Quasi-Classical Theory of Electron Correlations in Atoms

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The quasi-classical limit of the many-particle perturbation theory is considered for electrons moving in the Coulomb potential of the nucleus. The problem is analyzed using the Green's function formulation of many-particle physics. When corrections involving the gradient of the self-consistent potential are neglected, the results agree to all orders in the interaction strength with the procedure of Lewis for including correlation corrections in the Thomas-Fermi model. The disagreement between the work of Lewis and the recent work of Baraff is shown to be due to the latter's neglect of anomalous contributions to the perturbation theory which arise, because the local Fermi momentum is a function of the interaction strength. The calculation of inhomogeneity corrections is also considered.

I. INTRODUCTION

RECENTLY, there has been renewed interest in the theoretical basis for the statistical, or Thomas-Fermi, model of the atom. In particular, Kompaneets and Pavlovskii,[1] Kirzhnits,[2] Baraff and Borowitz,[3] and others have investigated the Thomas-Fermi model as the quasi-classical limit of the Hartree-Fock scheme and have derived expressions for exchange and inhomogeneity corrections to the Thomas-Fermi results. The question of incorporating many-particle effects outside the Hartree-Fock scheme into the quasi-classical model has been studied by Lewis[4] and most recently by Baraff.[5]

The work of Baraff (and BB), which incorporates the work of references 1 and 2, was based on the Green's function approach to the many-particle problem and leads to a result which differs from that of Lewis when electron correlation effects are taken into account. Lewis' work was based on the simple "local equilibrium" statistical model and made use of the calculation of the correlation energy of Gell-Mann and Brueckner[6] for the high-density electron gas.

One purpose of this paper is to show (on the basis of the quasi-classical limit of many-particle perturbation theory) that Lewis' result is correct. The incorrect result of Baraff is obtained by omitting the so-called anomalous contributions (in the sense of Luttinger and Ward[7]) which arise, because the local Fermi momentum in this model is a function of the interaction strength.

Secondly, we propose what we believe to be a consistent quasi-classical approximation. Our method is to consider many-particle perturbation theory to a given consistent order in the interaction strength. This expansion is then in turn expanded termwise in powers of the gradient which measures the inhomogeneities. This method avoids the ambiguities encountered[5] in attempting a strict expansion in powers of $\hbar$ and is the analog of the familiar WKB expansion in one-particle physics.

In Sec. II we establish the notation for our version of the Green's function formulation of the many-body problem. Here we note that if the states of the interacting and noninteracting system are related by the adiabatic hypothesis, a familiar Feynman-like expansion of the Green's functions is possible. This adiabatic expansion is valid for uniform systems with spherically symmetric interactions such as the free electron gas, but is not valid for the atomic electron system.[7] We therefore develop a Feynman-like expansion for the auxiliary propagator functions which does not involve the adiabatic hypothesis. The well-known Dyson integral equation for the propagator in terms of the self-energy part and the anomalous terms of LW which arise in the nonadiabatic theory are discussed here.

In Sec. III we discuss the quasi-classical expansion of the complete many-body Green's function formalism in powers of the gradient operator. We use the expansion technique of Theis[8] and BB.[3] In Sec. IV we consider the zero-order terms in this expansion which are identical to the homogeneous case. We show that by choosing our zero-order Hamiltonian in such a way as to eliminate the anomalous contributions, we obtain an equation for the local Fermi momentum identical to that of Lewis. This allows us to make contact with the adiabatic expansions previously used for the uniform electron gas.[9] Readers who are not interested in mathematical details can omit all but the summary paragraph of this section.

In Sec. V we briefly display the equations for the lowest order inhomogeneity corrections and discuss the calculation of certain quantities which arise there. In Sec. VI we calculate the electron density, which is important in determining the boundary conditions in an atom, and the total energy. To zero order in the inhomogeneities we again obtain Lewis' results. In Sec. VII we consider the relation of our work to that of

[1] A. S. Kompaneets and E. S. Pavlovskii, Soviet Phys.—JETP **31**, 328 (1957).
[2] D. A. Kirzhnits, Soviet Phys.—JETP **32**, 64 (1957).
[3] G. A. Baraff and S. Borowitz, Phys. Rev. **121**, 1704 (1961) (hereafter referred to as BB).
[4] H. W. Lewis, Phys. Rev. **111**, 1554 (1958).
[5] G. A. Baraff, Phys. Rev. **123**, 2087 (1961).
[6] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).
[7] J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960) (hereafter referred to as LW).
[8] W. R. Theis, Z. Physik **142**, 503 (1955).
[9] D. F. DuBois, Ann. Phys. (New York) **7**, 174 (1959).

Baraff. Finally, in Sec. VIII we discuss the limitations of the present work.

II. SUMMARY OF THE GREEN'S FUNCTION FORMALISM

The Green's function approach to the statistical-mechanical many-body problem has recently been developed and applied by many authors.[10–15] Our formulation is most closely related to the work of references 11–14 and the work of Martin and Schwinger.

We shall base our work here on the one-Fermion Green's function,

$$G(1,1')=\langle T\psi(1)\psi^\dagger(1')\rangle, \tag{2.1}$$

where $\psi(1)$ is the Heisenberg field operator for the Fermions, T is Wick's time ordering operator, and the average $\langle\ \rangle$ is with respect to the grand canonical ensemble,

$$\langle\mathbf{O}\rangle=\mathrm{Tr}(\varrho\mathbf{O}),$$
$$\varrho=e^{\beta\Omega}\exp[-\beta(\mathbf{H}-\mu\mathbf{N})],$$
$$\mathrm{Tr}(\varrho)=1.$$

Here k/β is the temperature and μ is the chemical potential; Ω is the thermodynamic potential. The Hamiltonian is

$$H=\int d^3x\ \psi^\dagger(\mathbf{x})\left[-\frac{1}{2m}\nabla^2+V(\mathbf{x})\right]\psi(\mathbf{x})$$
$$+\frac{\lambda}{2}\int d^3x\int d^3x'\ \psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')v(|\mathbf{x}-\mathbf{x}'|)$$
$$\times\psi(\mathbf{x}')\psi(\mathbf{x}), \tag{2.2}$$

where

$$V(x)=-Ze^2/|\mathbf{x}| \tag{2.3}$$

is the potential of the atomic nucleus located at the origin and the Coulomb interaction potential is

$$v(|\mathbf{x}-\mathbf{x}'|)=e^2/|\mathbf{x}-\mathbf{x}'|. \tag{2.4}$$

Now $G(1,1')$ can be expanded in powers of the interaction strength in two ways. First, in a case where the states of the interacting and noninteracting system are related by the adiabatic hypothesis, we can develop the usual Feynman-like rules.

The adiabatic theory is generally inapplicable to statistical-mechanical systems, except in the case of a uniform system with isotropic interaction forces at zero temperature. Since it is applicable in this case, it has been used in the calculation of correlation effects in an electron gas. In more general problems, the adiabatic theory can be applied only by redefining H_0 and H_1 in a self-consistent way so that the hypothesis applies. This appears feasible only at $T=0$ for uniform systems in which we can choose H_0 and H_1, so that H_0 and H_0+H_1 are described by the same Fermi surface. This adiabatic assumption allows us to write $G=G_A$ as

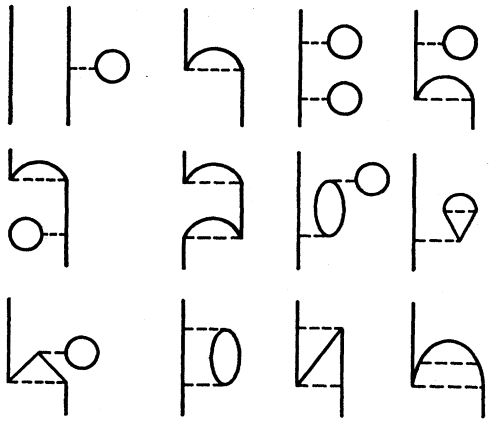


FIG. 1. Diagrams contributing to G_A through second order in the interaction. Solid lines indicate uncorrected propagator. Dashed lines indicate Coulomb interaction.

$$G_A(1,1')=\mathrm{Tr}[\rho_0 TU(\infty,-\infty)\psi(1)\psi^\dagger(1')]/\mathrm{Tr}[\rho_0 U(\infty,-\infty)], \tag{2.5}$$

where $U(t,t')$ is Dyson's matrix,

$$U(t,t')=T\exp\left[-\int_{t'}^{t}H_1(s)ds\right], \tag{2.6}$$

$$H_1(s)=e^{iH_0 s}H_1 e^{-iH_0 s}, \tag{2.7}$$

and ψ is the field operator in the interaction picture. The important ingredient in Eq. (2.5) is that ρ_0 is the grand canonical density matrix of the noninteracting system. Applying Wick's algebraic theorem, we derive the following rules for expanding G_A to order λ^n:

(i) Draw all topologically distinct diagrams leading from one Fermion at point $1'$ to one Fermion at point 1. (See Fig. 1 for examples.)

(ii) for each solid Fermion line between points i and j, there is a factor

$$G_A{}^0(i,j)=\mathrm{Tr}[\rho_0 T\psi(i)\psi^\dagger(j)]. \tag{2.8}$$

In a uniform system at zero temperature, if energies are measured with respect to the Fermi energy μ,

$$G_A{}^0(i,j)=-\int\frac{d^4p}{(2\pi)^4 i}e^{ip\cdot(x_i-x_j)}G_A{}^0(p). \tag{2.9}$$

[10] T. Matsubara, Progr. Theoret. Phys. (Kyoto) **14**, 351 (1955).
[11] L. Landau, Soviet Phys.—JETP **34**, 182 (1958).
[12] V. M. Galitskii and A. B. Migdal, Soviet Phys.—JETP **34**, 96 (1958).
[13] E. S. Fradkin, Soviet Phys.—JETP **36**, 912 (1959).
[14] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, Soviet Phys.—JETP **36**, 636 (1959).
[15] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

Here $p\cdot x=\mathbf{p}\cdot\mathbf{x}-p_0t$, and

$$G_A^0(p)=\frac{1}{p_0-[(p^2-p_F^2)/2m](1-i\epsilon)}$$
$$=\frac{\eta(p-p_F)}{p_0-[(p^2-p_F^2)/2m]+i\epsilon}+\frac{\eta(p_F-p)}{p_0-[(p^2-p_F^2)/2m]-i\epsilon}, \quad (2.10)$$

where $\mu=p_F^2/2m$, $\eta(x)=1$; $x>0$ and $\eta(x)=-1$; $x<0$.

For Fermion lines which begin and end on the same interaction line, take the limit $t_j\to t_i+0^+$.

(iii) For each dashed interaction line between points k and l, there is a factor

$$-i\lambda v(k,l)=-i\lambda v(\mathbf{x}_k-\mathbf{x}_l)\delta(t_k-t_l). \quad (2.11)$$

(iv) There is a factor of -1 for each closed Fermion loop.

(v) Integrate over all internal space-time points,

$$\int d^4x_i=\int d^3x_i\int_{-\infty}^{\infty}dt_i. \quad (2.12)$$

In the problem at hand, we will show that the adiabatic hypothesis does not apply. We will work with an expansion which does not involve this assumption. To do this, one defines an auxiliary "propagator function" $\tilde{G}(1,1')$ which is derived from $G(1,1')$ by setting $\beta=i\tau$, where τ is real and positive (except for an infinitesimal negative imaginary part to ensure convergence) for $|t-t'|\leqslant\tau$.

$$\tilde{G}(1,1')=\mathrm{Tr}[e^{i\tau\Omega}e^{-i\tau(H-\mu N)}T\psi(1)\psi^\dagger(1')], \quad |t-t'|\leqslant\tau. \quad (2.13)$$

With this function the adiabatic boundary condition is replaced by a periodicity condition,

$$\tilde{G}(\mathbf{x},\mathbf{x}';t-t')=-\tilde{G}(\mathbf{x},\mathbf{x}';t-t'-\tau). \quad (2.14)$$

Now using the cyclic invariance of the trace, it is easily shown that

$$\tilde{G}(1,1')=\mathrm{Tr}[e^{i\tau\Omega}e^{-i\tau(H_0-\mu N)}TU(\tau,0)\psi(1)\psi^\dagger(1')], \quad (2.15)$$

where U is the Dyson matrix and ψ is in the interaction picture. If we use Wick's theorem again, we derive a set of Feynman-like rules for the expansion of $\tilde{G}(1,1')$ similar to those of the adiabatic case for $G_A(1,1')$ with the following differences.

(ii') For each solid Fermion line between points i and j, there is a factor

$$\tilde{G}^0(i,j)=\mathrm{Tr}[e^{i\tau\Omega}e^{-i\tau(H_0-\mu N)}\psi(i)\psi^\dagger(j)]. \quad (2.16)$$

In a uniform system,

$$\tilde{G}^0(i,j)=\int\frac{d^3p}{(2\pi)^3}\frac{1}{-i\tau}\sum_{p_0}e^{ip\cdot(x_i-x_j)}\tilde{G}^0(p), \quad (2.17)$$

$$\tilde{G}^0(p)=[p_0-(p^2/2m-\mu)]^{-1}, \quad (2.18)$$

where $p_0=\pi\nu/\tau$, ν being an odd integer.

(v') Integrate over all internal space-time points,

$$\int d^4x_i=\int d^3x_i\int_{-\tau}^{\tau}dt_i. \quad (2.19)$$

For the atomic system at hand, the Green's functions depend only on the time differences

$$G(1,1')=G(\mathbf{x},\mathbf{x}';t-t'), \quad (2.20)$$

$$\tilde{G}(1,1')=\tilde{G}(\mathbf{x},\mathbf{x}';t-t'), \quad (2.21)$$

and we may introduce the Fourier analysis of the time dependence. For the $G(1,1')$ and $G_A(1,1')$, functions which are defined for all real values of $t-t'$, we may introduce Fourier transforms

$$G(1,1')=i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}G(\mathbf{x},\mathbf{x}';\omega), \quad (2.22)$$

$$G_A(1,1')=i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}G_A(\mathbf{x},\mathbf{x}';\omega). \quad (2.23)$$

However for $\tilde{G}(1,1')$, which is antiperiodic with period τ, we introduce a Fourier series expansion,

$$\tilde{G}(1,1')=\frac{1}{-i\tau}\sum_{p_0}\tilde{G}(\mathbf{x},\mathbf{x}';p_0)e^{-ip_0(t-t')}, \quad (2.24)$$

where the sum is over odd integers ν, and $p_0=\pi\nu/\tau$.

The connection between G and $\tilde{G}$ is made clear from the spectral representations of their Fourier coefficients:

$$G(\mathbf{x},\mathbf{x}';\omega)=\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\left\{\frac{1-f(\omega)}{\omega-\omega'+i\epsilon}+\frac{f(\omega)}{\omega-\omega'-i\epsilon}\right\}\times A_\beta(\mathbf{x},\mathbf{x}';\omega'), \quad (2.25)$$

$$\tilde{G}\left(\mathbf{x},\mathbf{x}';\frac{\pi\nu}{\tau}\right)=\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\frac{1}{\pi\nu/\tau-\omega'}A_{i\tau}(\mathbf{x},\mathbf{x}';\omega'), \quad (2.26)$$

where $A_\beta(x,x';\omega)$ is the spectral function which is a Hermitian matrix in $\mathbf{x}$ and $\mathbf{x}'$. Thus, it follows that we can obtain G by analytically continuing $\tilde{G}$ to continuous values of $\pi\nu/\tau=\omega+i\epsilon$ in the upper half-plane and then setting $\beta=i\tau$. The function

$$G^+(\mathbf{x},\mathbf{x}';\omega)=\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\frac{1}{\omega-\omega'+i\epsilon}A_\beta(\mathbf{x},\mathbf{x}',\omega'), \quad (2.27)$$

thus obtained, is related to G by

$$G(\mathbf{x},\mathbf{x}';\omega)=[1-f(\omega)]G^+(\mathbf{x},\mathbf{x}';\omega)+f(\omega)[G^+(\mathbf{x}\mathbf{x}';\omega)]^*. \quad (2.28)$$

In the case of the uniform electron gas, we can further introduce Fourier transforms for the space dependence and develop the Feynman-like rules in momentum space. This is discussed in Sec. IV.

The diagrammatic expansions for G and G_A may be partially summed in a well-known way and replaced by the integro-differential equations:

$$\left[\frac{i\partial}{\partial t_1}-\mathcal{E}(\mathbf{x}_1)\right]\tilde{G}(1,1')-\int_{|t_2|<\tau} d^4x_2\,\tilde{\Sigma}(1,2)\tilde{G}(2,1')=i\delta(1,1'), \quad (2.29)$$

$$\left[i\frac{\partial}{\partial t_1}-\mathcal{E}(\mathbf{x}_1)\right]G_A(1,1')-\int d^4x_2\,\Sigma_A(1,2)G_A(2,1')=i\delta(1,1'), \quad (2.30)$$

where

$$\mathcal{E}(\mathbf{x}_1)=-\nabla_1^2/2m+V(\mathbf{x}_1)-\mu, \quad (2.31)$$

and Σ and Σ_A are the proper self-energy parts calculated by the nonadiabatic[7] or adiabatic[16] rules, respectively.[17]

The proper self-energy diagrams to second order in e^2 are shown in Fig. 2. In the adiabatic theory for a uniform system, certain of these diagrams give vanishing contributions at $T=0$, namely, i, j, k, and l, because they require a particle and a hole to be in the same momentum-spin state. However, as Luttinger and Ward have shown, these diagrams do not generally vanish in the nonadiabatic theory and are examples of the anomalous contributions which arise in the $T=0$ limit of this theory. Finite anomalous contributions play an important part in the development of the quasi-classical theory of the atom which we treat in this paper.

Finally, we note that all the equilibrium properties of the system can be expressed in terms of the Green's functions or propagator functions. In particular, for the average number density we have[18]

$$n(\mathbf{x})=2\langle\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\rangle=-2\tilde{G}(1,1^+)\Big|_{i\tau=\beta}=-\frac{2}{\beta}\sum_{p_0}e^{ip_0 0^+}\tilde{G}(\mathbf{x},\mathbf{x};p_0), \quad (2.32)$$

$$N=\int d^3x\,n(\mathbf{x}),$$

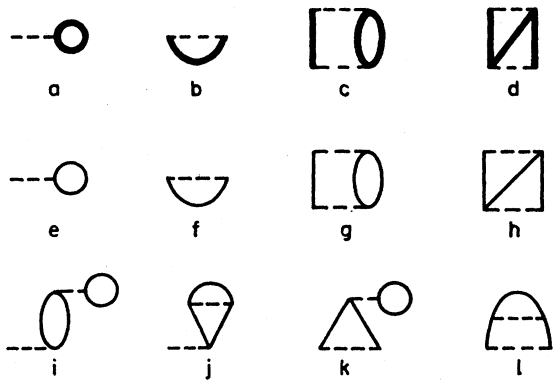


FIG. 2. (a–d) Irreducible proper self-energy diagrams to second order in the explicit interaction. Heavy lines indicate corrected Fermion propagators. (e–l) Explicit expansion of proper self-energy diagrams to second order in e^2. Solid lines indicate uncorrected propagator. In all these diagrams dashed lines indicate Coulomb interaction.

and for the total energy we have the equivalent expression:

$$E-N\mu=-\int d^3x_1\left(i\frac{\partial}{\partial t_1}+\mathcal{E}(\mathbf{x}_1)\right)\tilde{G}(1,1^+)\Big|_{i\tau=\beta} \quad (2.33)$$

$$=-2\int d^3x_1\,\mathcal{E}(\mathbf{x}_1)\tilde{G}(1,1^+)\Big|_{i\tau=\beta}-\int d^3x_1\int d^3x_2\,\tilde{\Sigma}(1,2)\tilde{G}(2,1)\Big|_{i\tau=\beta} \quad (2.34)$$

$$=2\int d^3x_1\int d^3x_2\,\frac{1}{\beta}\sum_{p_0}[\mathcal{E}(\mathbf{x}_1)\delta(\mathbf{x}_1-\mathbf{x}_2)+\tfrac{1}{2}\tilde{\Sigma}(\mathbf{x}_1,\mathbf{x}_2,p_0)]\tilde{G}(\mathbf{x}_1,\mathbf{x}_2,p_0)e^{ip_0 0^+} \quad (2.35)$$

III. EXPANSION IN POWERS OF ∇_R

We now consider a many-particle system, such as a large-Z atom, in which the inhomogeneities introduced by external fields, such as the nuclear potential, can be considered small over a distance comparable to an electron de Broglie wavelength. The one-Fermion Green's function $\tilde{G}$ should then possess an expansion in powers of the gradient operator which measures the inhomogeneities. This expansion can be carried out using the techniques of Theis and BB. We may write Eq. (2.29) as

$$\int d^4x_2\,\tilde{K}(1,2)\tilde{G}(2,1')=i\delta(1,1'), \quad (3.1)$$

where

$$\tilde{K}(1,2)=[i\partial/\partial t_1-\mathcal{E}(\mathbf{x}_1)]\delta(1,2)-\Sigma(1,2). \quad (3.2)$$

Introducing relative and "center-of-mass" coordinates, we may take the Fourier transforms over the relative

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

[17] In most of this paper we will discuss formal many-particle perturbation theory to all orders in λ. In any explicit calculation of Σ, involving the Coulomb interaction, it is well-known that certain classes of diagrams must be summed to all orders to remove divergences.[6,9] The necessity for these partial summations, which we will implicitly assume are carried out, does not affect the form of Eq. (2.30).

[18] The factor of 2 in this and succeeding equations arises if we take into account the two spin states of the electron.

coordinates:

$$\tilde{K}(\mathbf{R};p)=\int d^4(x_1-x_2)\, e^{-ip\cdot(x_1-x_2)}\tilde{K}(1,2), \quad (3.3)$$

where we have used a four-dimensional notation $p=(\mathbf{p},p_0)$, and $\mathbf{R}=(\mathbf{x}_1+\mathbf{x}_2)/2$.

Thus we have

$$\tilde{K}(\mathbf{R};p)=\omega-\mathcal{E}_p(\mathbf{R})-\tilde{\Sigma}(\mathbf{R};p), \quad (3.4)$$

$$\mathcal{E}_p(\mathbf{R})=(p^2/2m-\mu)+V(\mathbf{R}). \quad (3.5)$$

Then using the method and notation of BB, Eq. (3.1) may be written as an expansion

$$\theta[\tilde{K}(\mathbf{R};p),\tilde{G}(\mathbf{R};p)]=1, \quad (3.6)$$

where θ is the operator[19]

$$\theta[\tilde{K}(\mathbf{R};p),\tilde{G}(\mathbf{R};p)] = \lim_{\mathbf{R}'\to\mathbf{R},p'\to p}\{\exp[i/2(\nabla_R\cdot\nabla_{p'}-\nabla_{R'}\cdot\nabla_p)]\} \times\tilde{K}(\mathbf{R};p)\tilde{G}(\mathbf{R}';p'), \quad (3.7)$$

with the expansion in powers of ∇_R:

$$\theta=\sum_{j=0}^{\infty}\theta_j, \quad (3.8)$$

$$\theta_0(\tilde{K},\tilde{G})=\tilde{K}\tilde{G}, \quad (3.9)$$

$$\theta_1(\tilde{K},\tilde{G})=i/2[\nabla_R\tilde{K}\cdot\nabla_p\tilde{G}-\nabla_p\tilde{K}\cdot\nabla_R\tilde{G}], \quad (3.10)$$

$$\theta_2(\tilde{K},\tilde{G})=\tfrac{1}{2}(i/2)^2\lim_{\mathbf{R}'\to\mathbf{R},p'\to p}[(\nabla_R\cdot\nabla_{p'})^2 -2(\nabla_R\cdot\nabla_{p'})(\nabla_p\cdot\nabla_{R'})+(\nabla_p\cdot\nabla_{R'})^2] \times\tilde{K}(\mathbf{R};p)\tilde{G}(\mathbf{R}';p'). \quad (3.11)$$

To solve Eq. (3.6) we assume that each quantity $\tilde{K}$ and $\tilde{G}$ has an expansion in powers of ∇_R,

$$K(\mathbf{R};p)=\sum_{j=0}^{\infty}\tilde{K}_j(\mathbf{R};p),$$

$$\tilde{\Sigma}(\mathbf{R};p)=\sum_{j=0}^{\infty}\tilde{\Sigma}_j(\mathbf{R};p), \quad (3.12)$$

$$\tilde{G}(\mathbf{R};p)=\sum_{j=0}^{\infty}\tilde{G}_j(\mathbf{R};p),$$

and we compare coefficients on each side of the equation. It follows directly from Eqs. (3.4) and (3.10) that

$$\theta_1(\tilde{K}_0,\tilde{G}_0)=0, \quad (3.13)$$

so that the resulting equations may be written

$$\tilde{G}_0=1/K_0, \quad (3.14')$$

$$\tilde{G}_1=\tilde{G}_0\tilde{\Sigma}_1\tilde{G}_0, \quad (3.15')$$

$$\tilde{G}_2=\tilde{G}_0\tilde{\Sigma}_2\tilde{G}_0+\tilde{G}_0\tilde{\Sigma}_1\tilde{G}_0\tilde{\Sigma}_1\tilde{G}_0-\tilde{G}_0\theta_2(1/\tilde{G}_0,\tilde{G}_0). \quad (3.16')$$

These equations further simplify if we set $\tilde{\Sigma}_1=0$. We have verified that this is true to second order in the interaction (which is the order of the Gell-Mann Brueckner calculation),[6] but it appears that this is a general property true to all orders. With this assumption, which we will not discuss in more detail here, we obtain the equations

$$\tilde{G}_0=1/\tilde{K}_0, \quad (3.14)$$

$$\tilde{G}_1=0, \quad (3.15)$$

$$\tilde{G}_2=\tilde{G}_0\tilde{\Sigma}_2\tilde{G}_0-\tilde{G}_0\theta_2(1/\tilde{G}_0,\tilde{G}_0). \quad (3.16)$$

IV. ZERO ORDER IN ∇_R; CANCELLATION OF ANOMALOUS CONTRIBUTIONS

First let us concern ourselves with G_0, which is given by Eqs. (3.14) and (3.4) as

$$\tilde{G}_0=[p_0-\mathcal{E}_p(\mathbf{R})-\tilde{\Sigma}_0(\mathbf{R};p)]^{-1}. \quad (4.1)$$

The rules for calculating $\tilde{\Sigma}_0(\mathbf{R};p)$ are simple, since it is of zero order in ∇_R. We can replace $\tilde{G}(1.1')$ in the Feynman-like expansion by[20]

$$\tilde{G}_0(1,1')=\frac{-1}{\beta}\sum_{p_0}\int\frac{d^3p}{(2\pi)^3}\, e^{ip\cdot(x_1-x_{1'})}\tilde{G}_0(\mathbf{R};p) \quad (4.2)$$

to this order. In addition, to zero order in ∇_R we can set all the center of mass coordinates appearing in any term of $\tilde{\Sigma}$ equal to $\mathbf{R}$. This corresponds to the zeroth-order term in the successive application of the θ-expansion technique of Sec. III. It then follows that the rules for calculating $\tilde{\Sigma}_0(\mathbf{R};p)$ in terms of $\tilde{G}_0(\mathbf{R};p)$ are the same as the energy-momentum-space rules in the homogeneous case,[9–16] namely:

(i) Each line in the diagram expansion for $\tilde{G}_1(1,1')$ is labeled by an energy-momentum p_i.

(ii) For each corrected Fermion line with energy-momentum p, we have a factor $\tilde{G}_0(\mathbf{R};p)$.

(iii) A factor $-i\lambda v(q)$ for each dashed interaction line with momentum q, where $v(q)$ is the Fourier transform of the interaction potential

$$v(q)=\int d^4x\, e^{-iq\cdot x}v(\mathbf{x})\delta(t)=\int d^3x\, e^{-iq\cdot x}v(\mathbf{x}). \quad (4.3)$$

(iv) At each vertex with two Fermion lines and one interaction line, there is a delta function conserving energy-momentum:

$$(2\pi)^3\delta^3(\mathbf{p}_1+\mathbf{p}_2+\mathbf{q})\delta_{p_{10}+p_{20}+q_0}, \quad (4.4)$$

[19] In this expression and those to follow ∇_R and ∇_p are three-dimensional gradients.

[20] In the following formulas we have taken the limit $i\tau=\beta$.

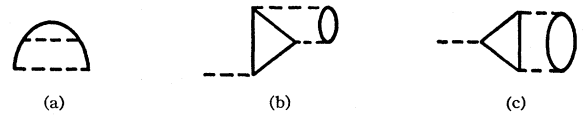


FIG. 3. Examples of anomalous and nonanomalous time orderings: (a) Anomalous in all orderings. (b) Anomalous ordering. (c) Same Feynman diagram as (b) in nonanomalous ordering.

where p_1, p_2, and q are momenta and energy coming in the vertex.

(v) All internal energy-momentum variables are summed and integrated out:

$$\int \frac{d^3p}{(2\pi)^3} \frac{1}{(-\beta)} \sum_{p_0} \left(p_0 = \frac{i\pi\nu}{\beta}, \ \nu \text{ odd integer} \right). \quad (4.5)$$

(Lines entering and leaving the same interaction require a convergence factor $e^{ip_0 0+}$.)

(vi) There is a factor of (-2) for each closed Fermion loop.

As things stand up to this point, the expansion of $\tilde{\Sigma}$ contains the so-called anomalous contributions as discussed in Sec. II. In momentum-energy space, these are characterized by time orderings of diagrams (see Fig. 3) in which a particle line and a hole line bear the same momentum-energy variable. As shown by LW, these time orderings give contributions which are singular on the Fermi surface. We will summarize their argument here. From the examples in Fig. 3 and the rules we see that diagrams containing anomalous orderings are generated by expanding the propagators for the corrected lines in $\tilde{G}_0$ in terms of

$$\tilde{G}_0^0(\mathbf{R}; p) = [p_0 - \mathcal{E}_p(\mathbf{R})]^{-1}. \quad (4.6)$$

Thus we have

$$\tilde{G}_0(\mathbf{R}; p) = \tilde{G}_0^0 + \tilde{G}_0^0\tilde{\Sigma}_0\tilde{G}_0^0 + \tilde{G}_0^0\tilde{\Sigma}_0\tilde{G}_0^0\tilde{\Sigma}_0\tilde{G}_0^0 \cdots. \quad (4.7)$$

If a diagram in the original expansion contains a factor

$$-\frac{1}{\beta} \sum_{p_0} \tilde{G}_0(\mathbf{R}; p) F(\mathbf{R}; p), \quad (4.8)$$

the anomalous diagrams obtained from it are of the form

$$-\frac{1}{\beta} \sum_{m=1}^{\infty} \sum_{p_0} [\tilde{G}_0^0(\mathbf{R}; p)]^{m+1} [\Sigma_0(\mathbf{R}; p)]^m F(\mathbf{R}; p). \quad (4.9)$$

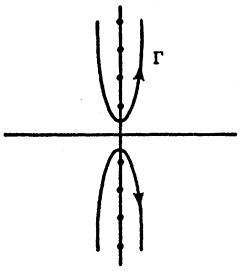
We can convert each term in this into a contour integral,

$$\frac{1}{2\pi i} \int_\Gamma dz \, f(z) [G_0^0(\mathbf{R}; \mathbf{p}, z)]^{m+1} [\Sigma(\mathbf{R}; \mathbf{p}, z)]^m \times F(\mathbf{R}; \mathbf{p}, z), \quad (4.10)$$

where $f(z) = (1+e^{\beta z})^{-1}$ and Γ is the contour in Fig. 4 which encloses the poles of $f(z)$ at $z = (i\pi\nu/\beta)$ $(\nu = \pm 1, \pm 3$, etc.). At $T=0$ in the vicinity of the (local) unperturbed Fermi surface, $\mathcal{E}_p(\mathbf{R}) = 0$, this term is singular near $z=0$, since $f(z)$ approaches a unit-step function with discontinuity at $z=0$. Thus, the $(m+1)$st order pole at $z=0$ contains terms as singular as

$$\delta^{(m)}(\mathcal{E}_p(\mathbf{R}))[\tilde{\Sigma}_0(\mathbf{R}, \mathbf{p}, 0)]^m F(\mathbf{p}, 0). \quad (4.11)$$

FIG. 4. Contour Γ.



The anomalous contributions can be eliminated by a self-consistent choice of the zero-order Hamiltonian.[21] By adding and subtracting a self-consistent potential $\Phi(\mathbf{R})$, we may write

$$\tilde{G}_0(\mathbf{R}; p) = \{p_0 - \mathcal{E}_p(\mathbf{R}) - \Phi(\mathbf{R}) - [\tilde{\Sigma}_0(\mathbf{R}; p) - \Phi(\mathbf{R})]\}^{-1}. \quad (4.12)$$

Thus, we may consider

$$\tilde{G}_0^0(\mathbf{R}; p) = [p_0 - \mathcal{E}_p(\mathbf{R}) - \Phi(\mathbf{R})]^{-1} \quad (4.13)$$

as our zero-order propagator if we replace $\tilde{\Sigma}_0$ everywhere by $\tilde{\Sigma}_0 - \Phi$. This propagator has a corrected Fermi surface given by

$$\mathcal{E}_{pF}(\mathbf{R}) + \Phi(\mathbf{R}) = 0. \quad (4.14)$$

Thus, in Eqs. (4.9) or (4.10) we can eliminate the anomalous contributions by choosing

$$\Phi(\mathbf{R}) = \tilde{\Sigma}_0(\mathbf{R}; \mathbf{p}_F, 0), \quad (4.15)$$

where $\mathbf{p}_F$ is the corrected Fermi momentum. With this choice of Φ and $\tilde{G}_0^0$, the integrand of Eq. (4.10) has at most a simple pole at $z=0$, and no anomalous contributions arise.

The motivation for this elimination of the anomalous contributions is twofold. First, once we have a perturbation theory without anomalous terms, we can make contact with the results of the usual "adiabatic" ground-state perturbation calculations which have been carried out for the electron gas. Secondly, the self-consistent potential $\Phi(\mathbf{R})$ is the natural generalization of the Thomas-Fermi potential to all orders in the interaction.

The connection with the usual ground-state perturbation theory follows by converting the sums over the discrete frequencies $p_0 = i\pi\nu/\beta$ into integrals in the $T=0$ $(\beta = \infty)$ limit in which these discrete points get

[21] This is closely related to the work of Klein [A. Klein, Phys. Rev. **121**, 950 (1961)] for the uniform system.

infinitely close together.

$$\frac{1}{\beta}\sum_{p_0}\tilde{G}_0(\mathbf{R};p)F(\mathbf{R};p)\rightarrow \int_{-i\infty}^{i\infty}\frac{d\omega}{2\pi i}\tilde{G}_0(\mathbf{R};\mathbf{p},\omega_0)F(\mathbf{R};\mathbf{p},\omega), \quad (4.16)$$

$$\frac{1}{\beta}\sum_{p_0}[\tilde{G}_0{}^0(\mathbf{R};p)]^{m+1}[\Sigma_0(\mathbf{R};p)-\Phi]^m F(\mathbf{R};p)\rightarrow \int_{-i\infty}^{i\infty}\frac{d\omega}{2\pi i}[\tilde{G}_0{}^0(\mathbf{R};\mathbf{p},\omega)]^{m+1}[\tilde{\Sigma}_0(\mathbf{R};\mathbf{p},\omega)-\Phi]^m \times F(\mathbf{R};\mathbf{p},\omega). \quad (4.17)$$

The integration over ω extends over the imaginary ω axis. This transformation can be carried out since the integrands have, at most, a simple pole at $\omega=0$.

The path of integration can now be deformed to lie slightly below the negative real axis and slightly above the positive real axis, since all the singularities of the integrand lie along the real axis. This is equivalent to replacing $\tilde{G}_0{}^0(\mathbf{R};\mathbf{p},\omega)$ by

$$G_A{}^0(\mathbf{R};p)=\{p_0-[\mathcal{E}_p(\mathbf{R})+\Phi(\mathbf{R})](1-i\epsilon)\}^{-1}, \quad 4.18)$$

where ϵ is a small positive quantity, and $\int_{-i\infty}^{i\infty}d\omega/2\pi i$ is replaced by

$$\int_{-\infty}^{\infty}dp_0/2\pi i, \quad \text{and} \quad \tilde{G}_0(\mathbf{R};\mathbf{p},\omega)$$

by

$$G_A(\mathbf{R};p)=\frac{G_A{}^0(\mathbf{R};p)}{1-G_A{}^0(\mathbf{R};p)[\tilde{\Sigma}_0(\mathbf{R};p)-\Phi(\mathbf{R})]}. \quad (4.19)$$

Thus, at $T=0$ we are led to the following modifications of the rules:

(i) The propagator for each Fermion line is replaced by $G_A(\mathbf{R};p)$;

(ii) The discrete sum over p_0 is replaced by a continuous integral, $\int_{-\infty}^{\infty}dp_0/2\pi i$.

These are just the Feynman rules for the usual adiabatic ground-state (or Goldstone-type) perturbation theory. Note that $G_A{}^0(\mathbf{R};p)$ has the usual separation between particles (positive frequencies) and holes (negative frequencies) described by the corrected local Fermi surface.

$$\mathcal{E}_{p_F}(\mathbf{R})+\Phi(\mathbf{R})=0, \quad (4.20)$$

or

$$\mu=p_F{}^2(\mathbf{R})/2m+V(\mathbf{R})+\tilde{\Sigma}_0(\mathbf{R};p_F(\mathbf{R}),0). \quad (4.21)$$

In terms of this Fermi momentum, we can write

$$G_A{}^0(\mathbf{R};p)=G_A{}^0(p)|_{p_F=p_F(\mathbf{R})}=\frac{1}{p_0-\{[p^2-p_F{}^2(\mathbf{R})]/2m\}(1-i\epsilon)} \quad (4.22)$$

$$=\frac{\eta(p-p_F(\mathbf{R}))}{p_0-[p^2-p_F{}^2(\mathbf{R})]/2m+i\epsilon}+\frac{\eta(p_F(\mathbf{R})-p)}{p_0-[p^2-p_F{}^2(\mathbf{R})]/2m-i\epsilon}, \quad (4.23)$$

which is the form of the propagator used in calculations for the homogeneous system.

We must still show the connection between $\tilde{\Sigma}_0(\mathbf{R};p)$ and the self-energy part $\Sigma_A(\mathbf{p},p_0)$ calculated from the adiabatic ground-state theory for the homogeneous case. The rules, propagators, and diagrams for $\tilde{\Sigma}_0$ are the same as those for the homogeneous adiabatic calculation except for the replacement of p_F by $p_F(\mathbf{R})$ *and* the rule that $\Phi(\mathbf{R})$ be subtracted from each internal self-energy part. However, this last additional rule has only a trivial effect since the Φ dependence is equivalent to changing the frequency variables in each propagator from p_0' to $p_0'+\Phi$. This dependence can be removed by a change of dummy variables $p_0''\rightarrow p_0'+\Phi$, and, thus, the net effect of the Φ dependence is to shift the external frequency variable from p_0 to $p_0+\Phi$. Thus,

$$\tilde{\Sigma}_0(\mathbf{R};p)=\Sigma_A(\mathbf{p},p_0+\Phi)|_{p_F=p_F(\mathbf{R})}, \quad (4.24)$$

where Σ_A is the usual self-energy part in the adiabatic expansion without any corrections to internal self-energy parts.

We can then write the equation for the Fermi momentum as

$$\mu=p_F{}^2(\mathbf{R})/2m+V(\mathbf{R})+\Sigma_A(p_F(\mathbf{R}),\Phi(\mathbf{R})), \quad (4.25)$$

or using Eqs. (4.20) and (4.21)

$$\mu=p_F{}^2(\mathbf{R})/2m+V(\mathbf{R})+\Sigma_A(p_F(\mathbf{R}),\mu-p_F{}^2(\mathbf{R})/2m-V). \quad (4.26)$$

Now the single-particle separation energy is, in the homogeneous case,[22]

$$E(p_F)=p_F{}^2/2m+V+\Sigma_A(p_F,E(p_F)-(p_F{}^2/2m)-V)=p_F{}^2/2m+E_H+V+E_{\rm ex}(p_F)+E_c(p_F), \quad (4.27)$$

where we have separated Σ_A explicitly into the Hartree potential, exchange energy, and correlation energy. In the inhomogeneous system, the Hartree self-energy

$$\Sigma_H(\mathbf{R})=\int d^3r\, v(\mathbf{R}-\mathbf{r})n(\mathbf{r}) \quad (4.28)$$

is included in the potential

$$\phi(\mathbf{R})=V(\mathbf{R})+\Sigma_H(\mathbf{R}), \quad (4.29)$$

which obeys the Poisson equation

$$\nabla^2\phi=4\pi Ze^2\delta(\mathbf{R})-4\pi e^2 n(\mathbf{R}). \quad (4.30)$$

Thus, we can express Eq. (4.26) as

$$\mu=p_F{}^2(\mathbf{R})/2m+\phi_0(\mathbf{R})+E_{\rm ex}(p_F(\mathbf{R}))+E_c(p_F(\mathbf{R})), \quad (4.31)$$

[22] Remember that in the ground-state formalism for the electron gas the energy is measured relative to $p_F{}^2/2m$ and the constant (infinite) potential energy of the uniform-positive background cancels the Hartree energy exactly.

where $\phi_0(\mathbf{R})$ is the local Thomas-Fermi potential [Eq. (4.29) to zero order in ∇_R], and where the quantities E_{ex} and E_c are obtained from the corresponding homogeneous quantities by replacing p_F by $p_F(\mathbf{R})$. This is exactly Lewis' equation for $p_F(\mathbf{R})$.

We can summarize the results of this section as follows: To zero order in the inhomogeneity corrections we can define a local Fermi momentum $p_F(\mathbf{R})$ which is a function of the interaction strength. Because of this, the ground states of the interacting and noninteracting systems cannot be related by the adiabatic hypothesis and anomalous contributions arise in the thermodynamic perturbation theory. Using the self-consistent potential $\Phi(\mathbf{R})$, we redefined the zero-order problem so its Fermi momentum coincided with $p_F(\mathbf{R})$. This eliminated the anomalous diagrams and allowed us to make the connection with the adiabatic ground-state perturbation theory. The result is that to zero order in ∇_R, the Feynman rules are the same as those in the homogeneous case with p_F replaced everywhere by $p_F(\mathbf{R})$ defined by Eq. (4.31).

We must emphasize the importance of the anomalous contributions. Their explicit appearance in the perturbation theory has been removed by the definition of $p_F(\mathbf{R})$. As we shall show in detail in Sec. VII, anomalous terms of the order of E_c are omitted by approximating $p_F(\mathbf{R})$ by its Fermi-Thomas value,

$$p_F^0(\mathbf{R})=\{2m[\mu-\phi_0(\mathbf{R})]\}^{\frac{1}{2}}. \tag{4.32}$$

In the case of an infinite uniform electron gas with Coulomb interactions, $V(\mathbf{R})=-\Sigma_H(p_F)$ is the infinite constant potential of the neutralizing background of positive charge. Since the uniform electron density must be the same with or without interactions, it follows simply by counting occupied states that the Fermi momentum is unchanged by including interactions beyond the Hartree approximation, i.e., $p_F=p_F^0$. The corrected chemical potential is determined by Eq. (4.20), which we can write as

$$\delta\mu=\mu-\mu_0=\tilde{\Sigma}(p_F,0)-\Sigma_H(p_F), \tag{4.33}$$

where $\mu_0=p_F^2/2m$. Thus, in the propagator G_0^0 the correction δ_μ cancels the self-consistent potential Φ so that if we merely set $\mu=\mu_0$, we can calculate using the adiabatic formalism, and no anomalous contributions arise. This is equivalent to the conclusions of LW.

In the atomic problem we cannot find $p_F(\mathbf{R})$ explicitly in general since the local density in the atom is dependent on the interactions. In this case we must solve Eqs. (4.21) and (6.6) numerically to determine μ and $p_F(\mathbf{R})$. To prove that $p_F(\mathbf{R})$ depends on interactions beyond the Hartree approximation in general, we note that $p_F(\mathbf{R})=p_F^0(\mathbf{R})$ if, and only if,

$$\delta\mu=\tilde{\Sigma}(\mathbf{R},p_F(\mathbf{R}),0)-\Sigma_H(p_F) \tag{4.33'}$$

holds for all $\mathbf{R}$, which is impossible.

V. LOWEST-ORDER INHOMOGENEITY CORRECTIONS

We will here briefly and formally consider the second-order inhomogeneity correction to G. From Eqs. (3.16) and (3.11), we find that

$$\tilde{G}_2=\tilde{G}_0^2\tilde{\Sigma}_2(\mathbf{R};p)+\tilde{G}_0^3\tilde{C}(\mathbf{R};p)+\tilde{G}_0^4\tilde{D}(\mathbf{R};p), \tag{5.1}$$

where

$$\begin{aligned}4C(\mathbf{R};p)=&-\frac{1}{m}\left[\frac{\partial^2\chi}{\partial R^2}+\frac{2}{R}\frac{\partial\chi}{\partial R}\right]\left[1+\frac{m}{p}\frac{\partial\chi}{\partial p}\right]\\&-\left[\frac{(\mathbf{R}\cdot\mathbf{p})}{pR}\frac{\partial^2\chi}{\partial R\partial p}\right]^2+\left[\frac{\partial^2\chi}{\partial p^2}-\frac{1}{p}\frac{\partial\chi}{\partial p}\right]\\&\times\left\{\left[\frac{\mathbf{p}\times\mathbf{R}}{pR}\right]^2\frac{1}{R}\frac{\partial\chi}{\partial R}+\left[\frac{\mathbf{p}\cdot\mathbf{R}}{pR}\right]^2\frac{\partial^2\chi}{\partial R^2}\right\},\end{aligned} \tag{5.2}$$

$$\begin{aligned}4D(\mathbf{R};p)=&\left[1+\frac{m}{p}\frac{\partial\chi}{\partial p}\right]^2\left\{\left[\frac{\mathbf{p}\cdot\mathbf{R}}{mR}\right]^2\frac{\partial^2\chi}{\partial R^2}\right.\\&\left.+\left[\frac{\mathbf{p}\times\mathbf{R}}{mR}\right]^2\frac{1}{R}\frac{\partial\chi}{\partial R}\right\}+\frac{1}{m}\left[1+\frac{m}{p}\frac{\partial\chi}{\partial p}\right]\\&\times\left\{\left[\frac{\partial\chi}{\partial R}\right]^2-\frac{2}{p}\left[\frac{\mathbf{p}\cdot\mathbf{R}}{R}\right]^2\frac{\partial\chi}{\partial R}\frac{\partial^2\chi}{\partial p\partial R}\right\}\\&+\left[\frac{\partial^2\chi}{\partial p^2}-\frac{1}{p}\frac{\partial\chi}{\partial p}\right]\left[\frac{\mathbf{p}\cdot\mathbf{R}}{pR}\right]^2\left(\frac{\partial\chi}{\partial R}\right)^2,\end{aligned} \tag{5.3}$$

and where

$$\chi(\mathbf{R};p)=\tilde{\Sigma}_0(\mathbf{R};p)+V(\mathbf{R}). \tag{5.4}$$

$\tilde{\Sigma}_2$ is the self-energy term second order in the gradient ∇_R. The prescription for calculating $\tilde{\Sigma}_2$ is more complicated than that for $\tilde{\Sigma}_0$ since the dependence on ∇_R arises from two sources: (i) the dependence of the propagators for each Fermion line on ∇_R, and (ii) the differences in the center-of-mass coordinate associated with each Fermion line. The expansion can be carried out formally by the successive application of the θ expansion technique to the original space-time rules for the calculation of $\Sigma(1,2)$. Note that, in general, we will get anomalous contributions in this order, since $\Phi(\mathbf{R})$ was chosen only to eliminate these in zeroth order in ∇_R. It is not unlikely that a generalization of this scheme could be used to eliminate the anomalous terms to higher orders, although we have not considered this problem.

For complete mathematical consistency, we should calculate $\tilde{G}_2$ to the same order in λ that we calculate $\tilde{G}_0$. However, if the inhomogeneity corrections are small first- or second-order quantities, it may be argued that we need only calculate $\tilde{G}_2$ to a lower order in λ to obtain the same order of "small quantities" as in the calculation of $\tilde{G}_0$. We will take this easy way out and calculate $\tilde{G}_2$ only in the Hartree approximation,

leaving the question open as to the importance of the higher-order terms in λ. We must stress that this result will have meaning only in the case in which the inhomogeneity terms are negligible and, as such, provides only an estimate for the conditions for which this is true. The calculation of these higher-order terms in λ appears to be straightforward, but tedious.

To zero order in λ, we have

$$\tilde{G}_2=\tilde{G}_2{}^0=[\tilde{G}_0{}^0]^3C^0(\mathbf{R};p)+[\tilde{G}_0{}^0]^4D^0(\mathbf{R};p)+[\tilde{G}_0{}^0]^2\phi_2(\mathbf{R}), \quad (5.5)$$

where

$$C^0(\mathbf{R};p)=(1/4m)[d^2\phi_0/dR^2+(2/R)d\phi_0/dR], \quad (5.6)$$

$$D^0(\mathbf{R},p)=\frac{1}{4}\left\{\left[\frac{\mathbf{p}\cdot\mathbf{R}}{mR}\right]^2\frac{d^2\phi_0}{dR^2}+\left[\frac{\mathbf{p}\times\mathbf{R}}{mR}\right]^2\frac{1}{R}\frac{d\phi_0}{dR}+\frac{1}{m}\left(\frac{d\phi_0}{dR}\right)^2\right\}. \quad (5.7)$$

Again, $\phi=\phi_0+\phi_2$ is the Thomas-Fermi potential of Eq. (4.29) to second order in ∇_R. This corresponds to the Hartree approximation for $\tilde{\Sigma}_0$. As mentioned in Sec. II, we consider the Hartree approximation as zeroth order in the interaction, since in the uniform electron gas $\phi=0$, i.e., the Hartree potential exactly cancels the potential of the uniform positive background.

VI. CALCULATION OF PHYSICAL PROPERTIES

A. Particle Density

The simplest quantity to calculate from this theory is the particle density. Using Eqs. (2.33) and (4.2), we have

$$n(\mathbf{R})=-2G(\mathbf{R},\mathbf{R}^+)=\frac{2}{\beta}\sum_{p_0}\int\frac{d^3p}{(2\pi)^3}\tilde{G}(\mathbf{R};p)e^{ip_00+}. \quad (6.1)$$

First we consider the zeroth order in ∇_R. In the $T=0$ limit, with our self-consistent choice of $\Phi(\mathbf{R})$, we can convert the sum over p_0 into an integral without being concerned with any anomalous contributions.

$$n_0(\mathbf{R})=2\int\frac{d^4p}{(2\pi)^4i}G_A(p)\Big|_{p_F=p_F(\mathbf{R})}e^{ip_00+}. \quad (6.2)$$

In the homogeneous case we know the result of this integration to be $n=(1/3\pi^2)p_F{}^3$ since the density does not depend on the interaction. Hence, according to the discussion in Sec. IV we obtain the value of $n_0(\mathbf{R})$ by merely replacing p_F by $p_F(\mathbf{R})$:

$$n_0(\mathbf{R})=(1/3\pi^2)p_F{}^3(\mathbf{R}). \quad (6.3)$$

The second-order correction in ∇_R we calculate only in the Hartree approximation. From Eqs. (5.5) to (5.7) and (6.1) we have

$$n_2(\mathbf{R})=\frac{1}{-2}\frac{1}{\beta}\sum_{p_0}\int\frac{d^3p}{(2\pi)^3}\tilde{G}_2(\mathbf{R};p)e^{ip_00+} \quad (6.4)$$

$$=-\frac{m}{\pi^2}p_F{}^0(\mathbf{R})\phi_2(\mathbf{R})-\frac{m}{24\pi^2p_F{}^0(\mathbf{R})}\times\left[2\nabla^2\phi_0+\frac{m}{[p_F{}^0(\mathbf{R})]^2}\left(\frac{d\phi_0}{dR}\right)^2\right], \quad (6.5)$$

where $p_F{}^0(\mathbf{R})$ is the zero-order Fermi momentum of Eq. (4.32). This is the same as Eq. (4.15) of BB without the exchange contribution, which in our formulation is included in $n_0(\mathbf{R})$ via Eq. (4.29) for $p_F(\mathbf{R})$.

B. Boundary Conditions for Atoms

The boundary conditions which, in effect, determine the chemical potential μ for an atom are expressed in terms of the particle density and it is primarily for this reason that $n(\mathbf{R})$ is of interest. We will consider an atom confined to a radius a outside of which the electron density vanishes. This is an often-used model for a gas of atoms under pressure. The boundary conditions then are

$$\int_{R\leqslant a}d^3R\,n(\mathbf{R})=Z, \quad (6.6)$$

where Z is the nuclear charge and hence the total number of electrons.

It is usually simpler to express this in terms of the generalized Thomas-Fermi potential ϕ which obeys Eq. (4.30). Inserting this equation into Eq. (6.6) and integrating by parts, we find

$$d\phi/dR|_{R=a}=0 \quad (6.7)$$

as an alternate expression of the boundary conditions.

C. Calculation of the Total Energy

From Eq. (2.35) we can derive the following expression for $E-N\mu$:

$$E-\mu N=2\int d^3R\int\frac{d^3p}{(2\pi)^3}\left(\frac{1}{\beta}\sum_{p_0}\right)\theta[p^2/2m+V(\mathbf{R})+\tfrac{1}{2}\tilde{\Sigma}(\mathbf{R};p),\tilde{G}(\mathbf{R};p)]e^{ip_00+}. \quad (6.8)$$

To zeroth order in ∇_R we have

$$E_0-\mu N_0=2\int d^3R\times\int\frac{d^3p}{(2\pi)^3}\frac{1}{\beta}\sum_{p_0}\{[p^2/2m+V(\mathbf{R})]\tilde{G}_0(\mathbf{R};p)+\tfrac{1}{2}\tilde{\Sigma}_0(\mathbf{R};p)\tilde{G}_0(\mathbf{R};p)\}. \quad (6.9)$$

In the limit as $\beta\rightarrow\infty$ we can convert the sum over p_0 to an integral in the manner described above to get

$$E_0=2\int d^3R\int\frac{d^4p}{(2\pi)^4i}\left\{\left[\frac{p^2}{2m}+V(\mathbf{R})\right]G_A(\mathbf{p},\,p_0+\Phi)+\tfrac{1}{2}\Sigma_A(\mathbf{p},\,p_0+\Phi)G_A(\mathbf{p},\,p_0+\Phi)\right\}\Big|_{p_F=p_F(\mathbf{R})} \quad (6.10)$$

This is obtained by expanding

$$\tilde{G}=\tilde{G}_0{}^0+\tilde{G}_0{}^0(\tilde{\Sigma}-\Phi)\tilde{G}_0{}^0+\tilde{G}_0{}^0(\tilde{\Sigma}-\Phi)\tilde{G}_0{}^0(\tilde{\Sigma}-\Phi)\tilde{G}_0{}^0+\cdots, \quad (6.11)$$

and noting Eq. (4.24), which leads to the following relations between $\tilde{G}_0$ and $\tilde{\Sigma}_0$ calculated by the non-adiabatic rules and the corresponding quantities G_A and Σ_A calculated in the adiabatic formalism for a uniform electron gas:

$$\tilde{G}_0(\mathbf{R};\,p)=G_A(\mathbf{p},\,p_0+\Phi)\,|_{p_F=p_F(\mathbf{R})}. \quad (6.12)$$

Changing dummy variables, $p_0\rightarrow p_0+\Phi$, we have

$$E_0=2\int d^3R\int\frac{d^4p}{(2\pi)^4i}\left\{\left[\frac{p^2}{2m}+V(\mathbf{R})\right]G_A(p)+\tfrac{1}{2}\Sigma_A(p)G_A(p)\right\}\Big|_{p=p_F(\mathbf{R})}. \quad (6.13)$$

It then follows that except for the term proportional to $V(\mathbf{R})$, that the $\mathbf{R}$ integrand is the ground-state energy per unit volume calculated in the adiabatic formalism with p_F replaced by $p_F(\mathbf{R})$, or in terms of the ground-state energy per particle:

$$\epsilon_0(p_F)=\frac{2}{n_0(\mathbf{R})}\int\frac{d^4p}{(2\pi)^4i}\left[\frac{p^2}{2m}+\frac{1}{2}\Sigma_A(\mathbf{R};\,p)\right]\times G_A(\mathbf{R};\,p)\,|_{p=p_F(\mathbf{R})}, \quad (6.14)$$

where $n_0(\mathbf{R})$ is the number density at $\mathbf{R}$.

$$n_0(\mathbf{R})=2\int\frac{d^4p}{(2\pi)^4i}G_A(\mathbf{R};\,p). \quad (6.15)$$

Thus, we have for the total energy

$$E_0=\int d^3R\,n_0(\mathbf{R})[\epsilon_0(p_F(\mathbf{R}))+V(\mathbf{R})]. \quad (6.16)$$

This is easily shown to be equivalent to Lewis' equations and leads to his results for the equation of state.

We have investigated the second-order inhomogeneity correction again only in the Hartree limit. From Eqs. (3.7) through (3.10) and (6.8), with $\Sigma=\Sigma_H=\phi-V$, we have

$$E_2=2\int d^3R\int\frac{d^3p}{(2\pi)^3}\frac{1}{\beta}\times\sum_{p_0}\{[p^2/2m+\tfrac{1}{2}V(\mathbf{R})+\tfrac{1}{2}\phi_0(\mathbf{R})]\tilde{G}_{(2)}{}^0(\mathbf{R};\,p)+\tfrac{1}{2}\phi_2(\mathbf{R})\tilde{G}_0{}^0(\mathbf{R};\,p)+\theta_2[p^2/2m+\tfrac{1}{2}V(\mathbf{R})+\tfrac{1}{2}\phi(\mathbf{R}),\,\tilde{G}_0{}^0(\mathbf{R};\,p)]\}. \quad (6.17)$$

Using the equations previously developed, after some manipulation we obtain

$$E_2=\int d^3R\left[\frac{p_F(\mathbf{R})^2}{2m}+\phi_0(\mathbf{R})\right]n_2(\mathbf{R})+\int\frac{d^3R}{24\pi^2}\times\frac{m}{[2m(\mu-\phi_0)]^{\frac{1}{2}}}\left[4(\mu-\phi_0)\nabla^2\phi_0-\left(\frac{d\phi_0}{dR}\right)^2\right]. \quad (6.18)$$

The first term of this energy expression arises as the correction to the zero-order energy (6.16) when the density $n_0(\mathbf{R})$ is corrected to second order. The second term, which we will label δ_2E, is an intrinsically second-order correction to the energy and agrees to lowest order in ∇_R with the expression given by Kirzhnits.[2] To compare with the Weizsäcker form of the inhomogeneity correction, we express ϕ_0 in terms of $\rho_0=en_0(\mathbf{R})$ and find

$$\delta_2E=\frac{1}{72m}\int d^3R\,\frac{1}{\rho_0}\left(\frac{d\rho_0}{dR}\right)^2-\frac{\pi a^2}{3}\left(\frac{d\rho_0}{dR}\right)_{R=a}, \quad (6.19)$$

where a is the radius of the atom. For the infinite atom the integrated term vanishes, leaving δ_2E just 1/9 the Weizsäcker correction.[1,2] An atom under pressure must be described as a cell in a crystal of high symmetry, for which the density is considered continuous at the boundary between cells, and by symmetry $(d\rho_0/dR)=0$ at $R=a$.

VII. RELATION TO OTHER WORK

We here want to consider the relation of our equations, which agree with Lewis to zero order in ∇_R, and with Baraff's results. To do this we eliminate $p_F(\mathbf{R})$ between Eqs. (4.30), (4.31), and (6.3). Solving Eq. (4.31) iteratively for $p_F(\mathbf{R})$, we find [with $E_s=E_{ex}(p_F)+E_c(p_F)$]

$$p_F{}^2(\mathbf{R})=2m[\mu-\phi_0-E_s(p_F)+(dE_{ex}/dp_F)(m/p_F)E_{ex}(p_F)]_{p_F=p_F{}^0(\mathbf{R})}, \quad (7.1)$$

where all the quantities on the right are evaluated at the Thomas-Fermi value $p_F{}^0$ of Eq. (4.32). The derivatives are with respect to the complete dependence of ϕ and E on p_F. The last term on the right-hand side can be identified as the anomalous contribution to the self-energy part coming from the diagram in Fig. 21.

This anomalous contribution arises if we try to express Σ_A in terms of $p_F{}^0$ rather than $p_F(\mathbf{R})$.[23]

We need only consider these terms in order $\lambda=e^2$ (Hartree-Fock) to get the total contribution to order $\lambda^2=e^4$. Explicitly, to this order we find

$$dE_{\rm ex}/dp_F=-(d/dp_F)[(e^2/\pi)p_F]=-e^2/\pi. \quad (7.2)$$

Substituting Eq. (7.1) in Poisson's Eq. (4.31), we have

$$\nabla^2\phi=\nabla^2(\phi_0+\phi_2)=-4\pi e^2[p_F{}^3(\mathbf{R})/3\pi^2+n_2(\mathbf{R})] \quad (7.3)$$

$$=-4\pi e^2\Big[\Big\{\frac{p_F{}^3}{3\pi^2}-\frac{1}{\pi^2}p_F m E_s(p_F)\Big\}+\delta n_0(\mathbf{R})+n_2(\mathbf{R})\Big]_{p_F=p_F{}^0(\mathbf{R})}, \quad (7.4)$$

where $\delta n_0(\mathbf{R})$ is the anomalous contribution:

$$\delta n_0(\mathbf{R})=\frac{1}{\pi^2}p_F m\frac{\delta E_{\rm ex}}{\delta p_F}\frac{m}{p_F}-E_{\rm ex}+\frac{1}{2\pi^2}\frac{m^2}{p_F}(E_{\rm ex})^2 \quad (7.5)$$

$$=\frac{3}{2\pi^4}e^4m^2p_F. \quad (7\,6)$$

If we drop the anomalous contribution $4\pi e^2\delta n_0(\mathbf{R})$ in Eq. (7.4), it is not hard to show that the result is the same as the equation for $\phi=\phi_0+\phi_2$ obtained by combining Baraff's Eqs. (4.3c) and (5.19). (Note however that our procedure of splitting ϕ into two parts ϕ_0 and ϕ_2 differs from Baraff's.) The anomalous term does contribute to the same order in e^2 as $E_{\rm corr}$. In fact, the correlation term contributes explicitly:

$$\frac{1}{\pi^2}p_F m E_{\rm corr}(p_F)$$

$$=+\frac{1}{\pi^2}p_F m\Big[\frac{1}{2\pi^2}me^4(1-\ln 2)\ln\Big(\frac{\alpha p_F}{me^2}\Big)+0.117\Big] \quad (7.7)$$

$$=\frac{1}{2\pi^4}e^4m^2p_F(1-\ln 2)\ln\Big(\frac{\alpha p_F}{me^2}\Big)+\frac{1}{2\pi^4}e^4m^2p_F(0.117). \quad (7.8)$$

Thus, the anomalous correction is quite comparable to the correlation correction.

[23] Note that since here we pick the Hartree approximation as our zero-order theory, fewer anomalous terms appear than in the usual case in which the completely noninteracting system is the zero-order theory. Diagrams 2 (i–k) are already included in the above equations because our zero-order propagator is corrected for the Hartree potential to all orders.

VIII. COMMENTS

By means of the rather complicated mathematical formalism of many-particle perturbation theory we have shown that Lewis' procedure, which is based on simple but sound physical reasoning, is indeed correct in the case where inhomogeneity effects are small. The actual calculation of correlation corrections in this limit is reduced to the case of a homogeneous electron gas for which several calculations already exist.

The basic physical fact that must be stressed is that the local Fermi momentum in this model is a function of the interaction strength, and one must be careful in applying a form of perturbation theory which is based on the adiabatic assumption.

We have left unanswered several important questions. First, we have not given an explicit expression for $E_c(p_F)$ which is valid over the whole range of densities encountered in an atom. Because of the poor convergence of perturbation theory at intermediate densities, the best one can do at present is to introduce a formula, as Lewis did, which interpolates between the exact high-density result of Gell-Mann and Brueckner and the accurate low-density result of Wigner.[4]

Secondly, we have not assessed the relative numerical importance of the anomalous terms although we have shown that they are of the same order in e^2 as the correlation terms. Tomishima, whose procedure is equivalent to Lewis', gives some numerical results which show that $n(\mathbf{R})$ is quite close to that predicted by the simple Thomas-Fermi theory. Baraff gives no numerical results so that we cannot compare the two methods numerically.

Thirdly, we have treated the inhomogeneity corrections only in the Hartree limit. These corrections are generally small except near the edge of the atom. Where they are important, the interaction effects beyond the Hartree approximation should be investigated. On the other hand, the inhomogeneity corrections to the total energy and equation of state are usually small.

The introduction of finite temperature effects in our formalism is straightforward, but quite tedious and numerically difficult when correlation effects and inhomogeneity corrections are taken into account. In the Hartree-Fock limit with no inhomogeneity corrections our procedure leads to the theory of Feynman, Metropolis, and Teller.[24]

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[24] R. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949).