Ground-State Energy of Metallic Hydrogen. I

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The ground-state energy of metallic hydrogen is calculated within the framework of a perturbation expansion by interpreting the perturbation series as that for two simpler systems weakly interacting, one being the electron gas system, the other that of electrons moving in the periodic potential of the lattice neutralized by a uniformly distributed negative charge. The decomposition is conveniently obtained by dividing the Rayleigh-Schrödinger perturbation expansion into three parts, the first two parts representing essentially the energy of the two simpler problems while the third part gives a series expansion for the small interaction terms. The first nonvanishing term in the latter comes from third order in the Rayleigh-Schrödinger series and has the small value $0.001\,r_s$ Ry per electron, where r_s is the radius of the unit sphere in atomic units. The interaction between the two systems is therefore assumed to have this order of magnitude.

The Fermi surface which leads to minimum energy of the total system in the high-density limit has been expressed in terms of anisotropy constants. The deviation from a spherical surface contributes no terms to the energy larger than order r_s^2, with a coefficient of order 10^{-5} Ry.

The ground-state energy for the N electrons then is given by

$$E = V_L + E_{eg}(0) + [E_p(0) - \epsilon_0 - \langle V_p \rangle] + 0.001 N r_s + O(r_s^2, r_s^2 \ln r_s),$$

where V_L is the energy of a lattice of positive charges in a uniform background negative charge, $E_{eg}(0)$ is the ground-state energy of the electron gas, $E_p(0)$ is the energy of the periodic potential problem for a spherical Fermi surface, ϵ_0 is the Fermi energy of free electrons, and $\langle V_p \rangle$ is the average value of the periodic potential. The uncertainty introduced by neglecting the $O(r_s^2)$ and higher order terms in the above equation is estimated, from previous considerations, to be of order $10^{-3} N r_s$ Ry.

The energy $E_p(0)$ may be calculated by conventional band methods or by means of many-body perturbation theory. The latter gives an expansion

$$E_p(0) = N(2.21/r_s^2 - 0.613/r_s - 0.0905 - 0.018 r_s + \cdots)$$

in powers of r_s, for a body-centered-cubic lattice. An estimate of the next or r_s^2 term is $-0.005 r_s^2$.

The use of this expansion for $E_p(0)$ and of previous estimates for $E_{eg}(0)$ gives a result for the energy of metallic hydrogen very close to the previous calculations of Wigner and Huntington.

INTRODUCTION

IN the application of many-body techniques toward understanding the properties of electrons in a crystalline solid, the simplest case to consider is that of a lattice of hydrogen atoms. Although such a crystal has not been found in nature, it presumably has properties similar to some of the alkali metals.

It is assumed that, as a function of density, the problem divides itself into two parts: a high-density or metallic region where the electrons are "itinerant," and a low-density, nonmetallic region where the electrons are "localized."

Progress toward a solution for the ground-state energy in the high-density case has been made by a number of authors, notably Wigner and Huntington,[1,2] who applied the Wigner-Seitz method to obtain an approximate solution for the Hartree-Fock equation and added to this solution an estimated "correlation energy;" and Bellemans and De Leener[3] who used the quantum statistical formalism of Bloch and de Dominicis.[4] (We make no attempt to give a complete list of formal analyses of the general problem.[5]) The principal uncertainty in these calculations is, in the first case, in the *a posteriori* estimate of a correction term; and for the second case, in questions as to the rate of convergence of the series expansion, if indeed it converges at

all in the region of interest, $r_s > 1$.[6] (The quantity r_s is the radius of the unit sphere in Bohr radii.) The result of reference 3, in fact, seems to lead to no binding energy.

It is our present intent to investigate the ground-state energy first in the high- and then in the low-density limit, and, as in the electron-gas problem,[7] to extrapolate the two solutions toward each other to indicate how well they match; although as Mott[8] has pointed out, a discontinuity in slope might be expected at the metal-to-nonmetal transition.

RESULTS OF THE HIGH-DENSITY CALCULATION

For the calculation in the high-density region we use Rayleigh-Schrödinger perturbation theory, with the total of Coulomb interactions as the perturbing term.[9]

In perturbation theory each unperturbed state, with degeneracy properly treated, leads to a perturbed level, and, in principle, the ground state is obtained by calculating all the perturbed levels and determining which of them lies lowest. Each unperturbed state may be classified by the surface enclosing the occupied momenta.

It is assumed at the outset that the ground state arises from a surface close to the Fermi sphere. Therefore, the perturbed states to be examined are restricted to those which come from zeroth order states that are simple distortions of the Fermi sphere, the distortions having crystal symmetry. Since these states occupy minimum volume in momentum space, they are specified

[1] E. Wigner and H. B. Huntington, J. Chem. Phys. **3**, 764 (1935).

[2] See also R. Kronig, J. DeBoer, and J. Korringa, Physica **12**, 245 (1946); and N. H. March, *ibid.* **22**, 311 (1956).

[3] A. Bellemans and M. De Leener, Phys. Rev. Letters **6**, 603 (1961).

[4] C. Bloch and C. de Dominicis, Nuclear Phys. **10**, 181 (1959).

[5] For example, J. Hubbard, Proc. Roy. Soc. (London) **A244**, 199 (1958); P. Nozières and D. Pines, Phys. Rev. **109**, 741 (1958); and W. Kohn and J. M. Luttinger, *ibid.* **118**, 41 (1960).

[6] R. A. Ferrell, Phys. Rev. Letters **1**, 443 (1958).

[7] W. J. Carr, Jr., R. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961).

[8] N. F. Mott, Phil. Mag. **6**, 287 (1961).

[9] This choice of the unperturbed Hamiltonian is dictated by the practical problems of computation, which make simple unperturbed functions highly desirable.

TABLE I. The energy V_L in rydbergs per positive particle of a lattice of positive charges neutralized by a uniform negative charge.

$V_L \times r_s$	Lattice	Reference
−1.79186	bcc	a
−1.79172	fcc	a
−1.760	sc	b
−1.79168	hcc	c

 a K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).
b W. J. Carr, Jr., Phys. Rev. **122**, 1437 (1961).
c W. Kohn and D. Schechter (unpublished).

simply by a set of $N/2$ momenta, where N is the number of electrons.[10]

In Rayleigh-Schrödinger theory it is very simple to divide the perturbation series so that it describes two simpler problems which weakly interact, the simpler problems being that for the electron gas and that for single electrons moving in a periodic potential, where the potential is for the fixed positive charges neutralized by a uniform background of negative charge. The essence of the procedure comes from arranging the series expansion into three parts. In two of these parts the analytic continuation of the series is readily apparent (as eigenvalues of the simpler systems), so that in the final analysis the perturbation expansion must be depended upon only to estimate the small interaction term between the two systems.

First, however, the complete series expansion will be considered.

The energy is shown to be

$$E(\nu) = V_L + E_{eg}(\nu) + [E_p(\nu) - \epsilon_\nu - \langle V_p \rangle] + E_{int}(\nu), \quad (1)$$

where ν is the particular set of momenta labeling the perturbed state that leads to minimum energy. The term $E_{eg}(\nu)$ is the eigenvalue of the electron gas problem which arises from the νth unperturbed state, $E_p(\nu)$ is the same for the periodic potential problem, and $E_{int}(\nu)$ measures the interaction between these systems. The quantity $\langle V_p \rangle$ is a diagonal element of the periodic potential (the same for all ν), ϵ_ν is the unperturbed energy (Fermi energy of free electrons) in the νth state, and V_L is the energy of the lattice of positive charges in a uniform background negative charge as given in Table I.

The formulation (1) is useful only if E_{int} is small, which indeed seems to be the case. The interaction term is defined only by the perturbation expansion [Eq. (25) in the following text]

$$E_{int}(\nu) = NC(\nu)r_s + \cdots, \quad (2)$$

which for exact results must converge. However, in any case there is some justification for using the first term in the series to estimate the order of magnitude of

the function which the series represents. The first constant in this series, $C(\nu)$, is finite and relatively easy to evaluate, although succeeding terms contain divergences, as in the case of the electron gas,[11] and would have to be treated by summing the proper diagrams.

The next step in the calculation involves finding the optimum unperturbed state ν which minimizes the energy of (1). Stated conversely, ν is the level into which the ground state of the system would go if the Coulomb interactions were adiabatically turned off.[12] We shall take the surface enclosing the unperturbed state ν as the definition of the "Fermi" surface. While the precise nature of the Fermi surface in an interacting system is still a matter of some controversy,[13] clearly it is closely related to the above definition, as others have previously recognized.[14–16]

If, for simplicity, only lattices with cubic symmetry are considered, the Fermi surface for high density may be expanded in terms of anisotropy constants K_1, K_2, $\cdots$, and powers of S and P, where $S = \alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2$, $P = \alpha_1^2\alpha_2^2\alpha_3^2$ with the α's the direction cosines, in momentum space, relative to cubic axes. We take orthogonal combinations of these functions, i.e., Kubic harmonics, and write

$$k_F{}^3 = k_{F_0}{}^3\{1 + K_1(5/2)(21)^{1/2}[S - \langle S \rangle]$$
$$+ K_2(231/8)(26)^{1/2}[P - \langle P \rangle - (1/11)(S - \langle S \rangle)]$$
$$+ K_3(65/8)(561)^{1/2}[S^2 - \langle S^2 \rangle$$
$$- (18/65)(S - \langle S \rangle) - (4/5)(P - \langle P \rangle)] + \cdots\}, \quad (3)$$

where $\langle S \rangle = 1/5$, $\langle P \rangle = 1/105$, and $\langle S^2 \rangle = 1/21$ are the averages of these functions over all solid angles. The Kubic harmonics are normalized to 4π and the volume enclosed by the surface (3) is constant and equal to $\frac{4}{3}\pi k_{F_0}{}^3$, where k_{F_0} is the radius of the spherical Fermi surface. As $r_s \to 0$, the anisotropy constants must approach zero since the kinetic energy dominates and the Fermi surface approaches a sphere; therefore, for small r_s the K's are small and the cube root of the right-hand side of (3) may be expanded to obtain

$$k_F(\alpha_1, \alpha_2, \alpha_3)$$
$$= k_{F_0}[1 + \tfrac{1}{3}K_1(5/2)(21)^{1/2}[S - \langle S \rangle] + \cdots]. \quad (4)$$

Quantities on the right-hand side of (1) may now be evaluated in terms of the anisotropy constants and the resultant expression minimized with respect to the K's.

[10] Except for the spherical surface, other states degenerate with these still exist. However, in a quasi-infinite system exact degeneracy of this type is assumed unimportant, as it is overwhelmed by the near degeneracy.

[11] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).
[12] For the particular class of states being investigated, it makes no difference whether only the interactions between electrons or all the Coulomb interactions are turned off. If it is only the electron interactions, a surface is obtained in the pseudo-momentum space of a set of Bloch functions. If now the electron-lattice interaction is turned off, the set of Bloch functions go over to a set of plane waves with the same surface in real momentum space; the wave vectors are preserved.
[13] J. M. Luttinger, *The Fermi Surface* (John Wiley & Sons, Inc., New York, 1960).
[14] W. Kohn and J. M. Luttinger, Phys. Rev. **118**, 41 (1960).
[15] A. Klein, Phys. Rev. Letters **4**, 601 (1960).
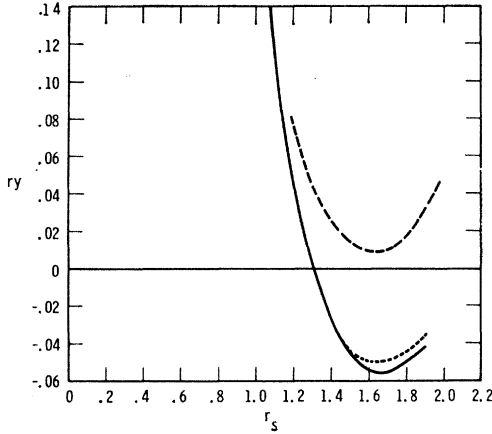[16] G. Wentzel, Phys. Rev. **120**, 659 (1960).

FIG. 1. The binding energy in rydbergs per atom plotted against r_s (negative values indicate binding). —— Eq. (9) with expansion (8) used for E_p and the values of E_{egc} taken from reference 7; . . . . . Wigner and Huntington; – – – – Bellemans and DeLeener. The dashed curve is for the s.c. case, the other two for bcc. Zero-point energy of the nuclei has not been included.

For symmetry reasons, the energy of the electron gas problem contains no linear terms in the K's; the leading terms are quadratic. (If it were otherwise, a sphere would not be the surface of lowest energy.) The energy of the periodic potential problem, however, contains linear terms, which allow the total energy to be minimized. The values of the K's leading to minimum energy are obviously a function of r_s. The leading term in K_1 (Appendix B) for a bcc lattice is $0.00115r_s{}^2$ and for fcc, $0.00294r_s{}^2$. The corresponding values for K_2 are $-0.00123r_s{}^2$ and $0.00153r_s{}^2$, and for K_3 are $0.000304r_s{}^2$ and $0.000280r_s{}^2$. The next terms in the K's are of the order $r_s{}^3$. The results indicate a bulging of the Fermi surface in the [110] direction for the bcc lattice and in the [111] for the fcc. These are the directions to the closest boundary.

Since the anisotropic Fermi surface contributes no energy terms of order less than $r_s{}^2$, it is proper to write (1) as[17]

$$E(\nu) = V_L + E_{eg}(0) + [E_p(0) - \epsilon_0 - \langle V_p \rangle]$$
$$+ NC(0)r_s + O(r_s{}^2, r_s{}^2 \ln r_s), \quad (5)$$

where the subscript zero indicates the isotropic Fermi surface or the ground state of the unperturbed system, and $C(0)$, given by Eq. (25), has the approximate value 1×10^{-3} Ry for both the bcc and fcc lattices.[18]

If the expansion for $E_p(0)$ obtained in the following text is substituted into (5), the results for bcc and fcc lattices are, in Ry units per particle,

$$E_{bcc} = E_{eg}(0) - 1.79186/r_s - 0.0905 - 0.017r_s$$
$$+ O(r_s{}^2, r_s{}^2 \ln r_s) \quad (6)$$

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[17] The results obtained here do not conflict with the calculations of Kohn and Luttinger in reference 14 who investigated terms of an order independent of r_s. Their specific application was for special potentials of no interest in the present problem.

[18] The author is indebted to Dr. A. E. Fein for advice and to Miss Esther Paran for programming the numerical calculation of these integrals.

and

$$E_{fcc} = E_{eg}(0) - 1.79172/r_s - 0.0922 - 0.017r_s$$
$$+ O(r_s{}^2, r_s{}^2 \ln r_s), \quad (7)$$

where the r_s term was computed only for the bcc case but used for both.

It is observed that for very small r_s, E_{bcc} lies lower, but for larger r_s it seems likely that the fcc crystal will have lower energy. If an expansion up to the $r_s{}^2$, $r_s{}^2 \ln r_s$ terms is made for $E_{eg}(0)$, then the resulting series (6) is exact up to this order. Because of the E_{eg} contribution, however, the series may have only a small radius of convergence.

Terms in this expansion up to those in r_s, $r_s \ln r_s$ agree with the previous results of Bellemans and De Leener. However, the additional r_s, $r_s \ln r_s$ contributions are of interest in that they and higher order terms must lead to most of the binding.

The expansion for $E_p(0)$ is of interest in itself from the point of view of band calculations. For the bcc case the value of $\langle V_p \rangle$ is[19] $-0.613r_s{}^{-1}N$ and

$$E_p(0) = N[2.21/r_s{}^2 - 0.613/r_s$$
$$- 0.0905 - 0.018r_s + O(r_s{}^2)]. \quad (8)$$

The coefficient of the $r_s{}^2$ term has been estimated to be about -0.005, and it seems apparent that the expansion (8) is accurate at least in the range $r_s < 2$.

APPROXIMATE CONTINUATION OF RESULT TO LARGER r_s

It will be assumed that the interaction term still is of the order NCr_s and may be neglected. Also the effect of anisotropy is assumed to be even smaller (see Appendix B), and, therefore, the first three terms in Eq. (5) apply approximately over a wider range of density than indicated by their series expansion.

It is convenient to rewrite these terms from (5) in the form

$$E \approx E_p(0) + \epsilon_x(0) + V_L - \langle V_p \rangle + E_{egc}(0), \quad (9)$$

where $\epsilon_x(0)$ is the ground-state exchange energy for free electrons, $\epsilon_x(0) = -0.916Nr_s{}^{-1}$, and $E_{egc}(0)$ is the correlation energy of the electron gas in its ground state.

The term $E_p(0)$, which as a perturbation series is

$$E_p(0) = \epsilon_0 + \langle V_p \rangle + \sum_{\mu}{}' \frac{|(V_p)_{0\mu}|^2}{\epsilon_0 - \epsilon_\mu} + \cdots, \quad (10)$$

is given by

$$E_p(0) = \sum_k \mathcal{E}_k, \quad (11)$$

where if the Hamiltonian for the periodic potential problem is $H_p = \sum_i H_{pi}$, the sum being over all electrons, then $H_{p1}\psi_k = \mathcal{E}_k\psi_k$. The sum on k is over the wave vectors inside the Fermi sphere.

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[19] J. Callaway and M. L. Glasser, Phys. Rev. 112, 73 (1958).

The result given in (9) has some resemblance to the Wigner-Seitz[20] approximation, where the energy is taken to be the Hartree-Fock energy plus the correlation energy of a free electron gas. This is particularly true when the various approximations used in the Wigner-Seitz method for the Hartree-Fock energy are made.[21] However, in the present formulation it is not, even in principle, the Hartree-Fock problem which must be solved, but rather the simpler one of electrons moving in the field of the positive charge neutralized by a uniform negative charge. Furthermore in this formulation the uncertainty in the result can be estimated, this uncertainty, in the range of metallic densities, being the E_{int} of order NCr_s or $10^{-3}r_s$ Ry per particle.

In Fig. 1 the energy is plotted with the expansion (8) (including the estimated value of the r_s^2 term) used for E_p and with E_{egc} as given in reference 7. The uncertainty coming from using these values for E_{egc} and from terminating the series expansion for E_p is estimated to be about 10^{-2} Ry. The result is very close to that of Wigner and Huntington. Minimum energy occurs at about $r_s = 1.66$.

DETAILS OF THE ENERGY CALCULATION

The unperturbed Hamiltonian is the kinetic energy operator and the perturbing term is

$$V = \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} + \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{R_{ij}} - \sum_i \sum_j \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_j|}, \quad (12)$$

in an obvious notation for the Coulomb interaction. The capital $\mathbf{R}$'s give the positions of the fixed nuclei, the small $\mathbf{r}$'s the coordinates of the electrons.

By adding and subtracting terms to (12) the following expression is obtained:

$$V = V_p + V_{eg} + \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{R_{ij}} - \tfrac{1}{2} \int \int \frac{e^2 \rho^2 d\mathbf{r}_1 d\mathbf{r}_2}{r_{12}}, \quad (13)$$

where ρ is the average density of electrons, or positive charge, and

$$V_p = \sum_i \left[\int \frac{e^2 \rho d\mathbf{r}}{|\mathbf{r}_i - \mathbf{r}|} - \sum_j \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_j|} \right] \quad (14)$$

is the periodic potential energy of electrons moving through a lattice neutralized by a uniform background of negative charge. The term V_{eg} is the Coulomb inter-

[20] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. X.

[21] For example, the calculations of Kronig, DeBoer, and Korringa in reference 2 as modified by March in reference 2 give for the energy of the Wigner-Seitz method, apart from the correlation energy, the expansion $2.21/r_s^2 - 2.716/r_s - 0.114 - 0.0239r_s + O(r_s^2)$, whereas (9) gives, if the expansion (8) is used for E_p, $2.21/r_s^2 - 2.708/r_s - 0.0905 - 0.018r_s + O(r_s^2)$. We have evaluated the next term in March's expansion, obtaining $-0.005r_s^2$ and this forms an estimate for the next term in Eq. (8).

action of an electron gas, given by

$$V_{eg} = \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} - \sum_i \int \frac{e^2 \rho d\mathbf{r}}{|\mathbf{r}_i - \mathbf{r}|} + \tfrac{1}{2} \int \int \frac{e^2 \rho^2 d\mathbf{r}_1 d\mathbf{r}_2}{r_{12}}. \quad (15)$$

Finally, V may be written as

$$V = V_p - \langle V_p \rangle + V_{eg} + V_L \quad (16)$$

since the last two terms on the right in Eq. (13) give $V_L - \langle V_p \rangle$, where V_L is the energy of a lattice of positive charges in a uniform background of negative charge.

The expression for V_L is

$$V_L = \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{R_{ij}} - \sum_j \int \frac{e^2 \rho d\mathbf{r}}{|\mathbf{r} - \mathbf{R}_j|} + \tfrac{1}{2} \int \int \frac{e^2 \rho^2 d\mathbf{r}_1 d\mathbf{r}_2}{r_{12}} \quad (17)$$

with values for various lattices given in Table I.

According to (16) a diagonal element of V is

$$V_{\mu\mu} = V_L + (V_{eg})_{\mu\mu} = V_L + \epsilon_x(\mu), \quad (18)$$

where μ indicates a set of wave vectors, and ϵ_x is the exchange energy for free electrons.

The unperturbed energies are ϵ_μ, with $\epsilon_0 = 2.21 N r_s^{-2}$, the Fermi energy. Therefore in Rayleigh-Schrödinger perturbation theory the ground-state energy of the system is represented by

$$E(\nu) = \epsilon_\nu + V_L + \epsilon_x(\nu) + \sum_{\mu \neq \nu} \frac{V_{\nu\mu} V_{\mu\nu}}{(\epsilon_\nu - \epsilon_\mu)} + \cdots, \quad (19)$$

where ν is the unperturbed state which leads to minimum E. For the present it is not necessary to assume that (19) converges.

Since constants have no effect on the second and higher order terms in (19), for these terms the replacement

$$V \rightarrow V_p + V_{eg} \rightarrow V' + V'' \quad (20)$$

may be made, where

$$V' = -\sum_i \sum_j e^2 / |\mathbf{r}_i - \mathbf{R}_j| \quad (21)$$

and

$$V'' = \tfrac{1}{2} \sum_{i \neq j} e^2 / r_{ij}. \quad (22)$$

Now let $V = V' + V''$ be substituted and expanded in all the higher orders of (19). The resulting series will contain terms in V' alone, others in V'' alone, and mixed terms containing both V' and V''. The series of terms from second order to infinity which contain only V'', with the addition of $\epsilon_\nu + \epsilon_x(\nu)$, gives the νth energy level of an electron gas, $E_{eg}(\nu)$. This result is true whether the series converges or diverges since the terms are just what would be obtained if the total Hamiltonian were reduced to that for the electron gas.

By a similar argument, the series of terms in V' alone, when $\epsilon_\nu + \langle V_p \rangle$ is added to them, gives an eigenvalue $E_p(\nu)$ of the periodic potential problem, whether or not the series converges.

If capital letters are used to designate one-particle functions in the set ν, and small letters designate functions outside the set ν, then it is readily established that this latter perturbation series is

$$E_p(\nu) - \epsilon_\nu - \langle V_p \rangle$$

$$= \sum_M \sum_m \frac{(M|V_1'|m)^2}{\epsilon_\nu - \epsilon_\nu(Mm)}$$

$$+ \sum_M \sum_{m \neq n} \frac{(M|V_1'|m)(m|V_1'|n)(M|V_1'|n)}{[\epsilon_\nu - \epsilon_\nu(Mm)][\epsilon_\nu - \epsilon_\nu(Mn)]}$$

$$- \sum_{M \neq L} \sum_m \frac{(M|V_1'|m)(M|V_1'|L)(L|V_1'|m)}{[\epsilon_\nu - \epsilon_\nu(Mm)][\epsilon_\nu - \epsilon_\nu(Lm)]}$$

$$+ \text{fourth and higher order terms}, \quad (23)$$

where $\epsilon_\nu(Mm)$ is the unperturbed energy for the case where M is removed and replaced by m, and V_i' is defined by $V' = \sum_i V_i'$.

The series is an expansion in powers of r_s. For the case where ν is the unperturbed ground state, evaluation of the matrix elements in (23) leads to

$$E_p(0) - \epsilon_0 - \langle V_p \rangle$$

$$= -\frac{N}{6\pi^2} \sum_{K \neq 0} \frac{1}{K^4} \left[\frac{(1-K^2)}{2K} \ln\left(\frac{K+1}{K-1}\right) + 1 \right]$$

$$- \frac{Nr_s\alpha}{72\pi^4} \sum_{K \neq K' \neq 0} \frac{1}{K^2 K'^2 |\mathbf{K} - \mathbf{K}'|^2}$$

$$\times \int_{p<1} \frac{d\mathbf{p}}{(\mathbf{K} \cdot \mathbf{p} + K^2)(\mathbf{K}' \cdot \mathbf{p} + K'^2)} + O(r_s^2), \quad (24)$$

where $\mathbf{K}/\pi$ is a reciprocal lattice vector, in units of the radius of the Fermi sphere and $\alpha^3 = 4/9\pi$.

Finally the mixed terms containing both V' and V'' must be considered. We shall calculate the first non-vanishing term in this series and show it is finite and proportional to Nr_s. Such behavior is in contrast to the series for E_{eg} where the corresponding term is infinite.

It is easy to see that no mixed terms appear in second-order perturbation. For any state $\mu \neq \nu$ such that $V_{\nu\mu}''$ does not vanish, $V_{\nu\mu}'$ will vanish. This result is true because of momentum considerations.

The mixed terms in third order are

$$E_{\text{int}}'''(\nu) = 2 \sum_{\mu \neq \eta \neq \nu} \frac{V_{\nu\mu}'' V_{\mu\eta}' V_{\eta\nu}'}{(\epsilon_\nu - \epsilon_\mu)(\epsilon_\nu - \epsilon_\eta)}$$

$$+ \sum_{\mu \neq \eta \neq \nu} \frac{V_{\nu\mu}' V_{\mu\eta}'' V_{\eta\nu}'}{(\epsilon_\nu - \epsilon_\mu)(\epsilon_\nu - \epsilon_\eta)}$$

$$+ \sum_{\mu \neq \nu} \frac{V_{\nu\mu}'(V_{\mu\mu}'' - V_{\nu\nu}'')V_{\mu\nu}'}{(\epsilon_\nu - \epsilon_\mu)^2}. \quad (25)$$

Terms containing V'' twice vanish because of momentum considerations and because $V_{\mu\mu}' - V_{\nu\nu}' = 0$. If $\psi_\nu(ML,ml)$ denotes a determinantal wavefunction in which the functions M and L in the set ν have been replaced by m and l outside ν, then

$$\sum_\mu V_{\nu\mu}'' = \sum_{M<L} \sum_{m<l} \int \psi_\nu^* V'' \psi_\nu(ML,ml) d\tau \quad (26)$$

and

$$\sum_\mu V_{\nu\mu}' = \sum_M \sum_m \int \psi_\nu^* V' \psi_\nu(M,m) d\tau. \quad (27)$$

With (26) and (27) the expression (25) is readily reduced to the integrals given in Appendix A.

Higher-order mixed terms are formally proportional to higher powers of r_s. However, divergent integrals begin to appear which must be combined, for example, in the manner of Gell-Mann and Brueckner[11] to obtain finite results.

The final result for the perturbation calculation (19) is

$$E(\nu) = E_{eg}(\nu) + V_L + [E_p(\nu) - \epsilon_\nu - \langle V_p \rangle]$$
$$+ E_{\text{int}}'''(\nu) + R(\nu), \quad (28)$$

where $R(\nu)$ is the remainder of the series of mixed terms. Insofar as this series converges, R depends on terms of higher order than r_s, and (28), with R neglected, is an exact expression up to and including order r_s.

APPENDIX A

The result for a spherical surface is

$$\sum_{\mu \neq \eta \neq 0} \frac{V_{0\mu}'' V_{\mu\eta}' V_{\eta 0}'}{(\epsilon_0 - \epsilon_\mu)(\epsilon_0 - \epsilon_\eta)}$$

$$= \frac{\alpha r_s N}{96\pi^5} \sum_{K \neq 0} \int \int \frac{d\mathbf{p}_1 d\mathbf{p}_2}{K^4} \left[\frac{1}{K^2} - \frac{2}{|\mathbf{p}_1 - \mathbf{p}_2 + 2\mathbf{K}|^2} \right]$$

$$\times \frac{1}{[2K^2 + \mathbf{K} \cdot (\mathbf{p}_1 - \mathbf{p}_2)](K^2 + \mathbf{K} \cdot \mathbf{p}_1)}, \quad (29)$$

$$\sum_{\mu \neq \eta \neq 0} \frac{V_{0\mu}' V_{\mu\eta}'' V_{\eta 0}'}{(\epsilon_0 - \epsilon_\mu)(\epsilon_0 - \epsilon_\eta)}$$

$$= \frac{\alpha r_s N}{96\pi^5} \sum_{K \neq 0} \int \int \frac{d\mathbf{p}_1 d\mathbf{p}_2}{K^4} \frac{1}{(K^2 + \mathbf{K} \cdot \mathbf{p}_1)(K^2 + \mathbf{K} \cdot \mathbf{p}_2)}$$

$$\times \left[\frac{1}{K^2} - \frac{2}{|\mathbf{p}_1 - \mathbf{p}_2|^2} \right], \quad (30)$$

and

$$\sum_{\mu \neq 0} \frac{V_{0\mu}'(V_{\mu\mu}'' - V_{00}'')V_{\mu 0}'}{(\epsilon_0 - \epsilon_\mu)^2}$$

$$= \frac{\alpha r_s N}{48\pi^5} \sum_{K \neq 0} \int \int \frac{d\mathbf{p}_1 d\mathbf{p}_2}{K^4} \left[\frac{1}{|\mathbf{p}_1 - \mathbf{p}_2|^2} - \frac{1}{|\mathbf{p}_1 - \mathbf{p}_2 + 2\mathbf{K}|^2} \right]$$

$$\times \frac{1}{(K^2 + \mathbf{K} \cdot \mathbf{p}_1)^2}, \quad (31)$$

where $\mathbf{K}/\pi$ is a reciprocal lattice vector in units of the radius of the spherical Fermi surface $[k_{F_0}(\mathbf{K}/\pi)\cdot\mathbf{R}_j$ =integer], $\alpha=(4/9\pi)^{1/3}$, and the $\mathbf{p}$ integrations are over a unit sphere.

APPENDIX B

The leading terms quadratic in the anisotropy constants come from the Fermi energy of the electron gas and are proportional to r_s^{-2}. From an expansion of Eq. (3) and the orthonormality of the Kubic harmonics we may write

$$\epsilon_\nu=\epsilon_0\langle(k_F/k_{F_0})^5\rangle$$
$$=\epsilon_0[1+(5/9)(K_1^2+K_2^2+K_3^2+\cdots)+O(K^3)]. \quad (32)$$

The leading linear terms in the anisotropy constants come from the energy of the periodic potential problem as given by Eq. (23).

For the case where the Fermi surface does not touch the zone boundary, which is the case when the Fermi surface is only slightly distorted from a sphere, we find upon evaluating the matrix elements that

$$E_p(\nu)-\epsilon_\nu-\langle V_p\rangle$$
$$=-\frac{N}{12\pi^3}\sum_{\mathbf{K}\neq0}\int\frac{d\mathbf{p}}{K^4(\mathbf{p}\cdot\mathbf{K}+K^2)}+O(r_S). \quad (33)$$

Here $\mathbf{K}$ is proportional to a reciprocal lattice vector as defined in Appendix A, and the integration is over the occupied region of momentum space, with $p=1$ defining the sphere.

The integral may be written

$$\int d\Omega\int_0^{k_F(\Omega)/k_{F_0}}\frac{p^2dp}{p(\mathbf{p}\cdot\mathbf{K}/p)+K^2}, \quad (34)$$

whence

$$\frac{1}{N}\frac{\partial[E_p(\nu)-\epsilon_\nu-\langle V_p\rangle]}{\partial K_i}\bigg|_{K_1,K_2\cdots=0}=-\frac{1}{12\pi^3}\sum_{\mathbf{K}\neq0}\frac{1}{K^4}\int\frac{d\Omega}{(\mathbf{p}\cdot\mathbf{K}/p+K^2)}\frac{1}{k_{F_0}}\frac{\partial k_F}{\partial K_i}\bigg|_{K_1,K_2\cdots=0}+O(r_s), \quad (35)$$

where $d\Omega$ is an element of solid angle.

The integral on the right-hand side has been evaluated by expressing the Kubic harmonics, $\partial k_F/\partial K_i$, in terms of Legendre polynomials and by making use of the addition theorem. The results for the first term on the right-hand side of (35) for $i=1$, 2, and 3 are, respectively, -2.82×10^{-3}, 3.02×10^{-3}, -7.46×10^{-4} for the bcc lattice, and -7.22×10^{-3}, -3.75×10^{-3}, and -6.87×10^{-4} for the fcc.

The values of K_1, K_2, and K_3 which minimize $\epsilon_\nu+[E_p(\nu)-\epsilon_\nu-\langle V_p\rangle]$ to first order are given in the text. Since the largest is of order $5\times10^{-3}r_s^2$, it has only a slight effect on the energy of the order of $10^{-5}r_s^2$ Ry per particle.