} \int_{1-\rho}^{(1-\rho^2)^{\frac{1}{2}}} \ln \frac{2c\epsilon'(\sigma_1)+2\sigma_1^2+2\sigma_1\rho}{2c\epsilon'(\sigma_1)+\sigma_1^2+1-\rho^2} \quad \left(\frac{3\sigma_1}{4}-\frac{\sigma_1^3}{16}\right)\frac{d\sigma_1}{\sigma_1^3} \\
& + \frac{4Ry}{3\pi^2\rho} \int_{(1-\rho^2)^{\frac{1}{2}}}^{1+\rho} \ln \frac{2c\epsilon'(\sigma_1)+2\sigma_1^2+2\sigma_1\rho}{2c\epsilon'(\sigma_1)+3\sigma_1^2+\rho^2-1} \quad \left(\frac{3\sigma_1}{4}-\frac{\sigma_1^3}{16}\right)\frac{d\sigma_1}{\sigma_1^3} \\
& + \frac{4Ry}{3\pi^2\rho} \int_{(1-\rho^2)^{\frac{1}{2}}}^{1+\rho} \ln \frac{2\sigma_1 v+\sigma_1^2+\rho^2-1}{2\sigma_1 v-\sigma_1^2-\rho^2+1} \quad \left(\frac{3\sigma_1}{4}-\frac{\sigma_1^3}{16}\right)\frac{d\sigma_1}{\sigma_1^2 v} \\
& + \frac{4Ry}{3\pi^2\rho} \int_{1+\rho}^{2} \ln \frac{v+\rho}{v-\rho} \quad \left(\frac{3\sigma_1}{4}-\frac{\sigma_1^3}{16}\right)\frac{d\sigma_1}{\sigma_1^2 v} + \frac{4Ry}{3\pi^2\rho} \int_{2}^{\infty} \ln \frac{v+\rho}{v-\rho} \quad \frac{d\sigma_1}{\sigma_1^2 v},
\end{aligned}
$$

where v stands for $(2c\epsilon'(\sigma_1)+\sigma_1^2)^{\frac{1}{2}}$. A calculation of this quantity for $r_s = 4$ shows that it is practically equal σ_1 if $\sigma_1 > 2$ and the last integral can be evaluated accordingly. It yields

$$
\frac{4Ry}{3\pi^2\rho}\left\{\left(\frac{1}{8}-\frac{1}{2\rho^2}\right)\ln\frac{2+\rho}{2-\rho}+\frac{1}{2\rho}\right\} \approx \frac{Ry}{9\pi^2}\left(1+\frac{\rho^2}{20}\right).
$$

The other integrals were evaluated numerically and the results are plotted against ρ. Fig. 6 shows the plots for $r_s = 1, 2, 4, 8$. From this, the mean value of the correlation energy which is the mean value of $-\frac{1}{2}F_\rho$ with the weight ρ^2, was calculated, and plotted against r_s. The $\frac{1}{2}$ enters, because the whole energy correction is present only for half of the electrons, that is, those with upward spin. In Fig. 7 the upper curve represents the values calculated in this way. The energy is given in multiples of e^2/r_s.

6.

One must remember, of course, that the preceding calculation is only an approximate one. Even if one confines oneself to wave functions of the form (2), the upper curve of Fig. 7 gives the correlation energy in first approximation only. The neglections are due to three causes: first to the use of an unnormalized wave function, second to the neglection of the terms with higher than the second power of α in ϵ_ν, when going over from (12) to (14a) and third to the non-complete orthogonality of the wave functions employed. Our approximation is good if the α's are small. One gets an idea about the accuracy of the approximation by calculating $\sum_\mu \int |\alpha_{\nu\mu}|^2 |y|^2 dy/n!$ (which is the reciprocal square of the normalization constant minus one), though an idea only, since $\sum_\mu |\alpha_{\nu\mu}|^2$ should really be small for all configurations of the y, not only its mean value. A calculation of the former quantity shows[9] that it stays well below one, except for large r_s and for ρ which are very near to 1. It is in these cases that our approximation must be expected to break down.

The real value of the correlation energy will be smaller in these cases than the calculated one. The correction with the normalization constant could easily be taken into account, as has been shown at another place.[10] It always decreases the correlation energy, not very much, however, as the magnitude of the normalization constant or the formulas in[10] show. The second neglection is probably more dangerous and also more laborious to correct. It has been done for one point ($r_s = 4$) only and for this one very roughly. The second neglection also increased the calculated value of the correlation energy, since it amounts to taking $1-2f$ instead of $(1-f)^2$ for the probability of the electron being at a certain point, and the minima of $1-2f$ are much deeper than those of $(1-2f)^2$ (the maxima are lower but less important).

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[9] The greatest part of the numerical work has been done by Dr. M. Vermes of Budapest. A table of the calculated values is given here:

ρ	$r=1$	4	8
0	0·006	0·10	0·45
0·4	0·009	0·14	0·54
1	0·04	0·30	0·94

[10] To appear shortly in the Bull. of the Hung. Acad.

If the electrons had no kinetic energy, they would settle in configurations which correspond to the absolute minima of the potential energy. These are closed-packed lattice configurations, with energies very near to that of the body-centered lattice. Here, every electron is very nearly surrounded with a spherical hole of radius r_s and the potential energy is smaller than in the random configuration by the amount $0.75 = e^2/r_s$. This would be the sum of the correlation energy and that due to the Fermi hole. Since the latter one is,[11, 1] $0.458e^2/r_s$, the maximum amount of the correlation energy is $0.292e^2/r_s$. This value will be attained only if the kinetic energy can be neglected, i.e., for $r_s = \infty$, and represents the asymptote to the real correlation energy curve, which is attempted to be drawn into Fig. 7. It appears to run much higher than one would have thought without calculation. I believe it to be in error everywhere by less than 20 percent.

The dotted line at $0.142e^2/r_s$ corresponds to a correlation energy as great as assumed in the first calculation[5] giving $0.6e^2/r_s$ together with the energy of the Fermi hole.

The calculated constants of the Na lattice with the correlation energy of Fig. 7 and the other quantities as in reference 1 are as follows: lattice constant 4.62A as compared with the observed value of 4.23A. The binding energy associated with this is 26.1 Calories, to be compared with the observed value of 26.9. The calculated value of the binding energy for the observed lattice
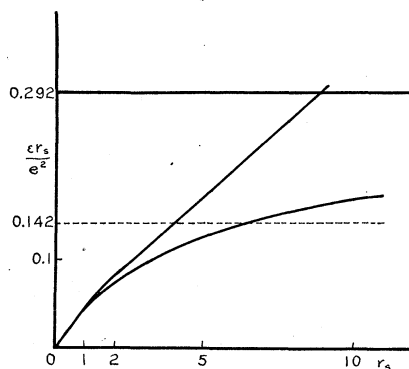

FIG. 7.

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[11] F. Bloch, Zeits. f. Physik **57**, 545 (1929).

constant is 22.3 Cal. As far as the lattice constant goes, one must remember, however, that both the correlation energy and that due to the Fermi hole are calculated for a flat wave function and the wave functions are flat only for $r_s = 4$ and its neighborhood.

The magnitude of the correlation energy is important for questions of paramagnetism and ferromagnetism as well as for questions of lattice energy. It modifies Bloch's original theory on the ferromagnetism of free electrons[11] in such a way that it yields ferromagnetism in fewer cases than in its original form.[12] I hope to return to this question at another time.

I wish to express my gratitude to Dr. F. Seitz for his kind help in connection with the preparation of this manuscript.

[12] A paper of S. Schubin and S. Wonsowsky, Proc. Roy. Soc. A145, 159 (1934) which appeared recently, points in the same direction.

Thermal Expansion and the Ferromagnetic Change in Volume of Nickel

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The coefficient of thermal expansion is measured at intervals of 2.5°C between 200°C and 500°C for single and polycrystalline specimens of nickel of varying known degrees of purity. The data yield the value $3.24 \pm 0.15 \times 10^{-4}$ for the ferromagnetic change in volume per unit volume of pure nickel.

INTRODUCTION

WHEN the coefficient of thermal expansion of nickel is plotted as a function of temperature the resulting graph has a hump which starts at about 200°C and terminates in the neighborhood of the Curie point. The area under the graph represents a change of length (and hence of volume), and the area under the hump may properly be taken as a measure of the change in volume associated with those interatomic forces (or energies) in terms of which the ferromagnetism of the material finds its explanation. Fowler and Kapitza[1] were the first to point out that Heisenberg's theory of ferromagnetism is competent to offer a quantitative description of this phenomenon. Their calculation has been extended by Powell,[2] who obtained an expression relating the change in volume per unit volume to the exchange energy between pairs of electrons belonging to neighboring atoms. The observations upon which Powell based his numerical estimate of the former quantity were obtained by Colby,[3] who worked with polycrystalline nickel of unspecified purity. It seemed worth while to repeat Colby's measurements upon single and polycrystalline nickel of varying known degrees of purity, and to extend them over a greater range of temperature in order to increase the precision of the base line from which the hump is reckoned. The present paper is a report based upon these experiments.

APPARATUS AND METHOD

The dilatometer (Fig. 1) is constructed entirely of fused quartz. A knife edge, A, and a table, B, rest upon a flat plate, C. The top of the table is ground flat and polished, and carries a ground roller about 1 mm in diameter. The specimen, S, is a circular cylinder about 5 mm in diameter and 6 cm to 7 cm long. A tiny lateral scratch is made near one end and the other end is polished. The scratch engages the knife edge and the polished end rests on the roller. Mirrors M_2 and M_4, of gold sputtered on quartz, are fused to the ends of the roller. These mirrors are rotated slightly with

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[1] Fowler and Kapitza, Proc. Roy. Soc. A124, 1 (1929).
[2] Powell, Proc. Phys. Soc. 42, 390 (1930).

[3] Colby, Phys. Rev. 30, 506 (1910).