Green's Function Method for Quantum Corrections to the Thomas-Fermi Model of the Atom*

GENE A. BARAFF† AND SIDNEY BOROWITZ
Physics Department, New York University, New York, New York

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A systematic method is presented for deriving the Thomas-Fermi equation for an atom and the quantum corrections from the many-body description. The novel feature of the method is that it does not require any *a priori* assumptions about the assignment of electrons to fully occupied single-particle states or about the distribution of electrons in phase space, but shows instead that the distribution which is usually assumed, or derived from the assumption of fully occupied single particle states, is a direct consequence of specifying that the many particle system is in its ground state. The procedure used in the derivation is the expansion of the mixed position-momentum representation of the Green's function in a series of powers of $\hbar$. The lowest order term is found to correspond with the Thomas-Fermi density. The form of the higher order terms, which are to be considered as corrections to zeroth order term, depends on the approximations made in the many-body equations for obtaining the Green's function. This paper deals only with the Hartree-Fock approximation, but the methods presented here allow generalization to other approximations which can include correlation effects.

I. INTRODUCTION

THE Thomas-Fermi model of the atom developed historically from reasonable physical assumptions about the nature of an atomic system.[1] However, because the development was not a systematic derivation from the many-body Schrödinger equation, it was difficult to incorporate corrections for certain higher order effects.

Dirac[2] in 1930 showed the connection between the Hartree-Fock theory and the Thomas-Fermi model. In this paper, the Hartree-Fock equations were expressed in terms of the density matrix, and the Fourier transform of the density matrix was identified as being the phase space distribution of electrons having a given spin direction. In order to proceed with the solution of his equations, Dirac made the plausible assumption that the distribution of electrons in phase space is the local Fermi density; that is, it equals $(2\pi\hbar)^{-3}$ for momenta less than the Fermi momentum $p_F(R)$ and is zero otherwise. The solution of his equations yielded the Thomas-Fermi equation plus an extra term due to exchange. This augmented equation has since become known as the Thomas-Fermi-Dirac equation.

In 1955,[3] Theis was able to show that Dirac's plausible assumption was a consequence of the fact that the system was in its ground state and that the single-particle density matrix is idempotent, $(\rho^2=\rho)$. This latter property of single-particle density matrices is satisfied for systems in which the n electrons can be assigned to n single-particle states, each of which has an occupation number equal to unity.

To complete this historical introduction, in 1957 Kompaneets and Pavlovskii[4] apparently independently of Theis, showed how, starting from Dirac's assumption, one could derive quantum corrections to the Thomas-Fermi model using the scheme proposed by Theis, namely, expansions in powers of $\hbar$. The extra terms included both exchange and inhomogeneity corrections. A somewhat different, but equivalent scheme was proposed by Kirzhnits[5] at about the same time. By assuming that the occupation number of each single-particle state depended on the expectation value of the Hamiltonian in that single-particle state, Kirzhnits was able to derive the Thomas-Fermi model at elevated temperatures. Thus, to date, all systematic corrections to the Thomas-Fermi model are based either on an *a priori* assumption about the momentum distribution of the electrons or on a model which, at zero temperature, approximates the wave function of the atom by a single Slater determinant.[6]

Before one attempts to introduce correlation corrections into the Thomas-Fermi model, it is necessary to investigate whether Dirac's assumption regarding the distribution of electrons in phase space depends on the description of an atomic system by a single Slater determinant. Löwdin[7] has shown that the introduction of correlation by using sums of Slater determinants re-

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† National Science Foundation Predoctoral Fellow.

[1] The basic references and the classical Thomas-Fermi model are described in the review article by P. Gombas in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXVI.

[2] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[3] W. R. Theis, Z. Physik **142**, 503 (1955).

[4] A. S. Kompaneets and E. S. Pavlovskii, Soviet Phys.-JETP **31**(4), 328 (1957).

[5] D. A. Kirzhnits, Soviet Phys.-JETP **32**(5), 64 (1957).

[6] An *apparent* exception to this statement is the work of S. Golden, Phys. Rev. **105**, 604 (1957); **107**, 1283 (1957); and Revs. Modern Phys. **32**, 322 (1960). Golden's work consists of two parts. In the first, he does not confine himself to single-particle Hamiltonians and makes no special assumption about the occupation number of single-particle states. However his working equations, while elegant, are not in the spirit of the Thomas-Fermi model in the sense that their greatest utility is for treating problems in which the number of particles is small. In the second part, he does indeed derive the Thomas-Fermi equation and quantum corrections from his formalism, but in doing so, he makes the usual assumption of introducing a single-particle Hamiltonian and a single-particle density matrix in which each single-particle state is either fully occupied or empty.

[7] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955), Sec. 4.

sults in fractional occupation numbers for the single-particle states.

By applying field-theoretic methods to the problem at hand, we show in this paper that Dirac's assumption can be derived from a statement that the atomic system is in its ground state, and that the Thomas-Fermi model with the previously derived quantum corrections can also be obtained using this formalism. But, by freeing ourselves at the outset from dependence on a determinantal wave function, we obtain a formalism capable of generalization to include correlation effects. We shall exploit this freedom in a future publication.

We use the Green's function formulation introduced by Schwinger,[8] discussed by Galitskii and Migdal[9] for the quantum mechanical many-particle system in the ground state, and by Martin and Schwinger[10] for the quantum mechanical many-particle system at nonzero temperature. This formalism for treating the N-particle system is a time-dependent description which resembles in some ways the time-independent description employing the set of 1, 2, $\cdots N$-particle density matrices. In it, the n-particle Green's function

$$G_n(\mathbf{r}_1 t_1 \cdots \mathbf{r}_n t_n;\, \mathbf{r}_1' t_1' \cdots r_n' t_n') \tag{1.1}$$

is analogous to the n-particle density matrix and can supply all of the information about the system contained in the latter.[11] As is the case for the density matrices, the Green's functions satisfy a hierarchy of equations in which the n-particle Green's function is coupled to the $(n-1)$-particle and the $(n+1)$-particle Green's function.

Explicit solutions to this set of equations coupling the various Green's functions are not known. Martin and Schwinger[10] discuss a systematic approximation scheme for truncating this set of equations, retaining the first n equations and approximating G_{n+1} in terms of the Green's functions for fewer particles. The simplest of these approximations is the Hartree-Fock approximation,[12] which results from approximating the two-particle Green's function by the antisymmetric product of one-particle Green's functions. We shall show by using an expansion similar to that used by Theis that the first term in the expansion of the solution of the Hartree-Fock approximation in powers of $\hbar$ yields the Thomas-Fermi model. The Dirac and inhomogeneity effects appear together in the equation determining the first nonvanishing correction to the Thomas-Fermi model. Higher order corrections can be generated in a manner similar to the method of Kompaneets and Pavlovskii.[4]

This technique of using the Green's function to derive the Thomas-Fermi model from the many-body equation is useful because it enables one to incorporate correlation corrections into the Thomas-Fermi model. We shall treat this problem in a forthcoming paper by replacing the Hartree-Fock approximation with the Gell Mann–Brueckner approximation.[13]

In Sec. II, we state without proof some useful properties of the Green's functions. We also state the first hierarchy equation satisfied by the single-particle Green's function and the Hartree-Fock approximation to it. We transform this equation to a mixed position-momentum representation. This transformation introduces an infinite order differential operator θ, which acts on the mixed representation single-particle Green's function to produce an equation completely equivalent to the original Hartree-Fock equation. In Sec. III, we make use of the structure of θ to expand the solution in a series involving powers of $\hbar$. We then show that the lowest order term yields the Thomas-Fermi density. In Sec. IV, we discuss higher order corrections. Sec. V contains the proof of the assertions made in Sec. II. Most important, however, it contains the discussion of the analytic properties of the exact Green's function which indicates clearly the connection between the appearance of the Thomas-Fermi density and the specification that the system be in its ground state. The derivation of the operator θ is to be found in the Appendix.

II. TRANSFORMATION TO THE MIXED REPRESENTATION

We 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. When we neglect spin-dependent forces and all relativistic effects in our system, the Hamiltonian is

$$H=\sum_i H_0(\mathbf{r}_i)+\tfrac{1}{2}\sum_{i\neq j} v(\mathbf{r}_i-\mathbf{r}_j), \tag{2.1a}$$

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

$$v(\mathbf{r}_i-\mathbf{r}_j)=e^2/|\mathbf{r}_i-\mathbf{r}_j|. \tag{2.1c}$$

We have mentioned the n-particle Green's function in the previous section: For the purposes of this section, we shall need only a few of its simplest properties. These properties follow directly from the basic definition (see Sec. V) and will be stated in the following paragraph. First, however, we must comment on notation. If the n-particle Green's function is denoted by (1.1), then each coordinate $\mathbf{r}_i$ and $\mathbf{r}_i'$ specifies both a spatial location and a spin direction. Consequently, equality of two coordinates indicates that the spatial locations are the same and that the associated spin indices are identical. Integration over a coordinate will be understood to imply summation over the corresponding spin index,

[8] J. Schwinger, Proc. Natl. Acad. Sci. U. S. **37**, 452 (1951).

[9] V. M. Galitskii and A. B. Migdal, Soviet Phys.-JETP **34**(7), 96 (1958).

[10] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

[11] A. Klein and R. Prange, Phys. Rev. **112**, 994 (1958); R. Prange and A. Klein, Phys. Rev. **112**, 1008 (1958).

[12] This approximation, in common with the usual Hartree-Fock equations for the self-consistent field, neglects dynamic correlation between the particles. It differs from them, however, in that it does allow for fractional occupation numbers, and does not by itself make any assignment of electrons to single-particle states.

[13] M. Gell Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

and a Dirac delta function of two coordinates will be understood to be multiplied by the Kronecker delta of the corresponding spin indices.

The n-particle Green's function contains all the information necessary to compute the expectation value of any n-particle property of the system.[11] In particular, the density of particles with a given direction of the spin is given by

$$n(\mathbf{r},t)=(-i)G_1(\mathbf{r}t;\,\mathbf{r}t^+), \tag{2.2}$$

where t^+ is a time infinitesimally later than t. The energy of the system is the expectation value of the Hamiltonian and is computed from the one- and two-particle Green's functions by the prescription

$$E=(-i)\int d\mathbf{r}\,\lim_{\mathbf{r}'\to\mathbf{r}}H_0(\mathbf{r})G_1(\mathbf{r}t;\,\mathbf{r}'t)$$
$$+(-i)^2\frac{1}{2}\int d\mathbf{r}_1d\mathbf{r}_2v(\mathbf{r}_1-\mathbf{r}_2)G_2(\mathbf{r}_1t\mathbf{r}_2t;\,\mathbf{r}_1t^+\mathbf{r}_2t^+). \tag{2.3}$$

For the system governed by the Hamiltonian (2.1), the Green's functions satisfy a set of integro-differential equations in which the n-particle Green's function is coupled to the $(n-1)$-particle and to the $(n+1)$-particle Green's functions. The first of these equations is

$$[i\hbar(\partial/\partial t_1)-H_0(\mathbf{r}_1)]G_1(\mathbf{r}_1t_1;\,\mathbf{r}_1't_1')$$
$$+i\int d\mathbf{r}_2\,v(\mathbf{r}_1-\mathbf{r}_2)G_2(\mathbf{r}_1t_1,\mathbf{r}_2t_1;\,\mathbf{r}_1t_1'\mathbf{r}_2t_1^+)$$
$$=\hbar\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(t_1-t_1'). \tag{2.4}$$

The Hartree-Fock approximation results from approximating G_2 in the equation above by the antisymmetrized product of one-particle Green's functions as follows:

$$G_2(1,2;\,1'2')\cong G_1(1;\,1')G_1(2;\,2')$$
$$-G_1(1;\,2')G_1(2;\,1'). \tag{2.5}$$

The functions appearing in (2.4) and (2.5) have the spin indices implicit in the coordinates and a spin summation implied by the integration. When we neglect spin-dependent forces of our system and choose a Hamiltonian (2.1), a single particle propagates without change of spin. That is, the single-particle Green's function vanishes unless the spin indices for the particle $\mathbf{r}_1$ and the spin coordinate for the particle $\mathbf{r}_1'$ are the same.

Substitute (2.5) into (2.4) and make the spin indices and summation explicit. If we use the fact that the Green's function for a spin-independent system is zero if the two spin indices are not alike and is otherwise independent of spin, then we find the only effect to be a factor of two multiplying the term arising from the first product on the right of (2.5). Accordingly, we shall include this factor of two, and in the future understand that there are no longer any implicit spin indices or summations in the equation which results:

$$[i\hbar(\partial/\partial t_1)-H_0(\mathbf{r}_1)]G_1(\mathbf{r}_1t_1;\,\mathbf{r}_1't_1')$$
$$+i\int d\mathbf{r}_2\,v(\mathbf{r}_1-\mathbf{r}_2)[2G_1(\mathbf{r}_2t;\,\mathbf{r}_2t^+)G_1(\mathbf{r}_1t;\,\mathbf{r}_1't_1')$$
$$-G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_1^+)G_1(\mathbf{r}_2t_1;\,\mathbf{r}_1't_1')]$$
$$=\hbar\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(t_1-t_1'). \tag{2.6}$$

It is in the spirit of the Hartree-Fock self consistent method to consider (2.6) as a pair of integral equations by writing it as

$$\int K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)d\mathbf{r}_2dt_2\,G_1(\mathbf{r}_2t_2;\,\mathbf{r}_1't_1')$$
$$=\hbar\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(t_1-t_1'), \tag{2.7}$$

$$K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)$$
$$=\left[i\hbar(\partial/\partial t_1)-H_0(\mathbf{r}_1)+2i\int d\mathbf{r}'\,v(\mathbf{r}_1-\mathbf{r}')G_1(\mathbf{r}'t;\,\mathbf{r}'t^+)\right]$$
$$\times\delta(t_1-t_2)\delta(\mathbf{r}_1-\mathbf{r}_2)-iv(\mathbf{r}_1-\mathbf{r}_2)$$
$$\times G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_1^+)\delta(t_1-t_1'). \tag{2.8}$$

Taking the Fourier transform of (2.7) with respect to $\mathbf{r}_1-\mathbf{r}_1'$ and t_1-t_1', keeping $\mathbf{R}=\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_1')$ fixed, we have

$$\int K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)dr_2dt_2\,G_1(\mathbf{r}_2t_2;\,\mathbf{r}_1t_1')d(\mathbf{r}_1-\mathbf{r}_1')d(t_1-t_1')$$
$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_1')-\omega(t_1-t_1')]/\hbar\}=\hbar. \tag{2.9}$$

The integral in (2.9) may be expressed in terms of the Fourier transforms $\tilde{K}$ and $\tilde{G}$,

$$\tilde{K}(\mathbf{R},\mathbf{p}\omega)$$
$$=\int d(\mathbf{r}_1-\mathbf{r}_2)d(t_1-t_2)\,K(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)$$
$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)-\omega(t_1-t_2)]/\hbar\}, \tag{2.10a}$$

$$\tilde{G}(\mathbf{R},\mathbf{p}\omega)$$
$$=\int d(\mathbf{r}_1-\mathbf{r}_2)d(t_1-t_2)\,G_1(\mathbf{r}_1t_1;\,\mathbf{r}_2t_2)$$
$$\times\exp\{-i[\mathbf{p}\cdot(\mathbf{r}_1-\mathbf{r}_2)-\omega(t_1-t_2)]/\hbar\}, \tag{2.10b}$$

$$\mathbf{R}=\tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2), \tag{2.10c}$$

by means of a differential operator of infinite order θ_{Rp}[14] as

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

[14] See Appendix.

Equation (2.9) then takes the form

$$\theta[\tilde{K},\tilde{G}]=\hbar. \tag{2.11}$$

$\tilde{K}(\mathbf{R},\mathbf{p}\omega)$ may be expressed in terms of $\tilde{G}$ by using the definitions (2.8) and (2.10), with the result that

$$\tilde{K}(\mathbf{R},\mathbf{p}\omega)=\omega-p^2/2m+Ze^2/|R|-2\int d\mathbf{r}'v(\mathbf{R}-\mathbf{r}')n(\mathbf{r}')+\int\frac{d\mathbf{p}'}{(2\pi\hbar)^3}n(\mathbf{R},\mathbf{p}')\tilde{v}(\mathbf{p}-\mathbf{p}'), \tag{2.12}$$

where

$$n(\mathbf{R},\mathbf{p})=-i\int\frac{d\omega}{(2\pi\hbar)}\tilde{G}(\mathbf{R},\mathbf{p}\omega)\exp(i\omega 0^+), \tag{2.13a}$$

$$n(\mathbf{R})=-iG(\mathbf{R}t;\mathbf{R}t^+)=\int\frac{d\mathbf{p}}{(2\pi\hbar)^3}n(\mathbf{R},\mathbf{p}), \tag{2.13b}$$

$$\tilde{v}(\mathbf{p})=\int v(\mathbf{r})e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}d\mathbf{r}. \tag{2.14}$$

The relationship between $n(\mathbf{R},\mathbf{p})$ and $n(\mathbf{R})$ permits us to interpret $n(\mathbf{R},\mathbf{p})$ as the phase-space density for electrons of a given spin direction. The system of Eqs. (2.11) and (2.12) is completely equivalent to the original Hartree-Fock equation (2.6). We next turn our attention to the expansion of the set (2.11) and (2.12) in a power series in $\hbar$.

III. EXPANSION IN POWERS OF $\hbar$

We refer to the Appendix and find that the operator θ_{Rp} consists of an infinite series of terms, each term containing explicitly some power of $\hbar$ as a factor

$$\theta_{Rp}=\sum_j\hbar^j\theta_j. \tag{3.1}$$

The zeroth order term is simply the product of the transforms $\tilde{K}$ and $\tilde{G}$ on which θ_{Rp} operates. Higher order terms all contain derivatives of the transform with respect to components of R. Hence, in an infinite homogeneous system for which neither $\tilde{K}$ nor $\tilde{G}$ can depend on $\mathbf{R}$, the zeroth order approximation to (2.11) is exact, within the Hartree-Fock approximation. For a non-infinite system, higher order terms of θ do contribute, and provide corrections for the effects of inhomogeneities. The higher order terms of the operator θ all contain the operator $\hbar(\partial/\partial R_i)(\partial/\partial p_i)$, which suggests that the physically significant parameter exhibited by θ is the fractional variation of $\tilde{K}$ and of $\tilde{G}$ within a cell of area $\hbar$ in the R_ip_i phase plane. If $\hbar$ were small enough relative to the extent of the phase plane occupied by the system, then higher order terms of the operator θ would again be unimportant.

This observation, that the operator θ involves powers of $\hbar$ in a series of terms whose relative size depends on the importance of the uncertainty principle, suggests that it might be useful to expand the density $n(R)$ in a series in which the size of $\hbar$ enters in a systematic manner. Accordingly, we write

$$n(\mathbf{R})=\sum_{j=0}\hbar^jn_j(\mathbf{R}). \tag{3.2}$$

In writing this expansion we do not imply that $n_j(\mathbf{R})$ is independent of $\hbar$; if it were, this would require that there be a classical charge density for the atomic system, namely, $n_0(\mathbf{R})$, which could be found in the limit $\hbar=0$. As we shall see, the quantum effect which prevents the atom from collapsing into the nucleus will be manifest in a negative power of $\hbar$ multiplying each of the terms $n_j(\mathbf{R})$.[15]

The expansion of the density $n(R)$ implies the possibility of similar expansions for $n(\mathbf{R},\mathbf{p})$ and $\tilde{G}(\mathbf{R},\mathbf{p}\omega)$:

$$n(\mathbf{R},\mathbf{p})=\hbar^3\sum\hbar^jn_j(\mathbf{R},\mathbf{p}), \tag{3.3}$$

$$G(\mathbf{R},\mathbf{p}\omega)=\hbar^4\sum\hbar^jG_j(\mathbf{R},\mathbf{p}\omega). \tag{3.4}$$

The powers of $\hbar$ appearing outside of the summations above have been so chosen that those relationships between the coefficients which are a consequence of (2.13) will be independent of $\hbar$. These relationships are

$$n_j(\mathbf{R},\mathbf{p})=-i\int\frac{d\omega}{2\pi}\exp(i\omega 0^+)G_j(\mathbf{R},\mathbf{p}\omega), \tag{3.5a}$$

$$n_j(R)=\int\frac{d\mathbf{p}}{(2\pi)^3}n_j(\mathbf{R},\mathbf{p}). \tag{3.5b}$$

We should now consider the effects of these expansions on the kernel $\tilde{K}(\mathbf{R},\mathbf{p}\omega)$. The exchange potential (2.14) for the Coulomb force (2.1c) is

$$\tilde{v}(\mathbf{p}-\mathbf{p}')=4\pi e^2\hbar^2/|\mathbf{p}-\mathbf{p}'|^2. \tag{3.6}$$

Substituting the expansions (3.2) and (3.3) into the definition (2.12) of the kernel $\tilde{K}$ gives

$$K(\mathbf{R},\mathbf{p}\omega)=\omega-p^2/2m+Ze^2/R-\sum 2h^i\int d\mathbf{r}\,v(\mathbf{R}-\mathbf{r})n_j(\mathbf{r})+\sum_{j=0}\hbar^{(j+2)}\frac{4\pi e^2}{(2\pi)^3}\int\frac{d\mathbf{p}'}{|\mathbf{p}-\mathbf{p}'|^2}n_j(\mathbf{R},\mathbf{p}'). \tag{3.7}$$

This form suggests that we can classify the terms in $\tilde{K}$ according to the explicit power of $\hbar$ they contain.

[15] Recall that the radial scale factor in the dimensionless Thomas-Fermi equation is proportional to $\hbar^2$. In the limit $\hbar\to 0$, the atom takes on zero extension. A physical way of looking at this is the following: The sole function of $\hbar$ in classical Thomas-Fermi theory is to establish a relationship between the local density and other physical quantities. This relation is such that the density is proportional to a negative power of $\hbar$. As $\hbar\to 0$, the density becomes infinite which means, since particles are conserved, that the density can differ from zero only at a single point.

Therefore, we write

$$K(\mathbf{R},\mathbf{p}\omega)=\sum_j \hbar^j K_j(\mathbf{R},\mathbf{p}\omega), \tag{3.8a}$$

$$K_0=\omega-\mathbf{p}^2/2m+Ze^2/|R| -2\int d\mathbf{r}\, v(R-\mathbf{r})n_0(\mathbf{r}), \tag{3.8b}$$

$$K_1=-2\int d\mathbf{r}\, v(\mathbf{R}-\mathbf{r})n_1(\mathbf{r}), \tag{3.8c}$$

$$K_j=-2\int d\mathbf{r}\, v(\mathbf{R}-\mathbf{r})n_j(\mathbf{r}) +\frac{4\pi e^2}{(2\pi)^3}\int\frac{d\mathbf{p}'}{|\mathbf{p}-\mathbf{p}'|^2}n_{j-2}(\mathbf{R},\mathbf{p}'). \tag{3.8d}$$

The expansions (3.1), (3.4), and (3.8a) are to be inserted in Eq. (3.11) and the explicit powers of $\hbar$ are to be separated in such a way that the zeroth order approximation is nonvanishing. The result is the series of equations below:

$$\theta_0[K_0,\hbar^4 G_0]=\hbar, \tag{3.9a}$$

$$\sum_{j+k+l=n}\theta_j[K_k(\mathbf{R},\mathbf{p}\omega),G_l(\mathbf{R},\mathbf{p}\omega)]=0. \tag{3.9b}$$

The solution to the set of Eqs. (3.8) and (3.9) can be obtained in principle by starting with the zeroth order equation of each set, solving simultaneously, then proceeding to the first order equation in each set, solving these simultaneously using the results of the zeroth order solutions, and so on. We shall now show that the solution of the zeroth order equations, i.e., of (3.8b) and (3.9a), yields the Thomas-Fermi model.

The operator θ_0 appearing in (3.9a) consists of the product of the transforms, so that this equation may be written

$$G_0(\mathbf{R},\mathbf{p}\omega)=\hbar^{-3}[K_0(\mathbf{R},p\omega)]^{-1} \tag{3.10a}$$

$$=\hbar^{-3}[\omega-E]^{-1}, \tag{3.10b}$$

where

$$E(R,p)=p^2/2m+\phi_0(R), \tag{3.10c}$$

$$\phi_0(R)=-Ze^2/|R|+2\int v(\mathbf{R}-\mathbf{r})n_0(r)d\mathbf{r}. \tag{3.11}$$

It is necessary to recover n_0 from G_0 by performing the integrations indicated by Eqs. (3.5). In order to carry these out, however, it is first necessary to specify a path in the complex ω plane. This choice of path is discussed in Sec. V. It turns out that the choice of a path is determined by the energy state of the ion or atom, and by the number of electrons N surrounding the nucleus. For a system in its ground state, the path of integration lies just below the real ω axis from $-\infty<\omega<\mu$, crosses the real axis at $\omega=\mu$, and lies just above the real axis from $\mu<\omega<+\infty$. The constant μ is the chemical potential, approximately the energy required to add another electron to the system. It determines the number of electrons surrounding the nucleus. This point is brought out in detail in Sec. V.

The exponential $\exp(i\omega 0^+)$ in (3.5a) makes it possible to complete the path by adding the integral over the infinite semicircle in the upper half of complex ω plane. $n_0(\mathbf{R},\mathbf{p})$ is then given by a contour integral, and is equal to $\hbar^{-3}$ or zero, depending on whether the point $\omega=E$ is inside or outside the contour. Since the contour crosses the real axis at $\omega=\mu$, this means that

$$n_0(R,p)=\hbar^{-3},\quad p^2/2m+\phi_0(R)<\mu \tag{3.12a}$$

$$=0,\quad p^2/2m+\phi_0(R)>\mu. \tag{3.12b}$$

The density $n_0(R)$ defined by (3.5b) is then

$$n_0(R)=(6\pi^2\hbar^3)^{-1}p_F{}^3(R), \tag{3.13}$$

where $p_F(R)$, the maximum momentum of electrons in the Fermi gas, is given by

$$p_F{}^2/2m+\phi_0(R)=\mu. \tag{3.14}$$

The density $n_0(R,p)$, which equals $\hbar^{-3}$ for $p<p_F(R)$, is of course the density usually *assumed* at the outset in derivations of the Thomas-Fermi model. Its appearance here is a consequence of the theory.

To complete the derivation of the model, one may obtain the integral form of the Thomas-Fermi equation by eliminating $\phi_0(R)$ from (3.14) and (3.11), and eliminating $n_0(R)$ from (3.11) with the result

$$p_F{}^2(R)/2m-Ze^2/|R| +(3\pi^2\hbar^3)^{-1}\int p_F{}^3(\mathbf{r})v(R-\mathbf{r})d\mathbf{r}=\mu. \tag{3.15}$$

The differential form of the Thomas-Fermi equation may be obtained by first combining (3.13) and (3.14) as

$$n_0(R)=(6\pi^2\hbar^3)^{-1}\{2m[\mu-\phi_0(R)]\}^{\frac{3}{2}}, \tag{3.16}$$

then taking the Laplacian of (3.11) with $v(\mathbf{R}-\mathbf{r})=e^2/|\mathbf{R}-\mathbf{r}|$. The result of this operation,

$$\nabla^2\phi_0=-8\pi e^2 n_0(R),$$

is combined with (3.16) to give

$$\nabla^2\phi_0(R)=-(4e^2/3\pi\hbar^3)\{2m[\mu-\phi_0(R)]\}^{\frac{3}{2}}, \tag{3.17}$$

which is the Thomas-Fermi equation in its usual form.

IV. HIGHER ORDER TERMS

Having found that the zeroth order term in the spatial density is the Thomas-Fermi density, we turn our attention to a consideration of the higher order terms. We shall find that the first-order correction vanishes, and that the second-order correction is identical with that discussed by Kompaneets and Pavlovskii.[4] We consider the $n=1$ equation of the set (3.9b). The operator θ_1 (see Appendix) constructs the Poisson bracket of

the functions on which it operates—in this case K_0 and G_0. The zeroth order result (3.10a) guarantees that this Poisson bracket vanishes. Moreover, since the operator θ_0 merely forms the product of the functions on which it operates, the solution of the first equation of (3.9b) is

$$G_1 = -K_1 G_0/K_0 = -\hbar^{-3} K_1/(\omega - E)^2. \tag{4.1}$$

The density $n_1(R)$ may be recovered from G_1 by the integration indicated in (3.5),

$$(2\pi\hbar)^3 n_1(\mathbf{R}) = K_1(\mathbf{R}) \int d\mathbf{p} \int \frac{d\omega}{2\pi i} \frac{\exp(i\omega 0^+)}{(\omega - E)^2}. \tag{4.2}$$

We have previously found that, over the path described in Sec. III,

$$\int \frac{d\omega \exp(i\omega 0^+)}{2\pi i(\omega - E)} = S(\mu - E), \tag{4.3a}$$

$$S(x) = 1, \quad x > 0 \tag{4.3b}$$

$$= 0, \quad x < 0. \tag{4.3c}$$

Repeated differentiations of (4.3) with respect to E will develop a series of relationships we shall use later in this section.

$$\int \frac{d\omega \exp(i\omega 0^+)}{2\pi i(\omega - E)^n} = -\frac{1}{(n-1)!}\left(\frac{\partial}{\partial E}\right)^{n-2} \delta(\mu - E). \tag{4.4}$$

Furthermore, if polar coordinates are introduced into momentum space, one may write

$$d\mathbf{p} = mpdEd\phi d\cos\theta. \tag{4.5}$$

The integral in (4.2) may be evaluated using (4.4) and (4.5). We note that when $E = \mu$, $p = p_F$.

$$n_1(\mathbf{R}) = (2\pi^2\hbar^3)^{-1} m p_F(R) K_1(\mathbf{R}). \tag{4.6}$$

An integral equation for $K_1(R)$ results by using this density in the definition of $K_1(R)$ given by (3.8c)

$$K_1(\mathbf{R}) = -(\pi^2\hbar^3)^{-1} m \int d\mathbf{r}\, p_F(r) K_1(\mathbf{r}) v(\mathbf{R} - \mathbf{r}). \tag{4.7}$$

The integration in (4.7) is over that region for which $p_F(R)$ is greater than zero because the density $n_1(R)$ given by (4.6) is nonzero for positive p_F only. Depending on the choice of μ, the region of integration may or may not be all space.

One solution to (4.7) is that $K_1(R)$ vanishes identically. To show that this is the only solution, multiply (4.7) by $K_1(R)p_F(R)$ and integrate over the region for which $p_F(R)$ is greater than zero. Making use of the specific form for $v(\mathbf{R} - \mathbf{r})$, the result is

$$\int [K_1(\mathbf{R})]^2 \mathbf{p}_F(R) d\mathbf{R} = -C \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} d\mathbf{r} d\mathbf{R},$$

where

$$C = me^2/(\pi^2\hbar^3),$$

$$\rho(\mathbf{r}) = p_F(r) K_1(\mathbf{r}).$$

The integral on the left is non-negative. The integral on the right is the self-energy of a distribution of charge with density ρ; it too is non-negative. The minus sign then requires that each integral vanish. Equation (4.1) indicates that G_1 also vanishes.

We may now consider the $n = 2$ equation of (3.9b), which we solve explicitly for G_2 using the fact that K_1 and G_1 are zero.

$$G_2 = -K_2 G_0/K_0 - \theta_2[K_0, G_0]/K_0,$$

or, equivalently,

$$-\hbar^3 G_2 = K_2(\mathbf{R}, \mathbf{p})/(\omega - E)^2 + (\omega - E)^{-1}\theta_2[(\omega - E), (\omega - E)^{-1}]. \tag{4.8}$$

When the set of differentiations which constitute θ_2 are performed, the result is

$$-\hbar^3 G_2 = (\omega - E)^{-2} K_2(\mathbf{R}, \mathbf{p}) + (\omega - E)^{-3} C(R) + (\omega - E)^{-4} D(R, p), \tag{4.9a}$$

$$C(R) = \frac{1}{4m}\left[\frac{d^2\phi_0}{dR^2} + \frac{2}{R}\frac{d\phi_0}{dR}\right], \tag{4.9b}$$

$$D(R,p) = \frac{1}{4}\left[\frac{d^2\phi_0}{dR^2}\left(\frac{\mathbf{p}\cdot\mathbf{R}}{mR}\right)^2 + \frac{1}{R}\frac{d\phi_0}{dR}\left(\frac{\mathbf{p}\times\mathbf{R}}{mR}\right)^2 + \frac{1}{m}\left(\frac{d\phi_0}{dR}\right)^2\right]. \tag{4.9c}$$

The density $n_2(\mathbf{R})$ is to be recovered from G_2 by integration, as before. In performing this integration, we note first that Eq. (3.8d) indicates that K_2 will depend only on the magnitudes of $\mathbf{R}$ and $\mathbf{p}$. Utilizing (4.4) and (4.5) and integrating by parts where necessary, we obtain

$$4\pi^2\hbar^3 n_2(R) = 2mp_F K_2(R, p_F) - mC(R)\left(\frac{dp}{dE}\right)_{E=\mu} + \frac{m}{6}\left[\frac{\partial^2}{\partial E^2} p \int D(R,p) d\cos\theta \frac{d\phi}{2\pi}\right]_{E=\mu}. \tag{4.10}$$

The remaining integration in (4.10) may be carried out by choosing the polar axis in the direction of R, after which the differentiations may be performed, resulting in

$$4\pi^2\hbar^3 n_2(R) = 2mp_F(R) K_2(R, p_F) - 2m^2 C(R)/(3p_F) - m^2\left(\frac{d\phi_0}{dR}\right)^2 \Big/ (12 p_F^3). \tag{4.11}$$

A single-integral equation for K_2 will result if the equa-

tion (3.8d) for K_2 is written using the density n_2 given by (4.11) and n_0 given by (3.12). Instead of doing this, however, we shall exhibit the differential equation which shows that the second-order term in our solution is the same as the first quantum correction found by Kompaneets and Pavlovskii. Define

$$\phi_2(R)=2\int n_2(r)v(\mathbf{R}-\mathbf{r})d\mathbf{r}. \tag{4.12}$$

Since $v(\mathbf{R}-\mathbf{r})$ is the Coulomb potential,

$$\nabla^2\phi_2=-8\pi e^2 n_2. \tag{4.13}$$

The n_0 of Eq. (3.12) used in the $j=2$ term of Eq. (3.8d) gives

$$\begin{aligned}K_2(R,p)&=-\phi_2+\frac{e^2}{2\pi^2}\int_{p'<p_F}\frac{\hbar^{-3}d\mathbf{p}}{|p-p'|^2}\\&=-\phi_2(R)+\frac{e^2}{\pi\hbar^3}\left[p_F-\left(\frac{p_F^2-p^2}{2p}\right)\ln\left|\frac{p_F-p}{p_F+p}\right|\right].\end{aligned} \tag{4.14}$$

Finally, n_2 is eliminated from (4.11) using (4.13) and $K_2(R,p_F)$ is eliminated from (4.11) using (4.14). In the equation which results, we evaluate $C(R)$ using (4.9b) as $(4m)^{-1}\nabla^2\phi_0$ and $p_F(R)$ using (3.14) as $[2m(\mu-\phi_0)]^{\frac{1}{2}}$

$$\begin{aligned}-\nabla^2\phi_2+\frac{4me^2}{\pi\hbar^3}[2m(\mu-\phi_0)]^{\frac{1}{2}}\phi_2&=8m^2e^4(\pi^2\hbar^6)^{-1}(\mu-\phi_0)-\frac{me^2[2m(\mu-\phi_0)]^{-\frac{1}{2}}}{12\pi\hbar^3}\\&\quad\times\left[4\nabla^2\phi_0+(\mu-\phi_0)^{-1}\left(\frac{d\phi_0}{dR}\right)^2\right].\end{aligned} \tag{4.15}$$

This equation was derived by Kompaneets and Pavlovskii using a different method in which the Thomas-Fermi distribution (3.12) is assumed at the outset. The authors discuss this equation and its numerical solution and point out that the exchange effect (first term on the right) and the inhomogeneity correction (last term on the right) appear together in this equation. Therefore the first nonvanishing correction to the Thomas-Fermi equation contains both exchange effects and inhomogeneity effects.

The higher corrections could presumably also be obtained by using systematic methods such as Kirzhnits or Golden has proposed. Retaining all higher corrections must ultimately lead back to the Hartree-Fock result. The utility of the Green's function method which we have presented here becomes apparent when we go to methods beyond Hartree-Fock, in which correlation effects preclude use of a scheme based on a single-particle Hamiltonian. This will be made more apparent in a future publication.

V. GENERAL PROPERTIES OF THE GREEN'S FUNCTION

In this section, our main concern is to establish the connection between the state of the ion or atom and the path of integration used to recover the density from the Green's function. This connection follows from certain general properties of the Green's function. These properties are best exhibited by starting with the well known definition of the Green's function and working in the formalism of second quantization. In this formalism, the Hamiltonian (2.1a) takes the form

$$\begin{aligned}H=\sum_\alpha\int\psi_\alpha^\dagger(\mathbf{r}t)H_0(\mathbf{r})\psi_\alpha(\mathbf{r}t)d\mathbf{r}&\\+\tfrac{1}{2}\sum_{\alpha\alpha'}\int\psi_\alpha^\dagger(\mathbf{r}t)\psi_{\alpha'}^\dagger(\mathbf{r}'t)v(\mathbf{r}-\mathbf{r}')&\\\times\psi_{\alpha'}(\mathbf{r}'t)\psi_\alpha(\mathbf{r}t)d\mathbf{r}d\mathbf{r}'.&\end{aligned} \tag{5.1}$$

$\psi_\alpha(rt)$ and $\psi_\alpha^\dagger(rt)$ are the annihilation and creation operators for the electrons; α is the spin index and takes on two values. These operators satisfy anti-commutation relationships

$$\begin{aligned}&\psi_\alpha(\mathbf{r}t)\psi_{\alpha'}(\mathbf{r}'t)+\psi_{\alpha'}(\mathbf{r}'t)\psi_\alpha(\mathbf{r}t)=0,\\&\psi_\alpha^\dagger(\mathbf{r}t)\psi_{\alpha'}^\dagger(\mathbf{r}'t)+\psi_{\alpha'}^\dagger(\mathbf{r}'t)\psi_\alpha^\dagger(\mathbf{r}t)=0,\\&\psi_\alpha(\mathbf{r}t)\psi_\alpha^\dagger(\mathbf{r}'t)+\psi_\alpha^\dagger(\mathbf{r}'t)\psi_\alpha(\mathbf{r}t)=\delta_{\alpha\alpha'}\delta(\mathbf{r}-\mathbf{r}').\end{aligned} \tag{5.2}$$

It will be convenient to suppress the spin index α by considering it to be implicitly contained in $\mathbf{r}$ and using the convention described in the beginning of Sec. II. We shall use the Heisenberg representation, in which the time dependence of the operators is

$$\begin{aligned}\psi(\mathbf{r}t)&=e^{iHt/\hbar}\psi(\mathbf{r},t=0)e^{-iHt/\hbar},\\\psi^\dagger(\mathbf{r}t)&=e^{iHt/\hbar}\psi^\dagger(\mathbf{r},t=0)e^{-iHt/\hbar}.\end{aligned} \tag{5.3}$$

States of the ion are specified by N, the number of electrons surrounding the nucleus, the energy E, and possibly some degeneracy parameter γ, i.e.,

$$H|N,E,\gamma\rangle=E|NE\gamma\rangle, \tag{5.4a}$$

$$N_{\text{op}}=|N,E,\gamma\rangle=N|N,E,\gamma\rangle. \tag{5.4b}$$

The operator giving the number of electrons surrounding the nucleus is

$$N_{\text{op}}=\int\psi^\dagger(rt)\psi(rt)dr, \tag{5.5}$$

and hence, the operator $n_{\text{op}}(rt)$ giving the spatial density of electrons with a given direction of spin is

$$n_{\text{op}}(rt)=\psi^\dagger(rt)\psi(rt). \tag{5.6}$$

We shall be especially concerned with the ground state of the system with N electrons, having energy $E_0(N)$, and for this state, we shall suppress the indices $NE\gamma$ and the vertical bar, leaving just the angular bracket to denote the state.

Green's functions for the many-particle system are

well known and have been widely studied.[9–11] To fix the definition we have been using, the n-particle Green's function for the ground state of the N electron system was defined by

$$G_n(1,2,\cdots n;1'\cdots n') = (-i)^n\langle(\psi(1)\psi(2)\cdots\psi(n)\psi^\dagger(n')\cdots\psi^\dagger(1'))_+\rangle. \quad (5.7)$$

The operators in (5.7) are the time dependent annihilation and creation operators; the bracket $(\ )_+$ indicates the time ordering of the operators enclosed: operators with later time coordinates stand to the left of operators with earlier time coordinates and the collection is multiplied by ± 1, the parity of the permutation of the operators from the sequence indicated in (5.7) to the time-ordered sequence. The expectation value is taken with respect to the ground state of the N-electron system.

It is now evident that Eqs. (2.2) and (2.3) are nothing other than the statements that the energy of the ground state is equal to the expectation value of the Hamiltonian in the ground state and that the particle density is the expectation value of the density operator.[9–11] The equation (2.4) linking the one-particle and two-particle Green's function may be derived[10,11] by differentiating (5.3):

$$i\hbar\partial\psi(\mathbf{r}t)/\partial t = \psi(\mathbf{r}t)H - H\psi(\mathbf{r}t), \quad (5.8)$$

evaluating the commutator on the right of (5.8) using the relations (5.2), multiplying the result by $-i\psi^\dagger(r't')$ from the right, and time-ordering the result. A delta function arises because

$$\frac{\partial}{\partial t}(\psi(\mathbf{r}t)\psi^\dagger(r't'))_+ = \left(\frac{\partial\psi}{\partial t}\psi^\dagger(\mathbf{r}'t')\right)_+ + \delta(\mathbf{r}-\mathbf{r}')\delta(t-t').$$

Finally, taking the ground-state expectation value results in Eq. (2.4).

We are especially concerned with the Fourier transform $\tilde{G}$ of the one-particle Green's function and its ω dependence. The transform was defined by (2.10b), which we rewrite, using the specific definition (5.7), as

$$\begin{aligned}\tilde{G}(\mathbf{R},\alpha;\ \mathbf{p}\omega) &= -i\int_{t_x>t_y} d(\mathbf{x}-\mathbf{y})d(t_x-t_y)\langle\psi_\alpha(\mathbf{x},t_x)\psi_\alpha^\dagger(\mathbf{y},t_y)\rangle \\ &\quad\times\exp\{-i[\mathbf{p}\cdot(\mathbf{x}-\mathbf{y})-\omega(t_x-t_y)]/\hbar\} \\ &\quad + i\int_{t_x>t_y} d(\mathbf{x}-\mathbf{y})d(t_x-t_y)\langle\psi_\alpha^\dagger(\mathbf{y},t_y)\psi_\alpha(\mathbf{x},t_x)\rangle \\ &\quad\times\exp\{-i[\mathbf{p}\cdot(\mathbf{x}-\mathbf{y})-\omega(t_x-t_y)]/\hbar\}, \quad (5.9)\end{aligned}$$

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{x}+\mathbf{y}).$$

There is no spin summation implied in (5.9). The time dependence of the matrix elements is exhibited by using a resolution of the identity between the two operators in each matrix element, and the Heisenberg time dependence (5.3):

$$\begin{aligned}&\langle\psi_\alpha(\mathbf{x}t_x)\psi_\alpha^\dagger(\mathbf{y},t_y)\rangle \\ &\quad = \textstyle\sum_{N'E\gamma}\langle\psi_\alpha(\mathbf{x}t_x)|N'E\gamma\rangle\langle N'E\gamma|\psi_\alpha^\dagger(\mathbf{y},t_y)\rangle \\ &\quad = \textstyle\sum_{N'E\gamma}\langle\psi_\alpha(\mathbf{x})|N'E\gamma\rangle\langle N'E\gamma|\psi_\alpha^\dagger(\mathbf{y})\rangle \\ &\qquad\times\exp\{i(t_x-t_y)[E_0(N)-E]/\hbar\}, \quad (5.10)\end{aligned}$$

with

$$\psi_\alpha(\mathbf{x}) \equiv \psi_\alpha(\mathbf{x},t_x=0),$$
$$\psi_\alpha^\dagger(\mathbf{y}) \equiv \psi_\alpha(\mathbf{y},t_y=0).$$

The summation in (5.10) is symbolic, and implies integration over the continuous range of eigenvalues also. The only intermediate states which will contribute are those for which $\langle N'|\psi^\dagger|N\rangle$ does not vanish, i.e., states where $N'=N+1$. The energy E appearing here specifies energy levels of the system with $(N+1)$ particles, and will be denoted $E(N+1)$. Similarly, for the other matrix element in (5.9), the same technique yields

$$\begin{aligned}&\langle\psi_\alpha^\dagger(\mathbf{y},t_y)\psi_\alpha(\mathbf{x},t_x)\rangle \\ &\quad = \textstyle\sum_{E,\gamma}\langle\psi_\alpha^\dagger(\mathbf{y})|N-1,E,\gamma\rangle\langle N-1,E,\gamma|\psi_\alpha(\mathbf{x})\rangle \\ &\qquad\times\exp[i(t_x-t_y)[E(N-1)-E_0(N)]/\hbar]. \quad (5.11)\end{aligned}$$

The spatial Fourier transforms are ω-independent, and will be denoted as

$$\begin{aligned}&\sum_\gamma\int d(\mathbf{x}-\mathbf{y})\langle\psi_\alpha(\mathbf{x})|N+1,E,\gamma\rangle\langle N+1,E,\gamma|\psi_\alpha^\dagger(\mathbf{y})\rangle \\ &\qquad\times\exp[-i\mathbf{p}\cdot(\mathbf{x}-\mathbf{y})/\hbar|] \\ &\qquad = \hbar^{-1}\bar{A}[\mathbf{R},\alpha;\ \mathbf{p},E(N+1)], \quad (5.12a)\end{aligned}$$

$$\begin{aligned}&\sum_\gamma\int d(\mathbf{x}-\mathbf{y})\langle\psi_\alpha^\dagger(\mathbf{y})|N-1,E,\gamma\rangle\langle N-1,E,\gamma|\psi_\alpha(\mathbf{x})\rangle \\ &\qquad\times\exp[-i\mathbf{p}\cdot(\mathbf{x}-\mathbf{y})/\hbar] \\ &\qquad = \hbar^{-1}\bar{B}[\mathbf{R},\alpha;\ \mathbf{p},E(N-1)]. \quad (5.12b)\end{aligned}$$

When (5.10), (5.11), and (5.12) are inserted into (5.9), the remaining time integration does not converge and is therefore ambiguous. The integration can be made unambiguous in the usual manner by inserting a convergence factor $\exp[-\eta|t_x-t_y|]$ into the integrand and taking the limit $\eta\to 0^+$ after the inversion to the time dependent form is performed. The result of the integration with the convergence factor inserted is

$$\begin{aligned}\tilde{G}(\mathbf{R},\alpha;\ \mathbf{p}\omega) &= \sum\frac{\bar{A}[\mathbf{R},\alpha;\ \mathbf{p},E(N+1)]}{E(N+1)-E_0(N)-i\eta-\omega} \\ &\quad + \sum\frac{\bar{B}[\mathbf{R},\alpha;\ \mathbf{p},E(N-1)]}{E_0(N)-E(N-1)+i\eta-\omega}. \quad (5.13)\end{aligned}$$

The sums in (5.13) are over the energy levels of the $(N+1)$-particle system and of the $(N-1)$-particle system.

At this point, we call attention to the fact that $E_0(N)$ appears in (5.13) because the state which ap-

peared in the definition of the Green's function was the ground state of the system with N particles. We can make use of this by introducing the excitation energy, a positive quantity defined by

$$\epsilon(N)=E(N)-E_0(N)\geq 0. \tag{5.14}$$

It is also convenient to introduce the chemical potential μ, defined as the minimum energy required to add another electron to the system, i.e.,

$$\mu(N)=E_0(N+1)-E_0(N). \tag{5.15}$$

These two definitions bring (5.13) to the form which exhibits its ω dependence most clearly, namely

$$\tilde{G}=\sum_{\epsilon(N+1)}\frac{A[\epsilon(N+1)]}{\mu(N)+\epsilon(N+1)-i\eta-\omega}+\sum_{\epsilon(N-1)}\frac{B[\epsilon(N-1)]}{\mu(N-1)-\epsilon(N-1)+i\eta-\omega}. \tag{5.16}$$

We observe that the singularities of (5.16) in the complex ω plane are poles and branch cuts adjacent to the real axis. The singularities below the real axis are contributed by the first sum in (5.16) and extend from $\mu(N)$ to infinity. The poles arise from the discrete (bound state) energies of the $(N+1)$-particle system. The branch cut arises from the continuum state eneriges of the $(N+1)$-particle system, for which the sum in (5.16) becomes an integral. The bound-state energies (if any) are expected to lie below the continuum-state energies, i.e., have lesser excitation energies. Therefore the poles, if any, are expected to lie to the left of the branch cut. No matter how many bound states of the $(N+1)$-particle system there are, all the singularities below the axis lie to the right of $\mu(N)$.

The singularities above the real axis are contributed by the second term in (5.16), and extend from $\mu(N-1)$ to minus infinity. This time the branch cut lies to the left of the poles, if any. All singularities above the real axis lie to the left of $\mu(N-1)$. The reason the two sets of singularities terminate at the μ is that the ground state of the N-particle system was used to define the Green's function. If the Green's function had been defined relative to an excited state, then each series of singularities would extend past its μ a distance equal to the excitation energy of this state. This statement is most easily verified by substituting for $E_0(N)$ in (5.13) the energy of the state used to define the Green's function.

In the inversion of (5.16) to recover the time dependent form, the path of integration of ω along the real axis defines a path which passes beneath one set of singularities and above the other. The relationship between the two sets of singularities depends on whether $\mu(N)$ is larger or smaller than $\mu(N-1)$. The exact relationship between these two will depend in detail upon the nature of the system. For an ion, however, the fact

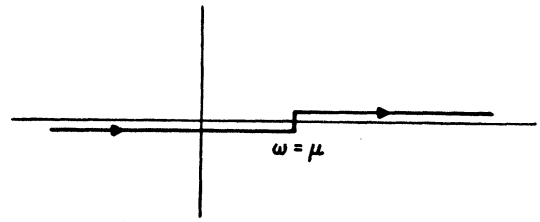

FIG. 1. Path of integration in complex ω plane.

that it becomes increasingly difficult to remove successive electrons indicates that μ increases with N. Hence, the set of singularities below the axis lies completely to the right of the set of singularities above the axis, with no overlap.

The nonoverlapping of the two sets of singularities makes it possible to shift slightly the path of integration off the real axis, so that it still passes beneath the one set of singularities and above the other, even as the operation of letting η go to zero moves all of the singularities onto the real ω axis. In this way, the imaginary part of the denominators in (5.16) may be discarded but the path used for recovering the time dependent form now lies below the real axis from minus infinity to μ, crosses the real axis at $\omega=\mu$ and lies above the real axis from μ to plus infinity. Here, μ is some real number such that

$$\mu(N-1)<\mu<\mu(N). \tag{5.17}$$

The path of integration discussed above is possible for the ground-state Green's function, because of the separation of the sets of singularities. But this path is precisely the one which in Sec. III yielded the Thomas-Fermi density.

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APPENDIX. THE OPERATOR $\theta_{\mathbf{R},\mathbf{p}}$

An operator $\theta_{R,p}$ was defined in Sec. II by the requirement that it produces the Fourier transform of the matrix product of two functions when it operates on the transforms of the individual functions. The precise definition is

$$\theta_{\mathbf{R},\mathbf{p}}[\tilde{K}(\mathbf{R},\mathbf{p}\omega),\tilde{G}(\mathbf{R},\mathbf{p}\omega)]\equiv\int e^{-i[\mathbf{p}\cdot(\mathbf{R}-\mathbf{y})-\omega(t_x-t_y)]/\hbar}d(\mathbf{x}-\mathbf{y})d(t_x-t_y)\times\int K(\mathbf{x}t_x;\mathbf{w}t_w)d\mathbf{w}dt_wG(\mathbf{w}t_w;\mathbf{y}t_y). \tag{A.1}$$

$$\mathbf{R}=\tfrac{1}{2}(\mathbf{x}+\mathbf{y}).$$

A four-dimensional notation will be convenient, in which

$$px=\mathbf{p}\cdot\mathbf{x}-\omega t,$$
$$dx=d\mathbf{x}dt,$$
$$dp=d\mathbf{p}d\omega$$
$$R=\tfrac{1}{2}(x+y).$$

The kernels K and G in (A.1) must be expressed in terms of their transforms, so that the right side of (A.1) becomes

$$(2\pi h)^{-8}\int d(x-y)dwdp_1dp_2\, e^{-i[p(x-y)-p_1(x-w)-p_2(w-y)]/\hbar}\times\tilde{K}\left(\frac{x+w}{2},p_1\right)\tilde{G}\left(\frac{w+y}{2},p_2\right). \quad \text{(A.2)}$$

Eliminate p_1 and p_2 by putting $p_1=p+q_1$ $p_2=p+q_2$. The preceding expression (A.2) becomes

$$(2\pi h)^{-8}\int d(x-y)dwdq_1dq_2\, e^{i[q_1(x-w)+q_2(w-y)]/\hbar}\times\tilde{K}\left(R+\frac{w-y}{2};p+q_1\right)\tilde{G}\left(R-\frac{x-w}{2};p+q_2\right). \quad \text{(A.3)}$$

Each of the transforms $\tilde{K}$ and $\tilde{G}$ may be expanded as a Taylor's series about R and p. For clarity we shall temporarily neglect the fact that R and p each have four components. Then the Taylor's series expansion is

$$\tilde{K}\left(R+\frac{w-y}{2};p+q_1\right)=\sum_{jk}\frac{1}{j!}\frac{1}{k!}\left(\frac{w-y}{2}\right)^j\times q_1{}^k\left(\frac{\partial}{\partial R}\right)^j\left(\frac{\partial}{\partial p}\right)^k\tilde{K}(R,p),$$

$$\tilde{G}\left(R-\frac{x-w}{2};p+q_2\right)=\sum_{lm}\frac{1}{l!}\frac{1}{m!}\left(\frac{x-w}{2}\right)^l\times q_2{}^m\left(-\frac{\partial}{\partial R}\right)^l\left(\frac{\partial}{\partial p}\right)^m\tilde{G}(R,p).$$

The powers of $(w-y)$ and of $(x-w)$ are derivatives of the exponential with respect to $iq_1/\hbar$ and $iq_2/\hbar$. On integration by parts, the derivatives of the exponential may be transferred to the other factors of the integrand, which, exclusive of the exponential, is then

$$\sum_{jklm}\frac{1}{j!k!l!m!}\left\{\left(\frac{\partial}{\partial R}\right)^j\left(\frac{\partial}{\partial p}\right)^k\tilde{K}(Rp)\right\}\times\left\{\left(-\frac{\partial}{\partial R}\right)^l\left(\frac{\partial}{\partial p}\right)^m\tilde{G}(R,p)\right\}\times\left(\frac{i\hbar}{2}\frac{\partial}{\partial q_1}\right)^l q_1{}^k\left(\frac{i\hbar}{2}\frac{\partial}{\partial q_2}\right)^j q_2{}^m. \quad \text{(A.4)}$$

The integration may be performed first over w, then over q_2, then over $(x-y)$ and finally q_1, with the result that the integral equals the value of (A.4) with $q_1=0$, $q_2=0$. Setting the q equal to zero deletes all terms from the summation except those for which $l=k$ and $m=j$. The result is

$$\theta[\tilde{K},\tilde{G}]=\sum_{jk}\frac{(i\hbar/2)^{j+k}}{j!k!}\left\{\left(\frac{\partial}{\partial R}\right)^j\left(\frac{\partial}{\partial p}\right)^k\tilde{K}(R,p)\right\}\times\left\{\left(-\frac{\partial}{\partial R}\right)^k\left(\frac{\partial}{\partial p}\right)^j\tilde{G}(R,p)\right\} \quad \text{(A.5)}$$

$$=\lim_{\substack{p'\to p\\ R'\to R}}\exp\left[\frac{i\hbar}{2}\left(\frac{\partial}{\partial R}\frac{\partial}{\partial p'}-\frac{\partial}{\partial R'}\frac{\partial}{\partial p}\right)\right]\times\tilde{K}(R,p)\tilde{G}(R',p'). \quad \text{(A.6)}$$

This latter form has been given by Theis. The modification brought about by the multicomponent nature of R and p is simply the appearance of an index for each component, i.e., the argument of the exponential becomes

$$\frac{ih}{2}\sum_{i=1}^{4}\left(\frac{\partial}{\partial R_i}\frac{\partial}{\partial p_i'}-\frac{\partial}{\partial R_i'}\frac{\partial}{\partial p_i}\right),$$

where

$$R_4=\tfrac{1}{2}(t_x+t_y)\quad p_4=-\omega.$$

There will be no R_4 dependence in either of the functions $\tilde{K}$ or $\tilde{G}$ because the ground-state system is time independent, and so the summation need be extended only over $i=1, 2, 3$. If we separate out terms according to the explicit power of $\hbar$ they contain as indicated by (3.1), then[16]

$$\theta_0[\tilde{K},\tilde{G}]=\tilde{K}\tilde{G}, \quad \text{(A.7)}$$

$$\theta_1[\tilde{K},\tilde{G}]=\tfrac{1}{2}i\sum_{xyz}\frac{\partial\tilde{K}}{\partial x}\frac{\partial\tilde{G}}{\partial p_x}-\frac{\partial\tilde{K}}{\partial p_x}\frac{\partial\tilde{G}}{\partial x}, \quad \text{(A.8)}$$

$$\theta_2[\tilde{K},\tilde{G}]=(\tfrac{1}{2}i)^2\left[\sum_{xyz}\frac{1}{2}\left(\frac{\tilde{K}\partial^2}{\partial x^2}\frac{\partial^2\tilde{G}}{\partial p_x{}^2}+\frac{\partial^2\tilde{K}}{\partial p_x{}^2}\frac{\partial^2\tilde{G}}{\partial x^2}\right)+\sum_{xyz}\left(\frac{\partial^2\tilde{K}}{\partial x\partial y}\frac{\partial^2\tilde{G}}{\partial p_x\partial p_y}+\frac{\partial^2\tilde{K}}{\partial p_x\partial p_y}\frac{\partial^2\tilde{G}}{\partial x\partial y}\right)-\sum_{p_xp_yp_z}\sum_{xyz}\frac{\partial^2\tilde{K}}{\partial x\partial p_y}\frac{\partial^2\tilde{G}}{\partial y\partial p_x}\right]. \quad \text{(A.9)}$$

[16] The summation of xyz means 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 $\mathbf{R}$ and a component of $\mathbf{p}$.