Inhomogeneous Electron Gas*

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This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\to\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

INTRODUCTION

DURING the last decade there has been considerable progress in understanding the properties of a homogeneous interacting electron gas.[1] The point of view has been, in general, to regard the electrons as similar to a collection of noninteracting particles with the important additional concept of collective excitations.

On the other hand, there has been in existence since the 1920's a different approach, represented by the Thomas-Fermi method[2] and its refinements, in which the electronic density $n(\mathbf{r})$ plays a central role and in which the system of electrons is pictured more like a classical liquid. This approach has been useful, up to now, for simple though crude descriptions of inhomogeneous systems like atoms and impurities in metals.

Lately there have been also some important advances along this second line of approach, such as the work of Kompaneets and Pavlovskii,[3] Kirzhnits,[4] Lewis,[5] Baraff and Borowitz,[6] Baraff,[7] and DuBois and Kivelson.[8] The present paper represents a contribution in the same area.

In Part I, we develop an exact formal variational principle for the ground-state energy, in which the density $n(\mathbf{r})$ is the variable function. Into this principle enters a universal functional $F[n(\mathbf{r})]$, which applies to all electronic systems in their ground state no matter what the external potential is. The main objective of theoretical considerations is a description of this functional. Once known, it is relatively easy to determine the ground-state energy in a given external potential.

In Part II, we obtain an expression for $F[n]$ when n deviates only slightly from uniformity, i.e., $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, with $\tilde{n}/n_0\to 0$. In this case $F[n]$ is entirely expressible in terms of the exact ground-state energy and the exact electronic polarizability $\alpha(q)$ of a *uniform* electron gas. This procedure will describe correctly the long-range Friedel charge oscillations[9] set up by a localized perturbation. All previous refinements of the Thomas-Fermi method have failed to include these.

In Part III we consider the case of a slowly varying, but *not* necessarily almost constant density, $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$, $r_0\to\infty$. For this case we derive an expansion of $F[n]$ in successive orders of r_0^{-1} or, equivalently of the gradient operator ∇ acting on $n(\mathbf{r})$. The expansion coefficients are again expressible in terms of the exact ground-state energy and the exact linear, quadratic, etc., electric response functions of a uniform electron gas to an external potential $v(\mathbf{r})$. In this way we recover, quite simply, all previously developed refinements of the Thomas-Fermi method and are able to carry them somewhat further. Comparison of this case with the nearly uniform one, discussed in Part II, also reveals why the gradient expansion is intrinsically incapable of properly describing the Friedel oscillations or the radial oscillations of the electronic density in an atom which reflect the electronic shell structure. A partial summation of the gradient expansion can be carried out (Sec. III.4), but its usefulness has not yet been tested.

I. EXACT GENERAL FORMULATION

1. The Density as Basic Variable

We shall be considering a collection of an arbitrary number of electrons, enclosed in a large box and moving

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[7] G. A. Baraff, Phys. Rev. **123**, 2087 (1961).
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[9] J. Friedel, Phil. Mag. **43**, 153 (1952).

under the influence of an external potential $v(\mathbf{r})$ and the mutual Coulomb repulsion. The Hamiltonian has the form

$$H=T+V+U, \tag{1}$$

where[10]

$$T\equiv-\frac{1}{2}\int \nabla\psi^*(\mathbf{r})\nabla\psi(\mathbf{r})d\mathbf{r}, \tag{2}$$

$$V\equiv\int v(\mathbf{r})\psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}, \tag{3}$$

$$U=\frac{1}{2}\int\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi^*(\mathbf{r})\psi^*(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})d\mathbf{r}d\mathbf{r}'. \tag{4}$$

We shall in all that follows assume for simplicity that we are only dealing with situations in which the ground state is nondegenerate. We denote the electronic density in the ground state Ψ by

$$n(\mathbf{r})\equiv(\Psi,\psi^*(\mathbf{r})\psi(\mathbf{r})\Psi), \tag{5}$$

which is clearly a functional of $v(\mathbf{r})$.

We shall now show that conversely $v(\mathbf{r})$ is a unique functional of $n(\mathbf{r})$, apart from a trivial additive constant.

The proof proceeds by *reductio ad absurdum*. Assume that another potential $v'(\mathbf{r})$, with ground state Ψ' gives rise to the *same* density $n(\mathbf{r})$. Now clearly [unless $v'(\mathbf{r})-v(\mathbf{r})=\text{const}$] Ψ' cannot be equal to Ψ since they satisfy different Schrödinger equations. Hence, if we denote the Hamiltonian and ground-state energies associated with Ψ and Ψ' by H, H' and E, E', we have by the minimal property of the ground state,

$$E'=(\Psi',H'\Psi')<(\Psi,H'\Psi)=(\Psi,(H+V'-V)\Psi),$$

so that

$$E'<E+\int[v'(\mathbf{r})-v(\mathbf{r})]n(\mathbf{r})d\mathbf{r}. \tag{6}$$

Interchanging primed and unprimed quantities, we find in exactly the same way that

$$E<E'+\int[v(\mathbf{r})-v'(\mathbf{r})]n(\mathbf{r})d\mathbf{r}. \tag{7}$$

Addition of (6) and (7) leads to the inconsistency

$$E+E'<E+E'. \tag{8}$$

Thus $v(\mathbf{r})$ is (to within a constant) a unique functional of $n(\mathbf{r})$; since, in turn, $v(\mathbf{r})$ fixes H we see that the full many-particle ground state is a unique functional of $n(\mathbf{r})$.

2. The Variational Principle

Since Ψ is a functional of $n(\mathbf{r})$, so is evidently the kinetic and interaction energy. We therefore define

$$F[n(\mathbf{r})]\equiv(\Psi,(T+U)\Psi), \tag{9}$$

where $F[n]$ is a universal functional, valid for any number of particles[11] and *any* external potential. This functional plays a central role in the present paper.

With its aid we define, for a given potential $v(\mathbf{r})$, the energy functional

$$E_v[n]\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n]. \tag{10}$$

Clearly, for the correct $n(\mathbf{r})$, $E_v[n]$ equals the ground-state energy E.

We shall now show that $E_v[n]$ assumes its minimum value for the correct $n(\mathbf{r})$, if the admissible functions are restricted by the condition

$$N[n]\equiv\int n(\mathbf{r})d\mathbf{r}=N. \tag{11}$$

It is well known that for a system of N particles, the energy functional of Ψ'

$$\mathcal{E}_v[\Psi']\equiv(\Psi',V\Psi')+(\Psi',(T+U)\Psi') \tag{12}$$

has a minimum at the correct ground state Ψ, relative to arbitrary variations of Ψ' in which the number of particles is kept constant. In particular, let Ψ' be the ground state associated with a different external potential $v'(\mathbf{r})$. Then, by (12) and (9)

$$\begin{aligned}\mathcal{E}_v[\Psi']&=\int v(\mathbf{r})n'(\mathbf{r})d\mathbf{r}+F[n'],\\ &>\mathcal{E}_v[\Psi]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n].\end{aligned} \tag{13}$$

Thus the minimal property of (10) is established relative to all density functions $n'(\mathbf{r})$ associated with some other external potential $v'(\mathbf{r})$.[12]

If $F[n]$ were a known and sufficiently simple functional of n, the problem of determining the ground-state energy and density in a given external potential would be rather easy since it requires merely the minimization of a functional of the three-dimensional density function. The major part of the complexities of the many-electron problems are associated with the determination of the universal functional $F[n]$.

3. Transformation of the Functional $F[n]$

Because of the long range of the Coulomb interaction, it is for most purposes convenient to separate out from

[10] Atomic units are used.

[11] This is obvious since the number of particles is itself a simple functional of $n(\mathbf{r})$.

[12] We cannot prove whether an arbitrary positive density distribution $n'(\mathbf{r})$, which satisfies the condition $\int n'(\mathbf{r})d\mathbf{r}=\text{integer}$, can be realized by *some* external potential $v'(\mathbf{r})$. Clearly, to first order in $\tilde{n}(\mathbf{r})$, any distribution of the form $n'(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$ can be so realized and we believe that in fact all, except some pathological distributions, can be realized.

$F[n]$ the classical Coulomb energy and write

$$F[n]=\frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+G[n], \tag{14}$$

so that $E_v[n]$ becomes

$$E_v[n]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+G[n], \tag{15}$$

where $G[n]$ is a universal functional like $F[n]$.

Now from the definition of $F[n]$, Eq. (9), and $G[n]$, Eq. (14), we see that

$$G[n]=\frac{1}{2}\int\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}n_1(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}d\mathbf{r}+\frac{1}{2}\int\frac{C_2(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{16}$$

Here $n_1(\mathbf{r},\mathbf{r}')$ is the one-particle density matrix; and $C_2(\mathbf{r},\mathbf{r}')$ is the two-particle correlation function defined in terms of the one- and two-particle density matrices as

$$C_2(\mathbf{r},\mathbf{r}')=n_2(\mathbf{r},\mathbf{r}';\mathbf{r},\mathbf{r}')-n_1(\mathbf{r},\mathbf{r})n_1(\mathbf{r}',\mathbf{r}'). \tag{17}$$

Of course $n_1(\mathbf{r},\mathbf{r})\equiv n(\mathbf{r})$.

From (16) we see that we can define an energy-density functional

$$g_{\mathbf{r}}[n]=\tfrac{1}{2}\nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}n_1(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}+\frac{1}{2}\int\frac{C_2(\mathbf{r}-\mathbf{r}'/2;\mathbf{r}+\mathbf{r}'/2)}{|\mathbf{r}'|}d\mathbf{r}' \tag{18}$$

such that

$$G[n]=\int g_{\mathbf{r}}[n]d\mathbf{r}. \tag{19}$$

The fact that $g_{\mathbf{r}}[n]$ is a functional of n follows of course from the fact that Ψ and hence n_1 and n_2 are.

It should be remarked, that while $G[n]$ is a unique functional of n, $g_{\mathbf{r}}[n]$ is of course not the only possible energy-density functional. Clearly the functionals

$$\bar{g}_{\mathbf{r}}[n]=g_{\mathbf{r}}[n]+\sum_{i=1}^{3}\frac{\partial}{\partial x_i}h_{\mathbf{r}}^{(i)}[n], \tag{20}$$

where the $h^{(i)}$ are entirely arbitrary, give equivalent results when used in conjunction with (19).

The following sections deal with $G[n]$ and $g_{\mathbf{r}}[n]$ in some simple cases.

II. THE GAS OF ALMOST CONSTANT DENSITY

1. Form of the Functionals $G[n]$ and $\bar{g}_r[n]$

We consider here a gas whose density has the form

$$n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r}), \tag{21}$$

with

$$\tilde{n}(\mathbf{r})/n_0\ll 1 \tag{22}$$

and

$$\int\tilde{n}(\mathbf{r})d\mathbf{r}=0. \tag{23}$$

Here we clearly must have a formal expansion of the following sort:

$$G[n]=G[n_0]+\int K(\mathbf{r}-\mathbf{r}')\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'+\int L(\mathbf{r},\mathbf{r}',\mathbf{r}'')\tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')\tilde{n}(\mathbf{r}'')d\mathbf{r}d\mathbf{r}'d\mathbf{r}''+\cdots. \tag{24}$$

In this equation there is no term linear in $\tilde{n}(\mathbf{r})$ since by translational invariance the coefficient of $\tilde{n}(\mathbf{r})$ would be independent of $\mathbf{r}$ leading to zero, by (23). The kernel appearing in the quadratic term is a functional of $|\mathbf{r}-\mathbf{r}'|$ only and may therefore be written as

$$K(\mathbf{r}-\mathbf{r}')=(1/\Omega)\sum_{\mathbf{q}}K(q)e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}. \tag{25}$$

The higher order terms will not be further discussed here.

One may also quite trivially introduce a density function

$$\bar{g}_{\mathbf{r}}[n]=g_0(n_0)+\int K(\mathbf{r}')\tilde{n}(\mathbf{r}+\tfrac{1}{2}\mathbf{r}')\tilde{n}(\mathbf{r}-\tfrac{1}{2}\mathbf{r}')d\mathbf{r}'+\cdots, \tag{26}$$

where $g_0(n_0)$ is the density function of a uniform gas of electron density n_0 (kinetic, exchange, and correlation energy).

2. Expression of the Kernel K in Terms of the Electronic Polarizability

We shall now see that the kernel K appearing in Eqs. (24) and (26) is completely and exactly expressible in terms of the electronic polarizability $\alpha(q)$. The latter is defined as follows: Consider an electron gas of mean density n_0 in a background of uniform charge plus a small additional positive external-charge density

$$n_{\text{ext}}(\mathbf{r})=(\lambda/\Omega)\sum a(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}}. \tag{27}$$

Write the electronic density, to first order in λ, as

$$n(\mathbf{r})=n_0+(\lambda/\Omega)\sum b_1(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}}. \tag{28}$$

Then

$$\alpha(q)\equiv b_1(\mathbf{q})/a(\mathbf{q}). \tag{29}$$

Let us now define the operator

$$\rho_{\mathbf{q}}\equiv\sum_{\mathbf{k}}c_{\mathbf{k}-\mathbf{q}}{}^{*}c_{\mathbf{k}}, \tag{30}$$

where $c_{\mathbf{k}}{}^{*}$, $c_{\mathbf{k}}$ are the usual creation and annihilation operators. Then, by first-order perturbation theory,

$$b_1(\mathbf{q})=-(8\pi)\frac{a(q)}{q^2}\sum_{n}\frac{(0|\rho_{\mathbf{q}}|n)(n|\rho_{-\mathbf{q}}|0)}{E_0-E_n}, \tag{31}$$

so that

$$\alpha(q)=\frac{-8\pi}{q^2}\sum_n\frac{(0|\rho_q|n)(n|\rho_{-q}|0)}{E_0-E_n}. \tag{32}$$

Next we express the change of energy in terms of $\alpha(q)$. By second-order perturbation theory we have

$$\begin{aligned}E&=E_0+\frac{\lambda^2(4\pi)^2}{\Omega}\sum_{\mathbf{q}}\frac{|a(\mathbf{q})|^2}{q^4}\sum_n\frac{(0|\rho_q|n)(n|\rho_{-q}|0)}{E_0-E_n},\\&=E_0-\frac{\lambda^2 2\pi}{\Omega}\sum_{\mathbf{q}}\frac{|a(\mathbf{q})|^2}{q^2}\alpha(q),\\&=E_0-\frac{\lambda^2 2\pi}{\Omega}\sum_{\mathbf{q}}\frac{|b_1(\mathbf{q})|^2}{\alpha(q)q^2}.\end{aligned}\tag{33}$$

On the other hand, combining Eqs. (15), (24), (25), and (28) gives

$$\begin{aligned}E&=\int v(\mathbf{r})n(\mathbf{r})+\frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+G[n]\\&=E_0-\frac{\lambda^2 4\pi}{\Omega}\sum\frac{|b_1(\mathbf{q})|^2}{\alpha(q)q^2}+\frac{\lambda^2 2\pi}{\Omega}\sum\frac{|b_1(\mathbf{q})|^2}{q^2}\\&\qquad+\frac{\lambda^3}{\Omega}\sum K(\mathbf{q})|b_1(\mathbf{q})|^2.\end{aligned}\tag{34}$$

Comparison of Eqs. (33) and (34) gives

$$K(q)=\frac{2\pi}{q^2}\left[\frac{1}{\alpha(q)}-1\right]. \tag{35}$$

Equivalently, in terms of the dielectric constant,

$$\epsilon(q)=\frac{1}{1-\alpha(q)}, \tag{36}$$

we may write

$$K(q)=\frac{2\pi}{q^2}\frac{1}{\epsilon(q)-1}. \tag{37}$$

3. The Nature of the Kernel K

The polarizability $\alpha(q)$ has the following properties, as function of q (see Fig. 1)

$$q\to 0: \quad \alpha(q)=1+c_2q^2+c_4q^4+\cdots; \tag{38}$$

$$q\to 2k_F: \quad d\alpha/dq\to-\infty; \tag{39}$$

$$q\to\infty: \quad \alpha(q)\to \text{const}/q^4. \tag{40}$$

These general properties are exemplified by the random-phase approximation in which

$$\alpha(q)=[1+(q^2/k_T^2)S(q)]^{-1} \tag{41}$$

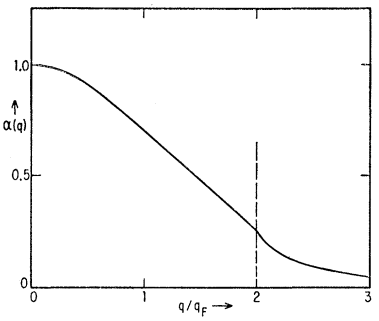

FIG. 1. Behavior of the electronic polarizability $\alpha(q)$, as function of q (electronic density $=4\times10^{23}$ cm^{-3}).

where k_T is the Thomas-Fermi screening constant,

$$k_T\equiv(4k_F)^{1/2} \tag{42}$$

and

$$S(q)\equiv\left[\tfrac{1}{2}+\frac{k_F}{2q}\left(1-\frac{q^2}{4k_F2}\right)\ln\left|\frac{q+2k_F}{q-2k_F}\right|\right]^{-1}. \tag{43}$$

This gives for $K(q)$, by (35),

$$q\to 0: \quad K(q)=2\pi[-c_2+(c_2^2-c_4)q^2+\cdots]; \tag{44}$$

$$q\to 2k_F: \quad dK/dq\to+\infty; \tag{45}$$

$$q\to\infty: \quad K(q)\to\text{const}\times q^2. \tag{46}$$

(See Fig. 2.)

The power-series expansion of $K(q)$, (43), leads to

$$K(\mathbf{r})=2\pi[-c_2+(c_2^2-c_4)\nabla^2+\cdots]\delta(\mathbf{r}), \tag{47}$$

which in turn gives

$$\begin{aligned}G[n]=G[n_0]+2\pi\Big[&-c_2\int\tilde{n}(\mathbf{r})^2d\mathbf{r}\\&+(c_2^2-c_4)\int|\nabla\tilde{n}(\mathbf{r})|^2d\mathbf{r}+\cdots\Big],\end{aligned}\tag{48}$$

i.e., a gradient expansion.

At this point an important remark must be made. One of the most significant features of $K(q)$ is its singularity at $q=2k_F$. This is responsible for the long-range Friedel oscillations[13] in $K(\mathbf{r})$,

$$r\to\infty: \quad K(r)\sim\text{const}\cos(2k_Fr+\delta)/r^3. \tag{49}$$

These obviously lie outside the framework of the power-series expansion (44) of $K(q)$ and hence outside the gradient expansion (49) of $G[n]$. This explains why neither the original Thomas-Fermi method [which for the present system reduces to keeping only the first term in (44)], nor its generalizations by the addition of gradient terms, have correctly yielded wave-mechanical density oscillations, such as the density oscillations in atoms which correspond to shell structure, or the Friedel oscillations in alloys which are of the same general origin.

[13] J. S. Langer and S. H. Vosko, Phys. Chem. Solids **12**, 196 (1960).

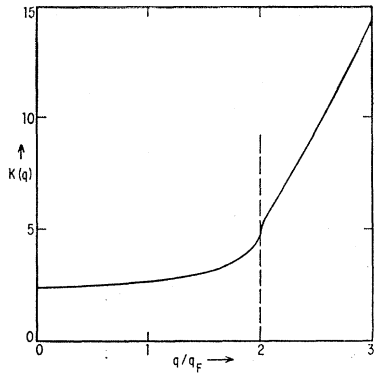

FIG. 2. Behavior of the kernel $K(q)$, as a function of q (electronic density $=4\times10^{23}$ cm^{-3}).

III. THE GAS OF SLOWLY VARYING DENSITY

1. The Thomas-Fermi Equation

For a first orientation we shall derive, from our general variational principle, the elementary Thomas-Fermi equation. For this purpose, we use the functional (18) and in (16) we neglect exchange and correlation effects, thus setting $C_2=0$. We approximate the kinetic-energy term by its form for a free-electron gas, i.e.,

$$g_r[n]=\tfrac{3}{10}[k_F(n)]^2 n, \tag{50}$$

where the Fermi momentum k_F is given by

$$k_F(n)=(3\pi^2 n)^{1/3}. \tag{51}$$

This results in

$$E_v[n]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' +\tfrac{3}{10}(3\pi^2)^{2/3}\int[n(\mathbf{r})]^{5/3}d\mathbf{r}. \tag{52}$$

To determine $n(\mathbf{r})$ we now set

$$\delta\left\{E_v[n]-\mu\int n(\mathbf{r})d\mathbf{r}\right\}=0, \tag{53}$$

where μ is a Lagrange parameter. This results in the equation

$$v(\mathbf{r})+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\tfrac{1}{2}(3\pi^2)^{2/3}[n(\mathbf{r})]^{2/3}-\mu=0. \tag{54}$$

If we now introduce the "internal" potential

$$v_i(\mathbf{r})\equiv\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{55}$$

(54) is equivalent to the pair of equations

$$n(\mathbf{r})=(1/3\pi^2)\{2[\mu-v(\mathbf{r})-v_i(\mathbf{r})]\}^{3/2}, \tag{56}$$

and

$$\nabla^2 v_i(\mathbf{r})=-4\pi n(\mathbf{r}). \tag{57}$$

From (56) and (57) we can eliminate $n(\mathbf{r})$ and arrive at the Thomas-Fermi equation

$$\nabla^2 v_i(\mathbf{r})=(-2^{7/2}/3\pi)[\mu-v(\mathbf{r})-v_i(\mathbf{r})]^{3/2}. \tag{58}$$

2. The Gradient Expansion

It is well known that one condition for the validity of the Thomas-Fermi equation is that $n(\mathbf{r})$ must be a slowly varying function of $\mathbf{r}$. This suggests study of the functional $G[n]$, where n has the form

$$n(\mathbf{r})=\varphi(\mathbf{r}/r_0), \tag{59}$$

with

$$r_0\to\infty. \tag{60}$$

It is obvious that this is quite a different class of systems than that considered in Part II ($n=n_0+\tilde{n}$, $\tilde{n}/n_0\ll1$), since now we shall allow φ to have substantial variations. On the other hand, whereas in Part II, $\tilde{n}$ could contain arbitrarily short wavelengths, these are here ruled out as r_0 becomes large.

We now make the basic assumption that for large r_0, the partial energy density $g_r[n]$ may be expanded in the form

$$g_r[n]=g_0(n(\mathbf{r}))+\sum_{i=1}^{3}g_i(n(\mathbf{r}))\cdot\nabla_i n(\mathbf{r}) +\sum_{i,j=1}^{3}[g_{i,j}^{(1,1)}(n(\mathbf{r}))\cdot\nabla_i n(r)\nabla_j n(\mathbf{r}) +g_{i,j}^{(2)}(n(\mathbf{r}))\cdot\nabla_i\nabla_j n(\mathbf{r})]+\cdots. \tag{61}$$

Here successive terms correspond to successive negative powers of the scale parameter r_0. Quantities like $g_0(n(\mathbf{r}))$, $g_i(n(\mathbf{r}))$ etc., are functions (not functionals) of $n(\mathbf{r})$. No general proof of the existence of such an expansion is known to us, although it can be formally verified in special cases, e.g., when $G[n(\mathbf{r})]$ can be expanded in powers of $[n(\mathbf{r})-n_0]$. At the same time, we know that, for a finite r_0, the series does not strictly converge (see the discussion at the end of Sec. II.3), but we may expect it to be useful (in the sense of asymptotic convergence) for sufficiently large values of r_0.

Now a good deal of progress can be made, using only the fact that $g_r[n]$ is a universal functional of n, independent of $v(\mathbf{r})$. This requires $g_r[n]$ to be invariant under rotations about $\mathbf{r}$. The coefficients $g_{i,j},\cdots(n(\mathbf{r}))$, being functions of the scalar n, are of course invariant under rotations. Hence one finds by elementary considerations that $g_r[n]$ must have the form

$$g_r[n]=g_0(n)+[g_2^{(a)}(n)\nabla^2 n+g_2^{(b)}(n)(\nabla n\cdot\nabla n)] +\text{terms of order }\nabla_i^4. \tag{62}$$

A further simplification results from the fact that we may eliminate from $g_r[n]$ an arbitrary divergence $\sum_i\nabla_i h_r^i[n]$ (see the end of Sec. I.3). It is then elementary to show that $g_r[n]$ may be replaced by

$$\bar{g}_r[n]=g_0(n)+g_2^{(2)}(n)\nabla n\cdot\nabla n +\{g_4^{(2)}(n)(\nabla^2 n)(\nabla^2 n)+g_4^{(3)}(n)(\nabla^2 n)(\nabla n\cdot\nabla n) +g_4^{(4)}(n)(\nabla n\cdot\nabla n)^2\}+O(\nabla_i^6). \tag{63}$$

Here the subscripts refer to the number of gradient operators (or the order in $1/r_0$) and the superscripts to the number of times that n appears to the right of $g_\mu^{(\nu)}(n)$.

It may be worth recalling that while $\bar{g}_r[n]$ is an admissible density function in the sense that

$$G[n]=\int \bar{g}_r[n]d\mathbf{r}, \tag{64}$$

it differs from the energy density function $g_r[n]$, Eq. (18), by a divergence.

3. Identification of the Coefficients of the Gradient Expansion

We shall now express the coefficients $g_\mu^{(\nu)}(n)$ appearing in Eq. (63) in terms of the expansion coefficients, in powers of $\mathbf{q}$, of the electronic polarizability $\alpha(q)$, and similar higher order, nonlinear, response functions.

We do this by applying our general expression (63) to the case of a nearly uniform electron gas, considered already in Sec. II.2. We go, however, beyond (28) and write

$$n(r)=n_0+\frac{\lambda}{\Omega}\sum b_1(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{r}}+\frac{\lambda^2}{\Omega}\sum b_2(q)e^{-i\mathbf{q}\cdot r}+\cdots. \tag{65}$$

The linear- and second-, third-, etc., order response functions are then defined by the relations

$$\begin{aligned} b_1(\mathbf{q})&=\alpha(q)a(\mathbf{q}),\\ b_2(\mathbf{q})&=\sum_{\mathbf{q}_1+\mathbf{q}_2=\mathbf{q}}\alpha(\mathbf{q}_1,\mathbf{q}_2)a(\mathbf{q}_1)a(\mathbf{q}_2),\\ &\text{etc.}\end{aligned} \tag{66}$$

Now let us compare these expressions with what one obtains with the use of (63). We require that

$$\frac{\delta}{\delta n}\left\{E_v[n]-\mu\int n(\mathbf{r})d\mathbf{r}\right\}=0. \tag{67}$$

This gives

$$\begin{aligned} &v(\mathbf{r})+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+g_0'-g_2^{(2)\prime}(\nabla n)^2\\ &-2g_2^{(2)}\nabla^2 n+3g_4^{(2)\prime}(\nabla^2 n)^2+2g_4^{(2)\prime\prime}(\nabla n)^2\nabla^2 n\\ &+2g_4^{(2)\prime}\nabla n\cdot\nabla(\nabla^2 n)+2g_4^{(2)}(\nabla^2\nabla^2 n)\\ &+g_4^{(3)\prime\prime}(\nabla n)^4+2g_4^{(3)}\nabla n\cdot\nabla(\nabla n)^2\\ &+g_4^{(3)}(\nabla^2(\nabla n)^2-2\nabla n\cdot\nabla(\nabla^2 n)-2(\nabla^2 n)^2)\\ &-3g_4(4)'(\nabla n)^4-4g_4^{(4)}\nabla^2 n(\nabla n)^2-4g_4^{(4)}\nabla n\cdot\nabla(\nabla n)^2\\ &+\cdots-\mu=0. \end{aligned} \tag{68}$$

Now let us set

$$v(\mathbf{r})=\frac{\lambda 4\pi}{\Omega}\sum_{\mathbf{q}}\frac{a(\mathbf{q})}{q^2}e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{69}$$

$$n=n_0+\frac{1}{\Omega}\sum_{\mathbf{q}}[\lambda b_1(\mathbf{q})+\lambda^2 b_2(\mathbf{q})+\cdots]e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{70}$$

$$\mu=\mu_0+\lambda\mu_1+\lambda^2\mu_2+\cdots. \tag{71}$$

Collecting terms of order λ^0, λ^1, λ^2, we find

$$g_0'(n_0)-\mu_0=0, \tag{72}$$

$$\begin{aligned} &-\frac{4\pi}{q^2}a(\mathbf{q})+\left\{\frac{4\pi}{q^2}+g_0''+2g_2^{(2)}q^2\right.\\ &\left.+2g_4^{(2)}q^4+\cdots\right\}b_1(\mathbf{q})=0, \end{aligned} \tag{73}$$

$$\mathbf{q}\neq 0,$$

giving

$$b_1(\mathbf{q})=\left\{1+\left(-\frac{g_0''}{4\pi}\right)q^2+\left[\left(\frac{g_0''}{4\pi}\right)^2-\frac{g_2^{(2)}}{2\pi}\right]q^4+\cdots\right\}a(\mathbf{q}). \tag{74}$$

Also clearly

$$\mu_1=0.$$

Similarly, we obtain

$$b_2(\mathbf{q})=\sum_{q'}\left\{\frac{g_0'''}{8\pi}q^2+\cdots\right\}a(\mathbf{q}')a(\mathbf{q}-\mathbf{q}'). \tag{75}$$

If we now expand the response functions in powers of q,

$$\alpha(q)=1+c_2q^2+c_4q^4+\cdots. \tag{76}$$

$$\alpha(\mathbf{q},\mathbf{q}')=\sum_{m,n}\sum_{i,j}c_{mn}{}^{ij}q_i{}^m q_j{}^n, \tag{77}$$

we can identify the functions $g_\mu^{(\nu)}$. Thus

$$g_0''/4\pi=-c_2, \tag{78}$$

$$g_2^{(2)}/4\pi=\tfrac{1}{2}(-c_4+c_2^2), \tag{79}$$

$$g_4^{(2)}/4\pi=\tfrac{1}{2}(-c_6+2c_2c_4-c_2^3). \tag{80}$$

Similarly all other coefficients $g_\mu^{(2)}(n)$ can be expressed in terms of the expansion coefficients c_n of the linear polarizability $\alpha(\mathbf{q})$ of an electron gas of density n.

In an analogous manner we can express all $g_\mu^{(3)}$ in terms of $\alpha(\mathbf{q}_1)$ and $\alpha(\mathbf{q}_1,\mathbf{q}_2)$; and generally $g_\mu^{(\nu)}$ in terms of $\alpha(\mathbf{q}_1)$, $\cdots\alpha(\mathbf{q}_1,\mathbf{q}_2,\cdots\mathbf{q}_{\mu-1})$.

On dimensional grounds we can see from (63) that the gradient expansion requires

$$|\nabla n|/n\ll k_F(n) \tag{81}$$

and

$$|\nabla_i\nabla_j n|/|\nabla n|\ll k_F(n). \tag{82}$$

Both of these conditions are necessary. For while (81) would admit the case of a nearly uniform gas with a small but short-wavelength nonuniformity, this and similar cases are excluded by (82), as they must be.

4. Partial Summation of Gradient Expansion

In the preceding section we have expressed the coefficient $g_\mu^{(2)}$ in terms of the expansion coefficient c_i of the polarizability $\alpha(q)$, Eq. (76). However, we may apply the expression (63) to the special case of the gas of almost constant density, discussed in Part II. This shows that the leading term $g_0(n)$ and the subsequent subseries involving coefficients $g_\mu^{(2)}(n)$ may be summed to yield

$$\bar{g}_r[n]=g_0(n(\mathbf{r}))+\int K_{n(\mathbf{r})}(\mathbf{r}')[n(\mathbf{r}+\tfrac{1}{2}\mathbf{r}')-n(\mathbf{r})]\times[n(\mathbf{r}-\tfrac{1}{2}\mathbf{r}')-n(\mathbf{r})]d\mathbf{r}'+\cdots \quad (83)$$

apart possibly from terms of the form of a divergence or of higher order in the superscript ν of $g_n^{(\nu)}$. Here

$$K_{n(\mathbf{r})}(\mathbf{r}')=\frac{1}{\Omega}\sum_{\mathbf{q}}\frac{2\pi}{q^2}\left(\frac{1}{\epsilon_{n(\mathbf{r})}(\mathbf{q})}\right)\cdot e^{-i\mathbf{q}\cdot\mathbf{r}'}. \quad (84)$$

The form (83) of $\bar{g}_r$ has the merit of being exact in both limiting cases where either the density has everywhere nearly the same value (see Part II) or is slowly varying. Its quantitative value for calculating the electronic structure of actual atomic, molecular, or solid-state systems is at present uncertain but is being examined. However, it is already clear that if applied to an atom it will, unlike the simple Thomas-Fermi theory, yield: (1) a finite density at the nucleus, and (2) oscillations in the charge density corresponding to shell structure.

5. Approximate Expressions for the Coefficients of the Gradient Expansion

In the previous section we have expressed the coefficients $g_\mu^{(\nu)}$ appearing in the gradient expansion (63) in terms of properties of the uniform electron gas. We now collect some results of existing calculations referring to the uniform electron gas which are useful for our present purposes.

a. $g_0(n)$

This is the sum of the kinetic+exchange+correlation energy density of a uniform gas of density n. Here one has available the high-density expansion of Gell-Mann and Brueckner[14];

$$g_0(n)=\left\{\frac{2.21}{r_s^2}-\frac{0.916}{r_s}+0.062\ln r_s-0.096+O(r_s)\right\}n, \quad (85)$$

where r_s is the radius of the Wigner-Seitz sphere defined by

$$\tfrac{4}{3}\pi r_s^3=1/n. \quad (86)$$

This expression is believed to be reasonably accurate only for $r_s\lesssim 1$. At lower densities, such as occur in metals ($2\lesssim r_s\lesssim 5$), various approximate expressions have been proposed. One is due to Wigner[15]

$$g_0(n)\sim\left\{\frac{2.21}{r_s^2}-\frac{0.916}{r_s}-\frac{0.88}{r_s+7.8}\right\}n. \quad (87)$$

Other approximations are due to Hubbard,[16] Nozières and Pines,[17] and Gaskell.[18]

b. $g_\mu^{(2)}(n)$

These coefficients are all determined in terms of the electronic polarizability, $\alpha(q)$. For this latter quantity there is available, at present, a random-phase expression, Eq. (41), which gives

$$\alpha(q)=\frac{2\pi}{k_T^2}\left[1+\frac{q^2}{k_T^2}S(q)\right]^{-1} \quad (88)$$

and

$$\frac{g_2^{(2)}}{4\pi}=\frac{1}{24}\frac{1}{k_T^2k_F^2}, \quad (89)$$

$$\frac{g_4^{(2)}}{4\pi}=\frac{1}{180}\frac{1}{k_T^2k_F^4}. \quad (90)$$

Inclusion of the first of these in the energy expression agrees with a correction to the Thomas-Fermi energy functional derived by Kompaneets and Pavlovskii.[3]

An expression for $\alpha(q)$, allowing in an approximate manner for exchange effects has been proposed by Hubbard.[16] It is

$$\alpha(q)=\left[\left(1+\frac{1}{2}\frac{q^2}{q^2+k_F^2}\right)+\frac{q^2}{k_T^2}S(q)\right]^{-1}, \quad (91)$$

where $S(q)$ is defined in Eq. (43). This form yields

$$\frac{g_2^{(2)}}{4\pi}=\frac{1}{24}\left(\frac{1}{k_T^2k_F^2}-\frac{6}{k_F^4}\right). \quad (92)$$

For typical metallic densities this has the opposite sign from the random-phase approximation expression (88). Thus we see that the lowest nonvanishing gradient correction to the Thomas-Fermi theory depends quite sensitively on refinements in the theory of the electronic polarizability, $\alpha(q)$.

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IV. CONCLUDING REMARKS

In the preceding sections we have developed a theory of the electronic ground state which is exact in two limiting cases: The case of a nearly constant density ($n=n_0+\tilde{n}(r)$, $\tilde{n}(r)/n_0 \ll 1$) and the case of a slowly varying density. Actual electronic systems do not belong to either of these two categories. The most promising formulation of the theory at present appears to be that obtained by partial summation of the gradient expansion (Sec. III.4). It has, however, not yet been tested in actual physical problems. But regardless of the outcome of this test, it is hoped that the considerations of this paper shed some new light on the problem of the inhomogeneous electron gas and may suggest further developments.

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Scattering of a High-Intensity, Low-Frequency Electromagnetic Wave by an Unbound Electron*

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"Thomson" scattering of a high-intensity, low-frequency, circularly-polarized electromagnetic wave by a free electron is considered. We find that by neglecting radiative corrections and pair effects, the Feynman-Dyson perturbation expansion is summable, and the sum can be analytically continued in the form of a sum of continued fractions. By imposing the boundary conditions that at $t=\pm\infty$ the photons and target electron propagate as free particles, we obtain results which differ from those reported by Brown and Kibble and by Goldman. In particular our results differ in two aspects. The first difference is in the kinematics; namely, we find no intensity-dependent frequency shift in the scattered photon. The second difference is in the dynamics; that is, we obtain a different expression for the scattering amplitude. Both of these changes originate in the choice of boundary conditions. Instead of treating the asymptotic radiation field classically, we choose our states as linear combinations of occupation-number states. Finally, contact is made with the results of Brown and Kibble and of Goldman using a mixed set of classical and quantum boundary values.

I. INTRODUCTION

THE advent of masers and lasers has stimulated a great deal of interest in the interaction of intense electromagnetic fields with matter. This activity has been focused on three different aspects of the subject. First, a great deal of attention has been devoted to the dynamics of production of high-intensity light.[1] A second area of concentration is the question of proper description of the electromagnetic radiation emanating from a laser; i.e., questions of coherence and correlation.[2] And finally, the problem of interaction of laser light with matter has attracted considerable interest.[3] It is this latter question to which we are devoting ourselves in this paper.

The particular problem of immediate interest is the effect of the presence of the high-intensity field on the Compton (Thomson) scattering amplitude. Recall that the Thomson amplitude describes the scattering of a

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