Correlation and Quantum Corrections in the Thomas-Fermi Model of the Atom*

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A new method is described for computing the effect of correlation, inhomogeneity, and exchange on the Thomas-Fermi model of the atom. The method makes use of the many-body point of view, rather than an independent-particle point of view, by considering the hierarchy equation linking the n-particle Green's functions. The hierarchy is truncated by a prescription equivalent to the Gell-Mann and Brueckner theory of the high-density electron gas, resulting in a description of the atom in which the exchange interaction is replaced by the effective interaction. The physical significance of this replacement is noted.

The Green's function for this model is then expanded as a series in powers of $\hbar$. The lowest order term is found to describe the Thomas-Fermi model of the atom. The equation for the next higher term contributing to this expansion is manipulated so as to yield an ordinary differential equation for the corresponding correction to the potential. This equation contains a term which expresses the effect of inhomogeneity and another which arises from the correlation of the electrons and from exchange. The inhomogeneity term is one which has been found previously. Study of the correlation term shows that it depends on the separation energy of an electron from an infinite electron gas, which suggests a generalization by which the method might be made applicable to those outer regions of the atom for which the electron density is below that to which the Gell-Mann and Brueckner theory would apply.

I. INTRODUCTION

IN a previous paper,[1] we presented a systematic method for deriving the Thomas-Fermi equation and quantum corrections (exchange and inhomogeneity) from the many-body equations of motion of an atomic system. This method was based on the Green's function formulation of the many-body problem,[2] and, in particular, made use of the Hartree-Fock approximation within that formalism. We showed that the single-particle Green's function in the Hartree-Fock approximation could be expanded as a series in powers of $\hbar$, and that the lowest order term in this series described the Thomas-Fermi distribution. The next nonvanishing higher order term was found to be the same as the quantum correction found by Kompaneets and Pavlovskii,[3] who had based their work on the Hartree-Fock approximation in the density matrix formalism, and independently by Kirzhnits,[4] who had used a method involving successive commutators, also within the Hartree-Fock scheme.

The effect, however, of including all the higher order terms of our infinite series can be to recover only the Hartree-Fock solution, and consequently neglects dynamic particle correlation. In this paper, we shall use the technique developed in I to include some of the correlation effects which are discarded *ab initio* in a Hartree-Fock approach. We shall do this by using the Gell-Mann–Brueckner theory of the high-density electron gas[5] as the basic approximation instead of the Hartree-Fock approximation. It will still be possible to express the single-particle Green's function as a series in powers of $\hbar$, and just as before, the lowest order term will describe the Thomas-Fermi distribution. This time, however, the higher order terms which may be regarded as corrections to the Thomas-Fermi model introduce not only the quantum corrections but also those correlation effects with which Gell-Mann and Brueckner were concerned.

The logical approach to this problem is divided into four parts, each of which is the subject of one of the following sections of this paper. In Sec. II, we formulate the many-body problem in the mixed position-momentum representation of the Green's function. The description of the interaction between particles is contained formally in the irreducible self-energy operator.[6] We choose an approximate form for this operator which describes the important interactions of the G.B. theory and find that the only difference between this approximation and that which corresponds to the Hartree-Fock method is the appearance of a time-dependent effective interaction instead of the instantaneous Coulomb potential in the exchange term. The direct-interaction term is unaltered. This result has physical significance which will guide our later steps.

In Sec. III, we expand the quantities of interest as series in powers of $\hbar$, employing the techniques presented in I. By series in powers of $\hbar$, we mean as $\hbar$ is considered to be made smaller, the lowest order terms dominate higher order terms to greater and greater extent. Some care is required in expanding the effective interaction in order to avoid recovering a series similar to the one summed by G.B. We can obtain a useful expansion of the effective interaction if we recognize why the straightforward expansion fails to work and

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[1] G. Baraff and S. Borowitz, Phys. Rev. **121**, 1704 (1961), hereafter denoted as I.

[2] V. M. Galitskii and A. B. Migdal, Soviet Phys.—JETP **34**, 96 (1958); P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

[3] A. S. Kompaneets and E. S. Pavlovskii, Soviet Phys.—JETP **31**, 328 (1957).

[4] D. A. Kirzhnits, Soviet Phys.—JETP **32**, 64 (1957).

[5] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957), hereafter referred to as G.B.

[6] A. Klein and R. Prange, Phys. Rev. **112**, 994 (1958).

proceed accordingly. The expansion which results is completely in accord with the physical significance of the result we noted in the preceding section.

In Sec. IV, we obtain equations for the lowest order terms in the expansion. We find that the zeroth order term describes the Thomas-Fermi distribution and that the first-order correction term vanishes, just as in I. The equation for the second-order term is quite similar to that found in I, the sole difference being in that term which in I arose from exchange and here arises from the effective interaction. We study this term in detail in Sec. V and find that it represents the nonkinetic part of the separation energy in both cases. This suggests a way to correct our work for an approximation made earlier and, also, for the approximation made in using the G.B. correlation corrections, which are valid only in the high-density limit.

Section VI contains a summary and a discussion of the similarities and differences between this work and an earlier paper by Lewis[7] on essentially the same problem. Our result in this work, then, is an equation which determines the lowest correction to the Thomas-Fermi model for the effect of correlation, exchange, and inhomogeneity. Solutions to this equation for various atoms are not presented.

II. FORMULATION OF THE PROBLEM

We again consider an atom or an ion to consist of a nucleus with charge Ze and infinite mass located at the origin, surrounded by N electrons, each of mass m. We neglect spin-dependent forces and all relativistic effects in our system. For such a system, the equation relating the one-particle and two-particle Green's function is

$$[i\hbar(\partial/\partial t_1)-H_0(\mathbf{r}_1)]G_1(1;1')$$
$$+i\int d(2)v(1-2)G_2(1,2;1',2^+)=\hbar\delta(1-1'), \quad (2.1a)$$

$$H_0(\mathbf{r})=(-\hbar^2/2m)\nabla^2-Ze^2/|\mathbf{r}|, \quad (2.1b)$$

$$v(1-2)=\delta(t_1-t_2)e^2/|\mathbf{r}_1-\mathbf{r}_2|. \quad (2.1c)$$

This notation is the same as in I: Each numerical argument 1, 1′, etc. specifies a spatial coordinate, a time, and a spin index. Integration over a numerical argument implies summation over the associated spin index; the delta function of numerical indices signifies the product of a Dirac delta function for each of the space and time coordinates with a Kronecker delta function of the spin index. The symbol + as a superscript to a numerical index indicates that the time associated with that index is to be made later by an infinitesimal amount.

The one- and two-particle Green's functions G_1 and G_2 are those defined in I [see I, (5.7)]. They are of use in computing the ground state expectation value of any one-particle or two-particle operator. For example, the density of particles at spatial point $\mathbf{r}_1$ having spin index σ_1 is given by $n(1)=-iG_1(1;1^+)$. The ground-state energy E is also easily determined [see I, (2.3)].

Klein and Prange[6] have introduced the irreducible self-energy operator M by giving an equation defining its effect:

$$i\int d(2)v(1-2)G_2(1,2;1',2^+)$$
$$=-\int d(2)M(1,2)G(2;1'). \quad (2.2)$$

We shall use this definition to define a kernel $K(1,2)$,

$$K(1,2)=[i\hbar(\partial/\partial t_1)-H_0(\mathbf{r}_1)]\delta(1-2)-M(1,2) \quad (2.3)$$

such that Eq. (2.1) takes the form

$$\int d(2)K(1,2)G_1(2;1')=\hbar\delta(1-1'). \quad (2.4)$$

For a system such as ours in which spin-dependent forces are neglected, a particle propagates without change of spin. That is, the single-particle Green's function vanishes unless its two spin indices are equal, but it is otherwise independent of the spin. Hence, we need consider Eq. (2.4) only for the case $\sigma_1=\sigma_2=\sigma_{1'}$. Let us transform this equation to the mixed position-momentum representation by taking the Fourier transform with respect to $\mathbf{r}_1-\mathbf{r}_1'$ and t_1-t_1', holding $\mathbf{R}=\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_1')$ fixed, denoting the transform variables by $\mathbf{p}$ and ω.

$$\int d(\mathbf{r}_1-\mathbf{r}_1')d(t_1-t_1')d(2)K(1,2)G_1(2;1')$$
$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_1')-\omega(t_1-t_1')]/\hbar\}=\hbar.$$

This transformation was used extensively in I, where it was shown that the left side of the preceding equation could be expressed in terms of the transforms of K and G by means of a differential operator of infinite order, θ, as

$$\theta[\tilde{K}(\mathbf{R},\mathbf{p}\omega),\tilde{G}(\mathbf{R},\mathbf{p}\omega)].$$

The transforms $\tilde{K}$ and $\tilde{G}$ are defined by

$$\tilde{K}(\mathbf{R},\mathbf{p}\omega)=\int d(\mathbf{r}_1-\mathbf{r}_2)d(t_1-t_2)K(1,2)_{\sigma_1=\sigma_2}$$
$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)-\omega(t_1-t_2)]/\hbar\}, \quad (2.5)$$

$$\tilde{G}(\mathbf{R},\mathbf{p}\omega)=\int d(\mathbf{r}_1-\mathbf{r}_2)d(t_1-t_2)G_1(1;2)_{\sigma_1=\sigma_2}$$
$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)-\omega(t_1-t_2)]/\hbar\}. \quad (2.6)$$

(The operator θ is defined fully and its effect given explicitly in I. Its first few terms are given in Appendix

[7] H. W. Lewis, Phys. Rev. 111, 1554 (1958).

B of this paper.) In terms of this notation, the transform of Eq. (2.4) is

$$\theta[\tilde{K}(\mathbf{R},\mathbf{p}\omega),\tilde{G}(\mathbf{R},\mathbf{p}\omega)]=\hbar. \quad (2.7)$$

From the definition of K, Eq. (2.3), we find that

$$\tilde{K}(\mathbf{R},\mathbf{p}\omega)=\omega-p^2/2m+Ze^2/|\mathbf{R}|-\tilde{M}(\mathbf{R},\mathbf{p}\omega), \quad (2.8)$$

where $\tilde{M}$ is the transform of $M(1,2)$ with $\sigma_1=\sigma_2$.

The equation defining M, Eq. (2.2), indicates that M can be found if both G_1 and G_2 are known. But knowledge of the exact G_1 and G_2 usually means that the entire many-body problem has been solved exactly. This is rarely feasible, and so it is at this point, specification of the form of the operator M, that various approximations are introduced. For example, the Hartree-Fock approximation which we used in I results from the choice

$$M(1,2)=-i\delta(1-2)\int d(3)v(1-3)G_1(3;3^+) +iv(1-2)G_1(1;2^+).$$

In this paper, we shall choose an M which embodies the approximation used by Gell-Mann and Brueckner in their study of the correlation energy of the high-density electron gas. The physical content of their theory may be stated as a prescription for the construction of the two-particle Green's function. The results of the original G.B. paper can be obtained from a two-particle Green's function of the form[8]

$$\begin{aligned}G_2(1,2;1',2')=&G_0(1;1')G_0(2;2')\\&-G_0(1;2')G_0(2;1')\\&+(i/\hbar)\int d(3)d(4)G_0(1;3)G_0(3;1')\\&\times v(3,4)G_0(2;4)G_0(4;2')\\&-(i/\hbar)\int d(3)d(4)G_0(1;3)G_0(3;2')\\&\times v(3-4)G_0(2;4)G_0(4;1'), \quad (2.9)\end{aligned}$$

where G_0 is the single-particle Green's function in the absence of interaction and $v(1,2)$ is the effective interaction, introduced by Hubbard,[9] which satisfies the integral equation

$$v(1,2)=v(1-2)-(i/\hbar)\int d(3)d(4)v(1-3)\times G_0(3;4)G_0(4;3)v(4,2). \quad (2.10)$$

The last term in Eq. (2.9) gives rise to the second order exchange energy ($\epsilon_b^{(2)}$ in G.B.) which, for the infinite electron gas, is independent of density. In a nonuniform electron gas, this energy might possibly be a function of density gradient and higher derivatives of the density.[10] The approximation procedure we shall be using, however, treats gradient dependence as a higher order effect than density dependence and in the low-order approximation, with which we shall be concerned, only the density dependence of $\epsilon_b^{(2)}$ would appear. We suspect, then, that in some way this last term will contribute a constant term to energies we may encounter. Let us suppress this term for the time being; it will become apparent (in Sec. V) how to allow for its effect.

It will be possible for us to work with the Green's function G_1 rather than the "unperturbed" Green's function G_0. This replacement does not follow strictly from the equations presented so far, but constitutes a simple extension of the Gell-Mann–Brueckner scheme.

We note that v is symmetric with respect to interchange of its arguments, as can be seen most readily from examination of the Neumann series solution of (2.10). In Eq. (2.9) we replace G_0 by G_1, interchange the arguments of v, and, for reasons explained above, suppress the last term to obtain

$$\begin{aligned}G_2(1,2;1',2')=&G_1(1;1')G_1(2;2')\\&-G_1(1;2')G_1(2;1')\\&+(i/\hbar)\int d(3)d(4)G_1(1;3)G_1(3;1')\\&\times v(4,3)G_1(2;4)G_1(4;2').\end{aligned}$$

This expression may be substituted into the left side of Eq. (2.2) and the result, after relabeling the variables of integration, is

$$\begin{aligned}\int d(2)v(1-2)G_2(1,2;1',2^+)=&\int d(2)\Big\{\delta(1-2)\\&\times\int d(3)v(1-3)G_1(3;3^+)-v(1-2)G_1(1;2^+)\\&+(i/\hbar)\int d(3)d(4)G_1(1;2)v(1-3)\\&\times v(4,2)G_1(3;4)G_1(4;3^+)\Big\}G_1(2;1'). \quad (2.11)\end{aligned}$$

Considered as a function of the difference between its two time coordinates, the single-particle Green's function is continuous except at zero. It follows, therefore, that the symbol + as a superscript of a numerical argument of a given single-particle Green's function has significance only if the two time variables of this given function are so tied together that they differ only by the infinitesimal which the symbol denotes. Thus, in the last term of Eq. (2.11)

[8] H. Kanezawa and M. Watabe, Progr. Theoret. Phys. (Kyoto) **23**, 408 (1960).

[9] J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957).

[10] We are indebted to Dr. M. Lax for this comment.

the factor $G_1(1;2^+)G_1(4;3)$ could replace the factor $G_1(1;2)G_1(4;3^+)$ without changing the value of the integral. Having made this replacement, we observe that the multiplier of $-G_1(1;2^+)$ within the brackets is just the right side of Eq. (2.10); i.e., it is the effective interaction itself. Finally, comparison of this result with Eq. (2.2), defining the self-energy operator, reveals that we have chosen an M defined by

$$M(1,2)=-i\delta(1-2)\int d(3)v(1-3)G_1(3;3^+) +iv(1,2)G_1(1;2^+). \quad (2.12)$$

This is the self-energy operator we shall use. It embodies the major feature of the G.B. theory in a form very similar to its Hartree-Fock counterpart. In Hartree-Fock theory, the exchange potential expresses the change from the average energy brought about by a correlation arising solely from the exclusion principle. In the G.B. theory, the repulsion arising from the Coulomb force induces a correlation which augments the one due to the exclusion principle. Both effects are included by substituting the effective interaction for the Coulomb interaction in the exchange term. The transform of this self-energy operator is readily evaluated and, when inserted into Eq. (2.8), gives

$$\tilde{K}(\mathbf{R},\mathbf{p}\omega)=\omega-p^2/2m+Ze^2/|R|-2\int\frac{n(\mathbf{r})e^2}{|\mathbf{R}-\mathbf{r}|}d\mathbf{r} -i(2\pi\hbar)^{-4}\int d\mathbf{p}'d\omega'\,\tilde{v}(\mathbf{R},\mathbf{p}-\mathbf{p}',\omega-\omega') \times G(R,\mathbf{p}',\omega')\exp(i\omega 0^+). \quad (2.13a)$$

$$n(r)=-iG_1(r,t;r,t^+). \quad (2.13b)$$

The factor of two in the fourth term on the right of Eq. (2.13a) arises from the spin summation. We have dropped the $\hbar$ from the exponent because the infinitesimal 0^+ renders the sign of ω, not its size, significant in the evaluation of such integrals. The same situation will occur with all quantities which must be set equal to zero after an integration is performed.

III. EXPANSION IN POWERS OF $\hbar$

We assumed in I that the transform of the single-particle Green's function could be expanded in powers of $\hbar$ as

$$\tilde{G}(\mathbf{R},\mathbf{p}\omega)=\hbar^4\sum_{j=0}\hbar^j\tilde{G}_j(\mathbf{R},\mathbf{p}\omega), \quad (3.1)$$

and that a similar expansion for the space-time form of the Green's function is also possible.[11]

$$G_1(1,2)=\sum_{j=0}\hbar^jG_j(1,2), \quad (3.2a)$$

$$G_j(1,2)=\int\frac{d\mathbf{p}d\omega}{(2\pi)^4}\tilde{G}_j(\mathbf{R},\mathbf{p}\omega)\exp[i(\mathbf{p}\cdot\mathbf{r}-\omega t)/\hbar], \quad (3.2b)$$

$$\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2,\quad t=t_1-t_2,\quad \mathbf{R}=\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2).$$

We shall have no further use for the symbol G_0 to denote the single-particle Green's function without interaction or for the symbol G_2 to denote the two-particle Green's function. To avoid confusion with the G_j used as expansion coefficients, we shall delete the subscript 1 from the single-particle Green's function with interaction, and shall denote this latter by $G(1,2)$ or sometimes, simply by G.

We found in I that the operator θ and the kernel $\tilde{K}$ could also be expanded in powers of $\hbar$ as

$$\theta=\sum_{j=0}\hbar^j\theta_j, \quad (3.3a)$$

$$\tilde{K}=\sum_{j=0}\hbar^j\tilde{K}_j. \quad (3.3b)$$

These expansions may be inserted into Eq. (2.7) and the powers of $\hbar$ separated in such a manner that the zeroth order approximation is nonvanishing. The resulting set of equations will be

$$\theta_0[\tilde{K}_0,\tilde{G}_0]=\hbar^{-3}, \quad (3.4a)$$

$$\sum_{j+k+m=n}\theta_j[\tilde{K}_k,\tilde{G}_m]=0,\quad n>0. \quad (3.4b)$$

The terms θ_j are given explicitly in the Appendix of I. The coefficients $\tilde{K}_j$ may be found by assuming the possibility of expanding $\tilde{v}$ as a series in powers of $\hbar$,

$$\tilde{v}(\mathbf{R},\mathbf{p}\omega)=\sum\hbar^j\tilde{v}_j(\mathbf{R},\mathbf{p}\omega), \quad (3.5)$$

inserting this series into Eq. (2.13), and separating out the various powers of $\hbar$. We find that

$$\tilde{K}_0(\mathbf{R},\mathbf{p}\omega)=\omega-p^2/2m+Ze^2/|\mathbf{R}|-2\int\frac{n_0(\mathbf{r})e^2d\mathbf{r}}{|\mathbf{R}-\mathbf{r}|} -i(2\pi)^{-4}\int d\mathbf{p}'d\omega'\,\tilde{v}_0(\mathbf{R},\mathbf{p}-\mathbf{p}',\omega-\omega') \times\tilde{G}_0(\mathbf{R},\mathbf{p}',\omega')\exp(i\omega' 0^+), \quad (3.6a)$$

$$\tilde{K}_j=-2\int\frac{n_j(\mathbf{r})e^2d\mathbf{r}}{|\mathbf{R}-\mathbf{r}|}-\frac{i}{(2\pi)^4} \times\int\sum_{k+m=j}d\mathbf{p}'d\omega'\,\tilde{v}_k\tilde{G}_m\exp(i\omega' 0^+), \quad (3.6b)$$

$$n_j(\mathbf{r})=-iG_j(\mathbf{r}t;\mathbf{r}t^+) =-i(2\pi)^{-4}\int d\mathbf{p}d\omega\tilde{G}_j(\mathbf{R},\mathbf{p}\omega)\exp(i\omega 0^+). \quad (3.6c)$$

[11] Neither the $\hbar^4$ which appears somewhat unexpectedly in (3.1) nor its unexpected omission in (3.2b) are essential to any of the results of I or of this paper. All that is required is that the transform and the Green's function be related by (2.6) and that the zeroth (lowest) order term of the transform corresponds to the zeroth (lowest) order term of the Green's function. Powers of $\hbar$ may be distributed in any way between (3.1) and (3.2b) that meets these requirements, and physical quantities such as the density, etc., will remain the same.

We should like at this point to remind the reader of footnote 11. Having reached this point, however, a difficulty arises if we follow the technique of simply expanding each object in terms of $\hbar$. Subsequent progress depends on our making a reasonable analysis of why this difficulty arises and what may be done to obviate it. The results, if any, one obtains, will depend on the assumptions one makes at this point, and a certain lack of uniqueness is introduced. Thus forewarned, the reader is free to label the subsequent argument as heuristic if he so chooses.

A calculation of the coefficients $\tilde{v}_n$ must start with consideration of the integral equation (2.10) defining the effective interaction. Before starting the calculation, however, we must point out that these expansions in powers of $\hbar$ were motivated by the desire to include the effects of the uncertainty principle in a systematic manner, as was explained in I. Although we are still motivated by that desire, the situation here is somewhat more complicated than that in I because of the appearance of $\hbar$ in a way that is not directly related to the uncertainty principle. We refer to the explicit appearance of $\hbar$ in Eqs. (2.9) and (2.10). These appearances of $\hbar$ have their origin in the perturbation expansion and diagrammatic analysis upon which these two equations are based. If this explicit $\hbar$ is used for expansion purposes, the effective interaction will be decomposed into a series of terms in which one of two things can happen. If we expand so that positive powers of $\hbar$ appear, that is, so that the series is dominated by its first few terms as $\hbar$ is made smaller, then the lowest order term which appears is independent of the strength of the actual force between particles and there is no way of recovering the exchange term in that limit in which correlation effects are assumed small. On the other hand, if we expand so that negative powers of $\hbar$ can appear, then the result is a series containing arbitrarily high negative powers of $\hbar$, which looks very much like the series of perturbation terms which G.B. have shown how to sum. Neither of these two possibilities is at all in accord with the physical interpretation attached to the circumstance that the effective interaction replaces the Coulomb potential in the exchange term. The interpretation of this, to which we called attention at the end of Sec. II, suggests very strongly that the effective interaction should be treated as an entity of the same sort as the exchange potential. This we propose to do, treating the effective interaction here in the same way as we treated the exchange potential in I. There, however, we had the advantage of knowing the exchange potential explicitly. Here, on the other hand, we have only a recipe, the integral equation, for calculating the effective interaction. This recipe calls for that $\hbar$ inherited from perturbation theory as one of the ingredients. This role of $\hbar$ should be suppressed before performing any expansion. The simplest method of suppressing this usage is to replace $\hbar$ temporarily by the symbol λ in each appearance in which it plays the role of the perturbation theory expansion parameter. Instead of Eq. (2.10), for example, we shall have

$$v(1,2)=v(1-2)-\int d(4)Q(1,4)v(4,2), \tag{3.7}$$

where

$$Q(1,4)=(i/\lambda)\int d(3)v(1-3)G(3,4)G(4,3). \tag{3.8}$$

If we now transform these equations to the mixed representation, the transform of the integrals may be expressed in terms of the transforms of the factors of the integrand using the operator θ once again. The result is

$$\tilde{v}=\tilde{v}-2\theta[\tilde{Q},\tilde{v}], \tag{3.9}$$

$$\tilde{Q}=(i/\lambda)\theta[\tilde{v},\tilde{\Gamma}], \tag{3.10}$$

where

$$\tilde{\Gamma}=\int d(\mathbf{r}_3-\mathbf{r}_4)d(t_3-t_4)G(3,4)G(4,3)$$

$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_3-\mathbf{r}_4)-\omega(t_3-t_4)]/\hbar\}. \tag{3.11}$$

Again, the factor of two in Eq. (3.9) arises from the spin summation. The integral in (3.11) may be also expressed using the transform of the Green's function as

$$\tilde{\Gamma}=(2\pi\hbar)^{-4}\int d\mathbf{p}'d\omega'\,\tilde{G}(\mathbf{R},\mathbf{p}'\omega')\tilde{G}(\mathbf{R},\,\mathbf{p}+\mathbf{p}',\,\omega+\omega')$$

or, using the expansion of the transform, as

$$\tilde{\Gamma}=\hbar^{-2}\sum_{j=0}\hbar^j\Omega_j(\mathbf{R},\mathbf{p}\omega), \tag{3.12a}$$

$$\Omega_j=\sum_{m+n=j}\int\frac{d\mathbf{p}'d\omega'}{(2\pi)^4}\hbar^3\tilde{G}_m(\mathbf{R},\mathbf{p}'\omega')$$

$$\times\hbar^3\tilde{G}_n(\mathbf{R},\,\mathbf{p}+\mathbf{p}',\,\omega+\omega'). \tag{3.12b}$$

Lest the handling of the powers of $\hbar$ here seem artificial, let us note that the form of the set of equations (3.4) indicates that each of the coefficients $\tilde{G}_j$ contains a factor $\hbar^{-3}$. The combination $\hbar^3\tilde{G}_j$ which appears in (3.12b) has been chosen only to remove this $\hbar$ dependence from the terms Ω_j.

We may insert the expansion of θ and of $\tilde{\Gamma}$ into Eq. (3.10) with the result that

$$\tilde{Q}(\mathbf{R},\mathbf{p}\omega)=\sum_{j=0}\hbar^j\tilde{Q}_j(\mathbf{R},\mathbf{p}\omega), \tag{3.13a}$$

$$\tilde{Q}_j=(4\pi e^2 i/\lambda)\sum_{m+n=j}\theta_m[(1/p^2),\Omega_n(\mathbf{R},\mathbf{p}\omega)]. \tag{3.13b}$$

Finally, we may insert the expansions of $\tilde{v}$, θ, and $\tilde{Q}$ into Eq. (3.9) and separate the various powers of $\hbar$.

The coefficient of $\hbar^n$ then satisfies the equation

$$\tilde{v}_n+2\sum_{j+k+m=n}\theta_j[\tilde{Q}_k,\tilde{v}_m]=(4\pi e^2/p^2)\delta_{n,2}. \quad (3.14)$$

Now let us consider each of the equations of this set in turn. The $n=0$ equation is

$$\tilde{v}_0+2\theta_0[\tilde{Q}_0,\tilde{v}_0]=0.$$

The operator θ_0 acts on a pair of transforms to produce the product of these transforms. Hence, the above equation indicates that $\tilde{v}_0$ is zero. Every term in Eq. (3.14) which contains $\tilde{v}_0$ may be deleted for this reason. Consider now the $n=1$ equation of this set. Only two terms survive the deletion, and they are related by the equation

$$\tilde{v}_1+2\theta_0[\tilde{Q}_0,\tilde{v}_1]=0.$$

Hence $\tilde{v}_1$ also vanishes, and all terms containing $\tilde{v}_1$ may be deleted from the set (3.14). In the $n=2$ equation, the terms surviving may be rearranged to yield

$$\tilde{v}_2(\mathbf{R},\mathbf{p}\omega)=\frac{4\pi e^2/p^2}{1+2\tilde{Q}_0(\mathbf{R},\mathbf{p}\omega)}. \quad (3.15)$$

The higher order coefficients $\tilde{v}_j$ may be expressed in terms of $\tilde{v}_2$ and the other $\tilde{Q}_n$ $(n<j)$ and certain differentiations of these which are prescribed by the other θ_n operators. We shall not need these higher order coefficients here, however. This completes as much of the expansion as we shall be using in this paper. λ is to be replaced by its value of $\hbar$, and $\tilde{Q}_0$ may be evaluated using (3.13b). The result, inserted in (3.15), gives

$$\tilde{v}_2=\frac{4\pi e^2}{p^2+8\pi e^2 i\Omega_0/\hbar}. \quad (3.16)$$

IV. EQUATION FOR THE CORRELATION CORRECTION

Having just found that $\tilde{v}_0$ and $\tilde{v}_1$ vanish, we may examine Eq. (3.6) for $\tilde{K}_0$ and $\tilde{K}_1$.

$$\tilde{K}_0=\omega-\frac{p^2}{2m}+\frac{Ze^2}{|\mathbf{R}|}-2e^2\int\frac{n_0(\mathbf{r})=\mathbf{r}}{|\mathbf{R}-\mathbf{r}|}, \quad (4.1a)$$

$$\tilde{K}_1=-2e^2\int n_1(\mathbf{r})d\mathbf{r}/|\mathbf{R}-\mathbf{r}|. \quad (4.1b)$$

The zeroth- and first-order equations of the set (3.4) may be rewritten as

$$\tilde{G}_0=\hbar^{-3}/\tilde{K}_0, \quad (4.2a)$$

$$\tilde{G}_1=-\tilde{K}_1\tilde{G}_0/\tilde{K}_0-\theta_1[\tilde{K}_0,\tilde{G}_0]/\tilde{K}_0. \quad (4.2b)$$

These equations are exactly the same as those we encountered in I [see I, Eqs. (3.8), (3.9), and (3.10)]. We found there that $2n_0(\mathbf{r})$ was the Thomas-Fermi distribution of electrons, and that $\tilde{K}_1$ and $\tilde{G}_1$ both vanished. It is convenient to express (4.1a) and (4.2a) in the following form:

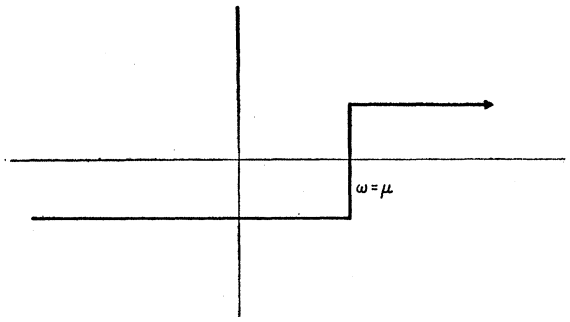

FIG. 1. Path of integration in the complex ω plane for recovering G_1 from $\tilde{G}_1$.

$$\tilde{G}_0(\mathbf{R},\mathbf{p}\omega)=\hbar^{-3}(\omega-E)^{-1}, \quad (4.3a)$$

$$E=E(R,p)=p^2/2m+\phi_0(R), \quad (4.3b)$$

$$\phi_0(R)=-\frac{Ze^2}{|\mathbf{R}|}+2e^2\int\frac{n_0(\mathbf{r})d\mathbf{r}}{|\mathbf{R}-\mathbf{r}|}. \quad (4.3c)$$

ϕ_0 is then the usual Thomas-Fermi potential for the atom.

The integrations which yield the space time form G_0, and the density n_0, as indicated by Eqs. (3.2b) and (3.6c), are to be carried out as if ω were a complex variable, with a path of integration in the complex ω plane which is displaced from the real ω axis by an infinitesimal amount. The path, shown in Fig. 1, lies slightly below the real axis for $-\infty<\omega<\mu$, crosses the real axis at $\omega=\mu$, and lies slightly above the real axis for $\mu<\omega<+\infty$. This choice of path is an expression of the fact that the system is in the ground state, as explained in I. The constant μ is the chemical potential, approximately the energy required to add another electron to the system.

The identity of these equations with those in I means that in this case too, the zeroth-order result is the Thomas-Fermi distribution and that corrections due to inhomogeneity effects, exchange, and correlations are not felt until the second order in $\hbar$. Our main interest is to obtain an equation for the first nonvanishing correction. This may be done as follows: Write Eq. (3.6b) for $\tilde{K}_2$ as

$$\tilde{K}_2(\mathbf{R},\mathbf{p}\omega)=-\phi_2(\mathbf{R})-\chi(\mathbf{R},\mathbf{p}\omega), \quad (4.4a)$$

$$\phi_2(\mathbf{R})=2e^2\int\frac{n_2(\mathbf{r})d\mathbf{r}}{|\mathbf{R}-\mathbf{r}|}, \quad (4.4b)$$

$$\chi(\mathbf{R},\mathbf{p}\omega)=-\int\frac{d\mathbf{p}'}{(2\pi)^3}\int\frac{d\omega'}{2\pi i}\tilde{v}_2(\mathbf{R},\mathbf{p}-\mathbf{p}',\omega-\omega')\times\tilde{G}_0(\mathbf{R},\mathbf{p}',\omega')\exp(i\omega'0^+). \quad (4.4c)$$

We may rearrange the $n=2$ equation of the set (3.4b) so as to exhibit $\tilde{G}_2$

$$\tilde{G}_2=-\tilde{K}_2\tilde{G}_0/\tilde{K}_0-\theta_2[\tilde{K}_2,\tilde{G}_0)/\tilde{K}_0.$$

By using the specific form for $\tilde{K}_0$ and $\tilde{G}_0$ given by Eqs. (4.1) and (4.3), this can also be written

$$-\hbar^3\tilde{G}_2=\tilde{K}_2/(\omega-E)^2 + (\omega-E)^{-1}\theta_2[(\omega-E),\,(\omega-E)^{-1}]. \quad (4.5)$$

The integral of $\tilde{G}_2$ indicated by (3.6c), using the path described above, yields the density $n_2(R)$.

$$(-2\pi\hbar)^3 n_2(\mathbf{R})=\int d\mathbf{p}\int\frac{d\omega}{2\pi i} \times\exp(i\omega 0^+)\frac{\tilde{K}_2(\mathbf{R},\mathbf{p}\omega)}{[\omega-E(R,p)]^2}+\int d\mathbf{p}\int\frac{d\omega}{d\pi i} \times\exp(i\omega 0^+)(\omega-E)^{-1}\theta_2[(\omega-E),(\omega-E)^{-1}]. \quad (4.6)$$

The second integral in Eq. (4.6) has been evaluated in I [see I, Eqs. (4.8)–(4.11)]. It is equal to

$$\frac{\pi m}{12p_F(R)}[4\nabla^2\phi_0+(2m/p_F{}^2(R))(d\phi_0/dR)^2], \quad (4.7)$$

where $p_F(R)$ is the Fermi momentum, defined by the equation

$$E[R,p_F(R)]=\mu. \quad (4.8)$$

Consider now the first integral in Eq. (4.6). The substitution of Eqs. (4.3) and (4.4) in this expression yields

$$-\phi_2(R)\int d\mathbf{p}\int\frac{d\omega}{2\pi i}\exp(i\omega 0^+)[\omega-E(R,p)]^{-2} +(2\pi\hbar)^{-3}\int d\mathbf{p}d\mathbf{p}'\int\frac{d\omega}{2\pi i}\frac{d\omega'}{2\pi i} \times\exp(i\omega 0^+)\exp(i\omega' 0^+)[\omega-E(R,p)]^{-2} \times[\omega'-E(R,p')]^{-1}\tilde{v}_2(\mathbf{R},\,\mathbf{p}-\mathbf{p}',\,\omega-\omega'). \quad (4.9)$$

The use of the special path for the ω and ω' integrations becomes somewhat inconvenient. It will be easier for us to integrate ω and ω' along their real axes, provided we compensate by adding small imaginary parts to the $\omega-E$ denominators so that the poles lie above or below the path of integration in the correct manner. This may be done by replacing each $E(R,p)$ in (4.9) by

$$A(p)=E(R,p)-i\alpha\epsilon(p-p_F);\quad \alpha\to 0^+. \quad (4.10)$$
$$\epsilon(x)=+1 \quad \text{for} \quad x>0$$
$$=-1 \quad \text{for} \quad x<0,$$
$$\epsilon(0)=0.$$

It is now possible to introduce new variables

$$\eta=\omega-\omega',\quad \eta'=\omega, \quad (4.11)$$

into the second integral in (4.9). The zeros appearing in the exponent are to be interpreted as if written t and t', each of which approach zero independently through positive values. The second integral becomes

$$(2\pi\hbar)^{-3}\int d\mathbf{p}d\mathbf{p}'\int\frac{d\eta}{2\pi i}\frac{d\eta'}{2\pi i} \times\exp\{i[\eta'(t+t')-\eta t']\}\tilde{v}_2(\mathbf{R},\,\mathbf{p}-\mathbf{p}',\,\eta) \times[\eta'-A(p)]^{-2}[\eta'-\eta-A(p')]^{-1}. \quad (4.12)$$

The η and η' integrations may be simplified by writing the factors following $\tilde{v}$ in the form

$$[\eta-A(p)+A(p')]^{-2}\{[\eta'-\eta-A(p')]^{-1} -[\eta'-A(p)]^{-1}\}-[\eta-A(p)+A(p')]^{-1} \times[\eta'-A(p)]^{-2}. \quad (4.13)$$

The η' integration associated with the first two terms of (4.13) may be performed by contour integration, treating η as real. In the limit $t,t'\to 0^+$, the contribution of these terms to the expression (4.12) will be

$$(2\pi\hbar)^{-3}\int d\mathbf{p}d\mathbf{p}'\int\frac{d\eta}{2\pi i} \times\tilde{v}_2(\mathbf{R},\,\mathbf{p}-\mathbf{p}',\,\eta)[\eta-A(p)+A(p')]^{-2} \times[\exp(i\eta 0^+)S(p_F-p')-\exp(-i\eta 0^+)S(p_F-p)],$$

where

$$S(x)=1 \quad \text{for} \quad x>0$$
$$=0 \quad \text{for} \quad x<0.$$

If the variables p and p' are interchanged in the second term of the integrand, and if the substitution of $-\eta$ for η is also made in this term, the result becomes

$$(2\pi\hbar)^{-3}\int d\mathbf{p}d\mathbf{p}'\int\frac{d\eta}{2\pi i} \times\exp(i\eta 0^+)S(p_F-p')[\eta-A(p)+A(p')]^{-2} \times[\tilde{v}_2(\mathbf{R},\,\mathbf{p}-\mathbf{p}',\,\eta)-\tilde{v}_2(\mathbf{R},\,\mathbf{p}'-\mathbf{p},\,-\eta)]. \quad (4.14)$$

We shall show later that $\tilde{v}_2$ is a function of the magnitude $|p-p'|$, and is an even function of η. Hence, the term above vanishes. The contribution of the last term in (4.13) to the expression (4.12) may be combined with the first term in (4.9) after the integration variable in this latter expression is changed

from ω to η'. We obtain

$$-\int d\mathbf{p}\Big\{\phi_2(R)+(2\pi\hbar)^{-3}\int d\mathbf{p}'\int\frac{d\eta}{2\pi i}\exp(-i\eta 0^+)\times[\eta-A(p)+A(p')]^{-1}\tilde{v}_2(\mathbf{R},|\mathbf{p}-\mathbf{p}'|,\eta)\Big\}\times\int\frac{d\eta'}{2\pi i}\exp(i\eta' 0^+)[\eta'-A(p)]^{-2}. \quad (4.15)$$

Again, the η' integration may be performed by contour integration, completing the path along the real axis by the infinite semicircle in the upper half of the η' plane. For p either greater than or less than p_F, this integral vanishes. For $p=p_F$, the singularity lies astride the contour and the integral becomes infinite. This suggests a delta-function, which leads us to evaluate the integral so as to exhibit it as follows:

$$\begin{aligned}&\int\frac{d\eta'}{2\pi i}\exp(i\eta' 0^+)[\eta'-A(p)]^{-2}\\&=\frac{m}{p}\frac{d}{dp}\int\frac{d\eta'}{2\pi i}\exp(i\eta' 0^+)[\eta'-A(p)]^{-1}+O(\alpha)\\&=\frac{m}{p}\frac{d}{dp}S(p_F-p)+O(\alpha)\\&=-\frac{m}{p}\delta(p_F-p)+O(\alpha).\end{aligned} \quad (4.16)$$

The term of order α arises from the imaginary addition we made so that the real axis could be used for a path of integration. It should be discarded. We choose spherical polar coordinates for $\mathbf{p}$ and $\mathbf{p}'$, taking the polar axis for $\mathbf{p}$ in the direction of $\mathbf{p}'$. The integrand of (4.15) is then independent of all angles except θ, the angle between $\mathbf{p}$ and $\mathbf{p}'$. Hence, expression (4.15) with ω replacing η, becomes

$$4\pi m p_F(R)\phi_2(R)+[mp_F(R)/\pi\hbar^3]J(R), \quad (4.17a)$$

$$J=\int_0^\infty p^2dp\int d\cos\theta\int\frac{d\omega}{2\pi i}\exp(-i\omega 0^+)\times[\omega-A(p_F)+A(p)]^{-1}\tilde{v}_2(R,|\mathbf{p}_F-\mathbf{p}|,\omega). \quad (4.17b)$$

We return to Eq. (4.6) in which expressions (4.17) and (4.7) may now replace the first and second terms on the right-hand side. It is possible to eliminate $n_2(R)$ from this equation using Eq. (4.4b) in the form

$$\nabla^2\phi_2(R)=-8\pi e^2 n_2(R).$$

The resulting equation for $\phi_2(R)$ is

$$\nabla^2\phi_2(R)-\frac{4me^2}{\pi\hbar^3}p_F(R)\phi_2(R)=\frac{me^2}{\pi^3\hbar^6}p_F(R)J(R)+\frac{me^2}{12\pi\hbar^3 p_F(R)}\left[4\nabla^2\phi_0+\frac{2m}{p_F{}^2}\left(\frac{d\phi_0}{Rd}\right)^2\right]. \quad (4.18)$$

This equation determines the first nonvanishing correction to the Thomas-Fermi potential, in terms of the Thomas-Fermi potential $\phi_0(R)$, the Fermi momentum $p_F(R)$, and the function $J(R)$, which arises from the exchange and correlation effects. In contrast to the situation in which only exchange is considered, it will no longer be possible to express the dependence of J on p_F in any simple manner. Still, the dependence of J on p_F can be exhibited much more explicitly than we have done in (4.17b) and, in its more explicit form, numerical calculation can be performed. Accordingly, the study of $J(R)$ is the subject of the next section.

V. STUDY OF $J(R)$

The definition of $J(R)$ by means of Eq. (4.17b) and that of $\tilde{v}_2$ by means of (3.16) leads us to Eq. (3.12b) for the definition of Ω_0:

$$\Omega_0(\mathbf{R},\mathbf{p}\omega)=(2\pi)^{-4}\hbar^6\int d\mathbf{p}'d\omega'\,\tilde{G}_0(\mathbf{R},\mathbf{p}'\omega')\times\tilde{G}_0(\mathbf{R},\mathbf{p}+\mathbf{p}',\omega+\omega'). \quad (5.1)$$

The Green's function $\tilde{G}_0$ which we shall need in order to evaluate the expression above is only partially defined by Eq. (4.3a). The missing part of the definition is the statement that the path of integration in the complex ω plane must be the one described in the paragraph immediately following Eq. (4.3a). This fact leads to manipulations which become quite cumbersome when two or more Green's functions are present, as in the expressions above. We may again avoid these manipulations by replacing the $E(R,p)$ of Eq. (4.3b) by the $A(p)$ of Eq. (4.10) and using the real ω' axis for the path of integration. In this manner, we obtain

$$(2\pi)^3 i\Omega_0=-\int_{\lim\alpha\to 0}d\mathbf{p}'\int\frac{d\omega'}{2\pi i}\times[\omega'-E(R,p')+i\alpha\epsilon(p'-p_F)]^{-1}\times[\omega+\omega'-E(R,|\mathbf{p}+\mathbf{p}'|)+i\alpha\epsilon(|\mathbf{p}+\mathbf{p}'|-p_F)]^{-1}.$$

The ω' integration may be performed by contour integration, with the result that

$$(2\pi)^3 i\Omega_0=\int_{R_1}d\mathbf{p}'[\omega-(p^2+2\mathbf{p}\cdot\mathbf{p}')/2m-2i\alpha]^{-1}-\int_{R_2}d\mathbf{p}'[\omega-(p^2+2\mathbf{p}\cdot\mathbf{p}')/2m+2i\alpha]^{-1}, \quad (5.2)$$

where the regions R_1 and R_2 are defined by

$$R_1:\ |\mathbf{p}'|>p_F \text{ and } |\mathbf{p}+\mathbf{p}'|<p_F;$$
$$R_2:\ |\mathbf{p}'|<p_F \text{ and } |\mathbf{p}+\mathbf{p}'|>p_F.$$

The variable of integration in the first term of (5.2)

may be changed from $\mathbf{p}'$ to $\mathbf{q}=-(\mathbf{p}+\mathbf{p}')$ so that

$$(2\pi)^3 i\Omega_0=\int_{|\mathbf{q}|<p_F;\ |\mathbf{p}+\mathbf{q}|>p_F} dq\{[\omega+(p^2+2\mathbf{p}\cdot\mathbf{q})/2m-2i\alpha]^{-1}-[\omega-(p^2+2\mathbf{p}\cdot\mathbf{q})/2m+2i\alpha]^{-1}\}. \quad (5.3)$$

The position dependence of Ω_0 comes about solely because the Fermi momentum is position dependent. There will be a marked similarity between many of the expressions we shall use and analogous expressions which appear in the study of the uniform electron gas. The expression (5.3) appears in the work of DuBois,[12] for example, where it is called Q_0, the propagator for density fluctuations in the bare-pair approximation. A quantity proportional to it is denoted $\mathcal{U}^*(k,\omega)$ in Hubbard's[9] work. The mathematical formalism we shall be using follows closest to that introduced by DuBois.

If we use dimensionless variables $\mathbf{x}$, y, and $\mathbf{u}$, defined by $\mathbf{x}=\mathbf{p}/p_F$, $y=\omega/(p_F^2/2m)$ and $\mathbf{u}=\mathbf{q}/p_F$, then

$$(2\pi)^3 i\Omega_0=2\pi m p_F(R) f(x,y), \quad (5.4a)$$

$$f=-\frac{1}{\pi}\int_{|\mathbf{u}|<1;\ |\mathbf{u}+\mathbf{x}|>1} d\mathbf{u}\left[\frac{1}{y+x^2+2\mathbf{x}\cdot\mathbf{u}-2i\alpha}+\frac{1}{-y+x^2+2\mathbf{x}\cdot\mathbf{u}-2i\alpha}\right]. \quad (5.4b)$$

The form of $f(x,y)$ gives us some valuable information even before the integration is performed. We note that f behaves as $1/y^2$ as $y\to\infty$, that it is an even function of y, and that it is analytic except along two separate lines in the complex y plane which are composed of those points for which one or the other of the denominators vanishes for some $\mathbf{u}$ within the domain of integration. These lines are depicted in Fig. 2. The function f depends on the magnitude of $\mathbf{x}$, rather than on its direction.

We may now reconsider the expression for $\tilde{v}_2$ given by Eq. (3.16). Using the definition (5.4), we have

$$\tilde{v}_2(R,\mathbf{p}_F-\mathbf{p},\omega)=4\pi e^2 p_F^{-2}(R)/[x^2+c(R)f(x,y)], \quad (5.5a)$$

where

$$c(R)=2me^2/(\pi\hbar p_F), \quad (5.5b)$$

$$x=|\mathbf{p}_F-\mathbf{p}|/p_F, \quad (5.5c)$$

$$y=\omega/(p_F^2/2m). \quad (5.5d)$$

Those assertions about $\tilde{v}_2$ which we made to justify setting (4.14) equal to zero are now seen to follow directly from some of those properties of $f(x,y)$ which we have just noted.

This expression for $\tilde{v}_2$ is to be inserted into the expression (4.17b) defining $J(R)$. The variables of integration may be transformed from p, $\cos\theta$, and ω to x, y, z, where $z=|\mathbf{p}|/p_F$ so that

$$x^2=1+z^2-2z\cos\theta. \quad (5.6)$$

Thus

$$J=4\pi e^2 p_F\int_0^\infty z\,dz\int_{|1-z|}^{|1+z|} x\,dx\int\frac{dy}{2\pi i}\exp(-iy0^+)\times[y-1+z^2-i\alpha\epsilon(z-1)]^{-1}[x^2+cf(x,y)]^{-1}. \quad (5.7)$$

The order of integration over x and z may be interchanged, and the z integration, whose limits become $1+x$ and $|1-x|$, may be performed. The result of this z integration will depend on whether or not the point $z=1$ lies within the range of integration.

$$J=2\pi e^2 p_F\int_0^\infty x\,dx\int\frac{dy}{2\pi i}\exp(-iy0^+)g(x,y)\times[x^2+cf(x,y)]^{-1}, \quad (5.8a)$$

$$g=\ln\frac{y+i\alpha}{y+i\alpha-x(2-x)}+\ln\frac{y-i\alpha+x(2+x)}{y-i\alpha} \quad : \quad x<2, \quad (5.8b)$$

$$g=\ln\frac{y-i\alpha+x(x+2)}{y-i\alpha+x(x-2)} \quad : \quad x>2. \quad (5.8c)$$

The integral over y can be considered to be a contour integral over a path enclosing the entire lower half of the complex y plane. Each singularity of the integrand will yield a contribution to $J(R)$ and so these singularities are of interest. They are depicted in Fig. 3. Figure 3 indicates the so-called plasmon poles[12,13] contributed by the last factor of the integrand, located at those points $y=\pm y_0$ for which

$$x^2+cf(x,y_0)=0. \quad (5.9)$$

A study of this equation indicates that for values of x and c for which the solution lies on the principal branch of f, that solution is in the second and fourth quadrant of the complex y plane. We go into this

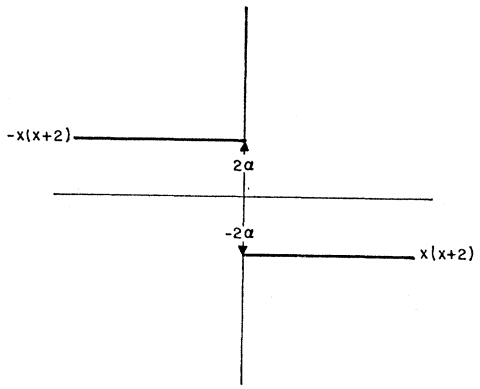

FIG. 2. Branch cuts of $f(x,y)$ in complex y plane.

[12] D. F. DuBois, Ann. Phys. 7, 174 (1959). This reference and the next contain references to work in this area.

[13] J. J. Quinn and R. A. Ferrell, Phys. Rev. 112, 812 (1958).

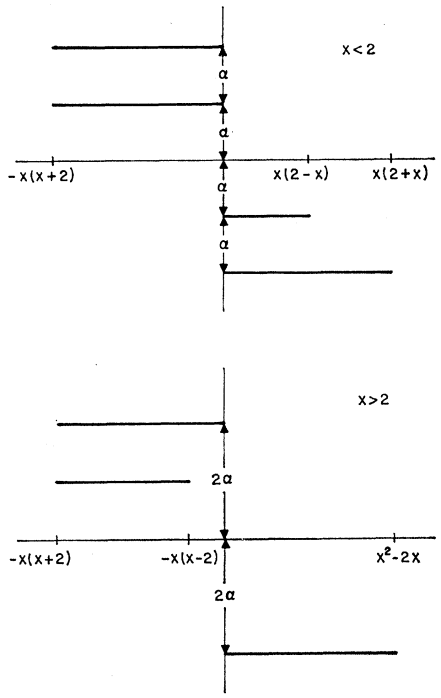

FIG. 3. Singularities of the integrand of Eq. (5.8) in complex y plane.

matter somewhat more carefully in Appendix A of this paper.

Instead of pursuing the steps which lead to the conversion of the y integral to integrations over the finite-length branch cuts in the lower half plane, we shall follow a course which will show the connection between this integral and the nonkinetic part of the separation energy, the energy required to remove a particle of momentum p_F. In this way, we shall be able to avoid the necessity of a numerical evaluation of that integral which results when the former course is followed, by taking advantage of numerical results others have obtained.[5,9,12,13] We rewrite (5.8a) as

$$J=2\pi e^2 p_F\int_0^\infty \frac{dx}{x}\int \frac{dy}{2\pi i}\exp(-iy0^+)g(x,y)$$
$$-2\pi e^2 p_F\int_0^\infty \frac{dx}{x}\int \frac{dy}{2\pi i}\exp(-iy0^+)g(x,y)$$
$$\times\left[\frac{cf(x,y)}{x^2+cf(x,y)}\right]. \quad (5.10)$$

The first integral on the right may be evaluated by contour integration. The only singularity of the integrand in the lower half of the y plane is the cut which extends from the axis to $x(2-x)$, and this, only for $x<2$. (See Fig. 3.) The discontinuity of the integrand across the cut is $-2\pi i$, and thus, the term is

$$J^{(1)}=-2\pi e^2 p_F\int_0^2 \frac{dx}{x}\int_0^{x(2-x)} dy=-4\pi e^2 p_F. \quad (5.11)$$

In the second term, the exponential serves to inform us that the singularities in the lower half plane contribute to the y integration—i.e., that the integral over the infinite semicircle on the lower half of the y plane vanishes. However, since $f(x,y)$ behaves as $1/y^2$ for large y (see 5.4b), this exponential is not needed, and can be set equal to unity. The path of integration may now be rotated from the real axis to the imaginary axis without crossing any singularities.[14] Rotation of the path of integration away from the real axis gives y such a large imaginary part that the small imaginary additions $i\alpha$ which appear in (5.8) and (5.4b) will have no effect. When α is set equal to zero in Eq. (5.4b) defining $f(x,y)$, the two terms of the integral cancel over that region for which the restriction $|\mathbf{u}+\mathbf{x}|>1$ is violated. Hence, this restriction may be dropped and the integration performed, yielding

$$f(x,y)=1+\frac{1}{2x}\left[1-\frac{1}{4}\left(x+\frac{y}{x}\right)^2\right]\ln\left[\frac{x(x+2)+y}{x(x-2)+y}\right]$$
$$+\frac{1}{2x}\left[1-\frac{1}{4}\left(x-\frac{y}{x}\right)^2\right]\ln\left[\frac{x(x+2)-y}{x(x-2)-y}\right]. \quad (5.12)$$

This form is closely related to Lindhard's dynamic dielectric constant $\epsilon(\mathbf{k},\omega)$,[15] a function of wave number $\mathbf{k}$ and frequency ω. In fact,

$$\epsilon(k,\omega)=1+[c(R)/x^2]f(x,y). \quad (5.13)$$

We may now insert (5.13) into the second term of (5.10) and, on setting the exponential there equal to unity and rotating the path of integration from the real to the imaginary axis, obtain

$$J^{(2)}=-e^2 p_F\int_0^\infty \frac{dx}{x}\int_{-\infty}^{\infty} dy g(x,iy)\left[\frac{1}{\epsilon(k,i\omega)}-1\right]. \quad (5.14)$$

We note that Eq. (5.12) indicates that $f(x,y^*)=f^*(x,y)$, and that $f(x,-y)=f(x,y)$. This establishes the reality of f, and consequently of ϵ, along the imaginary axis.

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[14] This is the so-called Wentzel transformation. See K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, Phys. Rev. **108**, 507 (1957). Another way of stating the legitimacy of this step in which the exponential is ignored and the path of integration is rotated in the complex y plane is the following: The path along the imaginary axis augmented by the infinite semicircle over the right half plane encloses the same singularities as does the path along the real axis augmented by the infinite semicircle over the lower half plane. In neither case does the integral over the infinite semicircle contribute.

[15] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **28**, No. 8 (1954).

We also note that setting $\alpha=0$ gives (5.8) a form

$$g(x,y)=\ln\frac{y+x(x+2)}{y+x(x-2)}, \tag{5.15}$$

with the property that $g(x,y^*)=g^*(x,y)$. Hence integration of the product of $g(x,y)$ with an even function of y along the imaginary y axis will not contain the contribution of the imaginary part of $g(x,y)$, and we may replace g by its real part:

$$\mathrm{Re}g(x,iy)=\tfrac{1}{2}\ln\left[\frac{y^2+x^2(x+2)^2}{y^2+x^2(x-2)^2}\right]$$
$$=-\int_{-1}^{1}d\mu\frac{\mu-x/2}{(\mu-\frac{1}{2}x)^2+(y/2x)^2}. \tag{5.16}$$

This expression may be inserted into (5.14). Introducing $v=y/2x$, $z=x/2$, we have

$$J^{(2)}=-4e^2p_F\int_{-\infty}^{\infty}dv\int_0^{\infty}dz\left(\frac{1}{\epsilon}-1\right)$$
$$\times\int_{-1}^{1}d\mu\frac{\mu-z}{(\mu-z)^2+v^2}. \tag{5.17}$$

We have achieved the desired connection between our quantity J and a quantity of physical significance which appears in the study of the infinite electron gas. Quinn and Ferrell[13] compute the correlation energy of an infinite electron gas by studying the self energy of an electron near the top of the Fermi sea. Comparison with their work reveals that $J^{(1)}$ is $4\pi^2\hbar$ times the exchange energy of an electron at the Fermi surface, and that $J^{(2)}$ is $4\pi^2\hbar$ times the correlation energy of an electron at the Fermi surface.[16]

In a uniform system, the separation energy is composed of kinetic energy, potential energy, exchange energy, and correlation energy—that is, designating the separation energy by $-E_S$,

$$E_S=p_F^2/2m+E_{\mathrm{ex}}(p_F)+E_{\mathrm{corr}}(p_F).$$

We have found now that

$$J(R)=4\pi^2\hbar\{E_S-p_F^2/2m\}. \tag{5.18}$$

This is a result we encountered before in I, although we did not recognize it there. The equation in I, (Eq. 4.15), can be written in the form of Eq. (4.18) of this paper so that a quantity in I can be defined which corresponds to the J of this paper. This quantity turns out to be equal to $-4\pi e^2p_F$, which is $4\pi^2\hbar$ times the nonkinetic part of the separation energy for an infinite electron gas in the Hartree-Fock approximation.

This fact suggests the way to include the effect of the term which we deleted from Eq. (2.9). Let us recall that when one calculates the nonkinetic part of the separation energy of an infinite electron gas using the theory of G.B., the result is a sum of terms, each term arising from one of the members of the right-hand side of Eq. (2.9). It seems likely that the contribution to J of the deleted term may be included along with the others merely by using an expression for E_S in which the contribution of this term appears. Such an expression can be derived from G.B.'s formula for the correlation energy per particle.[17] It also seems likely that the way to go past the Gell-Mann and Brueckner theory is to use an expression for the separation energy which has validity beyond the high-density limit. Therefore, we shall use the general equation, (5.18), for $J(R)$ without specifying in detail how the separation energy is to be calculated. Inserting this in Eq. (4.18) gives the equation for the first correlation and quantum correction to the Thomas-Fermi model:

$$\nabla^2\phi_2-\left(\frac{4me^2}{\pi\hbar^3}\right)p_F\phi_2=\frac{4me^2p_F}{\pi\hbar^5}\left\{E_S-\frac{p_F^2}{2m}\right\}$$
$$+\frac{me^2}{12\pi\hbar^3p_F}\left[4\nabla^2\phi_0+\frac{2m}{p_F^2}\left(\frac{d\phi_0}{dR}\right)^2\right]. \tag{5.19}$$

VI. SUMMARY AND DISCUSSION

An equation has been derived which determines the first correction to the Thomas-Fermi potential in terms of the Fermi momentum of the ordinary Thomas-Fermi model and the separation energy of an infinite electron gas. This correction describes the change from the Thomas-Fermi potential due to exchange, inhomogeneity, and correlation effects, and is the first term of a series whose higher members can, in principle, be found using the techniques described in this paper.

A recent paper by Lewis[7] describes a method of including correlation and exchange effects in the Thomas-Fermi model. His approach is based on the assumption that the electron cloud surrounding that atom behaves locally like an infinite electron gas, and therefore that a local separation energy can be ascribed to each point in the atom. This separation energy, he reasons, must be independent of position if the electron distribution is to be in equilibrium. By including successively the contributions of the potential, exchange, and correlation energies in his expression for the separation energy, he obtains successively the Thomas-Fermi, the Thomas-Fermi-Dirac, and the Thomas-Fermi-Dirac-correlation model of the atom.

Independently, Tomishima[18] proposed the same

[16] Their Eq. (5.4) has apparently omitted a minus sign. These authors work with $\hbar=1$.

[17] It is possible to relate the correlation energy for an electron at the top of the Fermi sea to the average energy per particle for the system, using a theorem due to Seitz. See F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940) p. 343. This technique is used by Quinn and Ferrell in reference 13.

[18] Y. Tomishima, Progr. Theoret. Phys. (Kyoto) **22**, 1 (1959).

sequence of models using a slightly different approach. This time, the assumption is that the energy of the atom is given by the volume integral of an energy density which depends only on the local density of particles. This energy is then minimized with respect to variation of particle density, subject to particle conservation. By including successively the various contributions to the energy density, Tomishima also obtains the various models mentioned before. The relationship between his work and that of Lewis, to which it is equivalent, arises because of the way the separation energy is related to the energy density.

Both authors utilize the G.B. expression for the correlation energy at high densities. Both recognize that the expression needs modification at low densities and propose changes of the G.B. expression which have more or less reasonable low-density limits. Some such prescription would have to be used in the application of our work. Tomishima's paper gives numerical results which show that the equation he and Lewis propose gives an electron distribution rather close to that predicted by the Thomas-Fermi-Dirac equation. In particular, the difficulty[19] of the discontinuity in density at the edge of the atom persists, even though correlation effects are included. A virtue of the technique we have proposed is that it does not yield, in the no-correlation case, the discontinuity at the edge of the atom.[20] Calculations are now in progress to determine if the distribution will behave sensibly at the edge of the atom for the present theory, in which the effect of correlations is included.

One may ask how our technique differs from that of Lewis and Tomishima for those more or less extended systems in which inhomogeneity would not be expected to play a major role. All inhomogeneity effects can be suppressed in our theory merely by discarding the θ_j operators for $j>0$. If we do this, we can sum the expansion and obtain equations almost identical to those which describe an infinite medium, the sole difference being that the Fermi momentum now depends on position. Such a procedure applied to the technique in I does, in fact, lead to the Thomas-Fermi-Dirac equation. So far, however, we have not been able to recover the starting point of the Lewis and Tomishima technique by ignoring the inhomogeneities and summing the expansion. The difficulty seems to be connected with the fact that when correlation effects are introduced, the electrons no longer occupy a Fermi distribution in momentum space. It may be possible in some other manner to derive the starting point of the Lewis and Tomishima theory from ours by ignoring inhomogeneities. We suspect, however, that there may be a real difference in content which makes it impossible to do so.

[19] N. H. March, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 7.

[20] The numerical solution to the equation for the first correction to the Thomas-Fermi model in I (4.15) is given in reference 3.

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APPENDIX

A. The Plasmon Poles

The integral (5.4b) defining $f(x,y)$ can be evaluated for real y in the limit $\alpha \to 0$ by splitting the integrand into its real and imaginary parts using the relationship

$$\lim_{\alpha\to 0} \frac{1}{z+i\alpha} = P\frac{1}{z} + i\pi\delta(z).$$

The result is

$$\lim_{\alpha\to 0^+;\ y \text{ real}} f(x,y) = A(x,y) + i\Sigma(x,y), \qquad \text{(A.1a)}$$

$$A = \frac{1}{\pi} P \int_{|\mathbf{u}|<1;\ |\mathbf{u}+\mathbf{x}|>1} d\mathbf{u} \left\{ \frac{1}{y+x^2+2\mathbf{x}\cdot\mathbf{u}} + \frac{1}{-y+x^2+2\mathbf{x}\cdot\mathbf{u}} \right\}, \qquad \text{(A.1b)}$$

$$\Sigma = \int_{|\mathbf{u}|<1;\ |\mathbf{u}+\mathbf{x}|>1} du\{\delta(y+x^2+2\mathbf{x}\cdot\mathbf{u}) + \delta(-y+x^2+2\mathbf{x}\cdot\mathbf{u})\}. \qquad \text{(A.1c)}$$

These expressions appear, in basically the same form, in DuBois'[12] paper. He credits Ferrell with the observation that the restriction $|\mathbf{u}+\mathbf{x}|>1$ is superfluous in the evaluation of A because the two terms of the integrand cancel over the region $|\mathbf{u}+\mathbf{x}|<1$. The evaluation of each term of Σ involves calculating the area of a plane, perpendicular to $\mathbf{x}$, whose distance from the origin depends on x and y and which cuts one, both, or neither of the unit spheres which bound the region of integration. These spheres are centered on the origin and on the point $-\mathbf{x}$. For $|\mathbf{x}|>2$, the spheres fail to intersect, and so the form of the result differs from that for $|\mathbf{x}|<2$. Upon evaluating the integrals, we obtain the result

$$A = \frac{1}{x}\left\{ x + \frac{1}{2}\left[1-\frac{1}{4}\left(\frac{y}{x}+x\right)^2\right] \ln\left|\frac{y+x(x+2)}{y+x(x-2)}\right| + \frac{1}{2}\left[1-\frac{1}{4}\left(\frac{y}{x}-x\right)^2\right] \ln\left|\frac{y-x(x+2)}{y-x(x-2)}\right| \right\}, \qquad \text{(A.2a)}$$

$$\Sigma(x>2;\ y) = 0; \quad x(x+2)<y$$

$$= \frac{\pi}{2x}\left[1-\frac{1}{4}\left(\frac{y}{x}-x\right)^2\right]; \quad x(x-2)<y<x(x+2)$$

$$= 0; \quad 0<y<x(x-2)$$

$$\Sigma(x<2, y)=0; \quad x(2+x)<y \tag{A.2b}$$
$$=\frac{\pi}{2x}\left[1-\frac{1}{4}\left(\frac{y}{x}-x\right)^2\right];$$
$$x(2-x)<y<x(2+x)$$
$$=\frac{\pi y}{2x}; \quad 0<y<x(2-x)$$
$$\Sigma(x,-y)=\Sigma(x,y).$$

This result was obtained previously by Hubbard,[9] although his A and Σ differ from ours by a factor involving p_F and x^2. The utility of this result is twofold. Firstly, integrals over y involving f can be frequently transformed to contour integrals to be evaluated by shrinking the contour down around the singularities of f. Once these have been identified the limit $\alpha\to 0$ may be taken. It will turn out that the integrals remaining will involve only A and Σ, to be integrated over finite lengths of the real y axis. Secondly, this result determines the appropriate branch of the function which describes f when $\alpha\neq 0$, and y is anywhere in the complex plane. That is, the integral (5.4b) for f can be evaluated just as it stands, with the result

$$f(x<2, y)=\frac{1}{x}\Big\{x-i\alpha+\frac{1}{2}\Big[1-\frac{1}{4}\Big(\frac{y-2i\alpha}{x}+x\Big)^2\Big]$$
$$\times\ln\Big[\frac{y-2i\alpha+x(2+x)}{y-2i\alpha+x(2-x)}\Big]-\tfrac{1}{2}(y-2i\alpha)$$
$$\times\ln\Big[\frac{y-2i\alpha+x(2-x)}{y-2i\alpha}\Big]+\tfrac{1}{2}(y+2i\alpha)$$
$$\times\ln\Big[\frac{y+2i\alpha-x(2-x)}{y+2i\alpha}\Big]$$
$$+\frac{1}{2}\Big[1-\frac{1}{4}\Big(\frac{y+2i\alpha}{x}-x\Big)^2\Big]$$
$$\times\ln\Big[\frac{y+2i\alpha-x(2+x)}{y+2i\alpha-x(2-x)}\Big]\Big\}, \tag{A.3a}$$

$$f(x>2, y)=\frac{1}{x}\Big\{x-\frac{2i\alpha}{x}+\frac{1}{2}\Big[1-\frac{1}{4}\Big(\frac{y-2i\alpha}{x}+x\Big)^2\Big]$$
$$\times\ln\Big[\frac{y-2i\alpha+x(x+2)}{y-2i\alpha+x(x-2)}\Big]$$
$$+\frac{1}{2}\Big[1-\frac{1}{4}\Big(\frac{y+2i\alpha}{x}-x\Big)^2\Big]$$
$$\times\ln\Big[\frac{y+2i\alpha-x(x+2)}{y+2i\alpha+x(x-2)}\Big]\Big\}. \tag{A.3b}$$

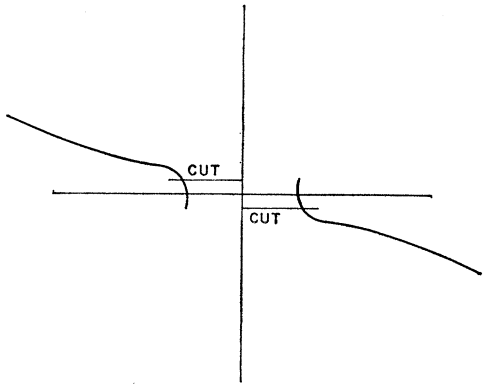

FIG. 4. The curve $\mathrm{Im}f(x,y)=0$.

The phase of the logarithm of each divisor or dividend should be restricted to $-\pi<\phi<+\pi$, and (A.3) will then go over into (A.2) in the limits y real and $\alpha\to 0$.

This form (A.3) is useful in locating the plasmon pole at that y_0 for which

$$x^2+cf(x,y_0)=0,$$
$$\mathrm{Re}f(x,y_0)=-x^2/c, \tag{A.4}$$
$$\mathrm{Im}f(x,y_0)=0. \tag{A.5}$$

We regard the position of the pole as being determined by the intersection of the curves in the y_0 plane defined by (A.4) and (A.5). Since the curve (A.5) is independent of c, it is convenient to study this curve, and to regard the position of the pole along it as being determined by (A.4). The general behavior of the curve is depicted in Fig. 4. The relevant features of the curve are these:

For y far from the imaginary axis, the curve is asymptotic to a straight line whose angle with the real axis is proportional to α.

For y closer to the imaginary axis, the curve approaches the end of the branch cut of $f(x,y)$, and, crossing the cut, continues on a different sheet of the function. The distance of this crossing from the end of the cut is also proportional to α.

The plasmon pole on the sheet of the function which is of interest to us always lies in the second and fourth quadrant, if it is present at all, and thus the rotation of the axis used in Sec. V can be performed without crossing any singularities.

In the limit $\alpha\to 0$, the plasmon pole in the fourth quadrant lies just below the real axis to the right of the cut. As x^2/c is varied, this pole reaches the end of the cut. The value of x for which this occurs is determined by (A.4) by setting $y_0=x(x+2)$. This value of x, which depends on c, is called x_c,[12,13] the cutoff momentum, or the critical momentum, since for greater values of x, the plasmon pole does not appear but seems to be imbedded in the continuum. As x is reduced from values greater than x_c to values less than x_c, the plasmon state appears at the end of the continuum represented by the cut, and detaches itself from this continuum.

This behavior was somewhat mysterious when the plasmon state was regarded as one of the states arising from the continuum. Now that we have traced its position onto the nonphysical sheet for $x>x_c$, this mystery is dispelled.

B. Terms in the Operator[21] θ

$$\theta_0[\tilde{K},\tilde{G}]=\tilde{K}\tilde{G},$$

$$\theta_1[\tilde{K},\tilde{G}]=\tfrac{1}{2}i\sum_{xyz}\left(\frac{\partial\tilde{K}}{\partial x}\frac{\partial\tilde{G}}{\partial p_x}-\frac{\partial\tilde{K}}{\partial p_x}\frac{\partial\tilde{G}}{\partial x}\right),$$

$$\theta_2[\tilde{K},\tilde{G}]=(\tfrac{1}{2}i)^2\Bigg[\sum_{xyz}\frac{1}{2}\left(\frac{\partial^2\tilde{K}}{\partial x^2}\frac{\partial^2\tilde{G}}{\partial p_x{}^2}+\frac{\partial^2\tilde{K}}{\partial p_x{}^2}\frac{\partial^2\tilde{G}}{\partial x^2}\right)+\sum_{xyz}\left(\frac{\partial^2\tilde{K}}{\partial x\partial y}\frac{\partial^2\tilde{G}}{\partial p_x\partial p_y}+\frac{\partial^2\tilde{K}}{\partial p_x\partial p_y}\frac{\partial^2\tilde{G}}{\partial x\partial y}\right)-\sum_{p_xp_yp_z}\sum_{xyz}\frac{\partial^2\tilde{K}}{\partial x\partial p_y}\frac{\partial^2\tilde{G}}{\partial y\partial p_x}\Bigg].$$

The full θ is given by

$$\theta[\tilde{K},\tilde{G}]=\lim_{R'\to R;\,p'\to p}\exp\left[\frac{i\hbar}{2}\sum_{xyz}\left(\frac{\partial}{\partial R_x}\frac{\partial}{\partial p_x{}'}-\frac{\partial}{\partial p_x}\frac{\partial}{\partial R_x{}'}\right)\right]\times\tilde{K}(\mathbf{R},\mathbf{p}\omega)\tilde{G}(\mathbf{R}',\mathbf{p}'\omega).$$

[21] The summation of xyz means that xyz are to replace each other cyclically. The double summation means that xp_y is to be replaced by each of the eight other combinations of a component of **R** and a component of **p**.

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Absolute Measurement of a Set of Energy Calibration Standards*

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A 180° magnetic spectrometer has been employed to measure the energy of several neutron thresholds and γ-ray resonances, as well as the energy of the alpha particles emitted by Po^{210}. The primary reason for performing these experiments was to obtain a set of energy standards with consistent experimental techniques for all the measurements. The neutron thresholds studied were $Li^7(p,n)Be^7$, $B^{11}(p,n)C^{11}$, $C^{13}(p,n)N^{13}$, and $F^{19}(p,n)Ne^{19}$. The γ-ray resonances at 872 kev in $F^{19}(p,\alpha\gamma)O^{16}$ and at 992 kev in $Al^{27}(p,\gamma)Si^{28}$ were observed. The same instrument used to make the energy measurements for these experiments was also employed to determine the energy of the alpha particles emitted by Po^{210}.

INTRODUCTION

CONSIDERABLE effort has been devoted in recent years to precise energy measurements of several nuclear reactions frequently employed for calibration purposes. These measurements have consisted primarily of the energy determination of neutron thresholds, γ-ray resonances, and the measurements of the energy of alpha particles emitted by radioactive substances. Generally speaking, the reason for the continuous effort to obtain increased accuracy in these measurements has stemmed from the extensive use of these reactions in calibrating analyzing magnets associated with accelerator energy determinations and with Q-value and nuclear mass measurements. It seemed of some importance to perform a representative set of calibrations by employing a single instrument and a single analysis technique. This paper describes such a set of measurements.

The present work has been concerned with (1) the neutron thresholds in the reactions $Li^7(p,n)Be^7$, $B^{11}(p,n)C^{11}$, $C^{13}(p,n)N^{13}$, and $F^{19}(p,n)Ne^{19}$ and (2) the γ-ray resonances at 872 kev for the reaction $F^{19}(p,\alpha\gamma)O^{16}$ and at 992 kev for $Al^{27}(p,\gamma)Si^{28}$. In addition, (3) the energy of the alpha particles emitted by Po^{210} has been measured with the same instrument. These particular reactions were chosen as being those most frequently employed in energy calibration measurements.

EXPERIMENTAL PROCEDURE

The Rice University Van de Graaff accelerator, with associated 90° magnetic analysis, has served as the source of monoenergetic protons for these experiments, with a 180° magnetic spectrometer[1] employed to determine the proton energy. The basic procedure has been to determine the accelerator bombarding energy as a function of the magnetometer frequency of the Van de Graaff analyzing magnet by measuring the energy of

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[1] K. F. Famularo and G. C. Phillips, Phys. Rev. **91**, 1195 (1953).