

Background reading for Nicola Spaldin's  
lectures :-

Density functional theory for  
magnetic systems.

I will use the Kohn-Sham equations  
as my starting point - these notes  
describe their derivation. (It's not  
necessary to work through this booklet  
if you're happy to believe them  
without knowing how they're derived!)

THE THOMAS-FERMI APPROXIMATION

6, 1 (1957)

assume ①  $e^- - e^-$  interaction arises solely from the Coulomb interaction

$$E_{\text{int}}[n] = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

② K.E. is given by

$$T[n] = \int d\mathbf{r} t[n(\mathbf{r})]$$

where  $t[n]$  is the K.E. density for a system of noninteracting electrons with uniform density  $n(\mathbf{r})$  - A LOCAL APPROXIMATION  
This should be a good approximation if  $n(\mathbf{r})$  varies sufficiently slowly in space that an electron at point  $\mathbf{r}$  sees an essentially homogeneous medium with density  $n(\mathbf{r})$ .

From free  $e^-$  theory,

$$t[n] = 2 \frac{1}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_F} \frac{\hbar^2 k^2}{2m} d\mathbf{k}$$

and  $n = 2 \left(\frac{4\pi}{3}\right) \frac{k_F^3}{(2\pi)^3}$

so  $T[n] = C_k \int d\mathbf{r} [n(\mathbf{r})]^{5/3}$

where  $C_k = \frac{3\hbar^2 (3\pi^2)^{2/3}}{10m}$

∴ the energy functional,

$$E[n] = C_k \int d\underline{r} [n(\underline{r})]^{5/3} + \frac{e^2}{2} \int d\underline{r} \int d\underline{r}' \frac{n(\underline{r})n(\underline{r}')}{|\underline{r}-\underline{r}'|} + \int d\underline{r} n(\underline{r}) V_{\text{external}}(\underline{r}) \quad \textcircled{1}$$

(eg. e<sup>-</sup>-ion and ion-ion interactions)

③ for the ground state, the electron density minimizes the energy functional E[n], under the constraint

$$N = \int n(\underline{r}) d\underline{r} \quad \textcircled{2}$$

where N is the total number of e<sup>-</sup>s in the system

∴ by the method of Lagrange multipliers, the ground state e<sup>-</sup> density must satisfy the variational principle

$$\delta \{ E[n] - \mu_{TF} (\int n(\underline{r}) d\underline{r} - N) \} = 0$$

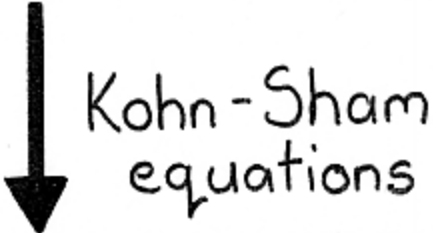
giving the Thomas-Fermi equation :-

$$\mu_{TF} = \frac{\delta E[n]}{\delta n(\underline{r})} = \frac{5}{3} C_k n(\underline{r})^{2/3} + V_{\text{ext}}(\underline{r}) + e^2 \int d\underline{r}' \frac{n(\underline{r}')}{|\underline{r}-\underline{r}'|} \quad \textcircled{3}$$

Eqn. ③ can be solved in conjunction with the constraint ②, + the resulting e<sup>-</sup> density inserted into ① to give the total energy.

Density Functional Theory

interacting many-electron system



system of non-interacting electrons

Hohenberg and Kohn (1964)

Kohn and Sham (1965)

# The Kohn-Sham Equations

single particle kinetic energy

Hartree potential

$$[T + V_{ei}(r) + V_H(r) + V_{xc}(r)] \psi_i(r) = \epsilon_i \psi_i(r)$$

Coulomb potential due to nuclei (use Pseudopotentials)

Exchange Correlation potential - use LDA.

where both  $V_H$ :

[also Vion-ion - calculate using an Ewald summation (see attached article)]

$$V_H(r) = e^2 \int \frac{\rho(r')}{|r - r'|} d^3r'$$

and  $V_{xc}$ :

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}$$

depend on the density:

$$\rho(r) = \sum_{occ} \psi_i^*(r) \psi_i(r)$$

solve KS eqns  $\rightarrow$  KS eigenvalues,  $\epsilon_i$   
 KS wavefunctions,  $\psi_i$   
 TRUE (within LDA) charge density,  

$$\rho(r) = \sum_{i \text{ occupied}} \psi_i^*(r) \psi_i(r)$$

then  $E_{TOT} = E_{KINETIC ENERGY} + E_{e-ION} + E_{Hartree e^-e^-} + E_{xc e^-e^-} + E_{ION-ION}$

$$= \sum_i \epsilon_i - \frac{1}{2} \int \rho(r) V_H(r) + \int \rho(r) [E_{xc}(r) - \mu_{xc}(r)] dr + E_{ION-ION}$$

$\nearrow$   
 sum over occupied  
 KS eigenvalues

$\underbrace{\hspace{10em}}$   
 subtract  $\frac{1}{2}$  the  
 Hartree energy  
 because you've  
 double  
 counted

$\underbrace{\hspace{10em}}$   
 $+ E_{ION-ION}$   
 summing over  $\epsilon_i$   
 gives  $\sum \mu_{xc}(r)$ ,  
 whereas we want  
 $\sum E_{xc}(r)$  - this is  
 the correction.



- The proofs of this follow - go through them once some time!

## DENSITY FUNCTIONAL FORMALISM

### References

- ① Hohenberg + Kohn PR 136, B 864 (1964)
- ② Kohn + Sham, PR 140, A 1133 (1965)
- ③ Schlüter + Sham, Physics Today, p.36, Feb. 1982

For an interacting inhomogeneous electron gas in a static potential  $v(r)$

- I) The ground state energy can be written as (a.u.s)

$$E[n] = \int v(r)n(r)dr + F[n]$$

charge density

where  $n(r)$  = density distribution  
 $F[n]$  is a universal functional of  $n(r)$  which doesn't depend on the potential

- II)  $E$  is a minimum for the correct  $n(r)$   
 $\Rightarrow$  variational principle
- III)  $n(r)$  can in principle be exactly obtained from the solution of an

associated one-body problem, whose effective one-body potential,  $V_{\text{eff}}[r, n(r)]$  is a unique functional of  $n(r)$ .

### Proof of (I)

- consider a collection of  $e^-$ 's moving in an external potential  $v(r)$

Coulomb repulsion is  $\frac{e^2}{r_{ij}}$

- then  $H = T + V + U$ 
  - KE  $\rightarrow T$
  - $e^- v(r)$   $\rightarrow V$
  - $e^- e^-$  interaction  $\rightarrow U$

- prove by contradiction

denote  $\Psi = \text{grd. state wavefn.}$

$$n(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle$$

number density operator

= ground state density (clearly a functional of  $v(r)$ )



now show that  $v(r)$  is a unique functional of  $n(r)$  :-

(by contradiction)

assume  $v'(r) \rightarrow \Psi' \rightarrow n'(r)$

with  $v'(r) \neq v(r)$  BUT  $n(r) = n'(r)$

(ie. assume the converse is true)

THEN  $\Psi' \neq \Psi$  because they satisfy different Schrodinger equations

$\Rightarrow E' = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle$   
 $= \langle \Psi | p^2 + v' - v | \Psi \rangle$

(ground state energy must be less than any other energies)

ie.  $E' < E + \int [v'(r) - v(r)] n(r) dr$

$\nearrow$   
 $\langle \Psi | H | \Psi \rangle$

similarly

$$E < E' + \int [v(r) - v'(r)] n'(r) dr$$

$$< E' + \int [v(r) - v'(r)] n(r) dr$$

(assuming  $n(r) = n'(r)$ )

adding eqns  $\Rightarrow$

$$E + E' < E + E' \Rightarrow \text{a contradiction}$$

ie. if we have a different potential we MUST have a different charge density

$\Rightarrow v(r)$  is a unique function of  $n(r)$

$$\Rightarrow E = \int v(r) n(r) dr + F[n]$$

because  $E = \langle \psi | T + V + U | \psi \rangle$   
↑ depends on ext. pot.  
↑ indep. of ext. pot.

$$= \langle \psi | V | \psi \rangle + \langle \psi | T + U | \psi \rangle$$

$\psi[v[n]]$

PROOF OF II - THE VARIATIONAL PRINCIPLE

For a given potential  $v(r)$ , the energy functional,

$$E_v [n(r)] = \int v(r)n(r)dr + F [n(r)]$$

We will show that  $E_v [n]$  assumes its minimum value for the correct  $n(r)$  if the admissible functions are restricted by the condition

$$N [n] = \int n(r)dr = N$$

It's well known that, for a system of  $N$  particles, the energy functional of  $\Psi'$ ,  $E_v [\Psi']$  has a minimum at the correct ground state  $\Psi$ , relative to arbitrary variations of  $\Psi'$  in which the number of particles is kept constant, i.e.

$$E_v [\Psi'] > E_v [\Psi]$$

BUT  $E_v [\Psi'] = \int v(r)n'(r)dr + F [n'] = E_v [n']$   
and  $E_v [\Psi] = \int v(r)n(r)dr + F [n] = E_v [n]$

$\therefore$  the minimum property of

$$E_v [n] = \int v(r)n(r)dr + F [n(r)]$$

is established relative to all density functions  $n'(r)$  associated with some OTHER external potential  $v'(r)$ .

Proof of (III) ( $\exists$  a set of self-consistent one-particle equations which exactly determine  $n(r)$ )

$$F[n] = \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + G[n]$$

ex-corr + K.E. of  $n$

so  $E_v[n] = \int v(r)n(r)dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + G[n]$

rewrite  $G[n] \equiv T_s[n] + E_{xc}[n]$

KE of a non-interacting system with the same  $n(r)$       Kohn-Sham exchange-correlation energy

now derive a set of self-consistent equations (the Kohn-Sham equations)



real system

non-interacting system  
- generates a trial density to start search

plug into expression for  $E_V[n']$  with TRUE  $V$

vary  $v' \rightarrow$  a set of  $n'$   $\xrightarrow{\delta}$   $E_V[n']$  to find minimum in  $E_V$   
- true density is at minimum in  $E_V[n']$

for the non-interacting system :-

$$\left[-\frac{1}{2}\nabla^2 + v'(r)\right]\phi_{i'}(r) = \epsilon_{i'}\phi_{i'}(r)$$

construct  $n'(r) = \sum_{i=1}^N |\phi_{i'}|^2$

lowest  $N$  occupied eigenstates

(this is the usual way of obtaining the charge density for a 1-body problem)

now  $T_S[n'] = \sum_i \epsilon_i - \int v'(r) n'(r) dr$

want to minimize  $T_S[n']$  interac<sup>n</sup>. with ext<sup>l</sup> pot<sup>l</sup>. due to charge

$$E_V[n'] = \sum_i \epsilon_i - \int v'(r) n'(r) dr + \int v(r) n'(r) dr$$

+  $\frac{1}{2} \iint \frac{n'(r) n'(r')}{|r-r'|} dr dr'$  ↖ Hartree term

+  $E_{xc}[n']$  ↖ we don't know th. term yet

we want to do variation in the functional space: take frat. derivatives:

$$\delta E_V[n] = \sum_{i=1}^n \delta \epsilon_i + \int \delta n'(r) \left\{ -v'(r) - \int \frac{\delta v'(r'')}{\delta n'(r')} n'(r'') dr'' + v(r) + \int \frac{n'(r'')}{|r''-r|} dr'' + \frac{\delta E_{xc}[n]}{\delta n(r)} \right\} dr'$$

(Hartree potential)

now  $\sum_i \delta \epsilon_i = \sum_i \langle \phi_i | \delta v | \phi_i \rangle$  (using 1st order P.T.)

$$= \sum_i \langle \phi_i | \delta v | \phi_i \rangle = \sum_i |\phi_i|^2 \delta v = \int \delta v(r') n'(r') dr'$$

$$= \int \delta n'(r) \int \frac{dv'(r') n'(r')}{\delta n'(r)} dr' dr \quad (\text{chain rule})$$

ie. term ① cancels with term ③ !

\* at the minimum,  $\delta E_V[n] = 0$

\* since  $\int$  is arbitrary, the integrand in  $\{ \}$  must = 0

$$\text{i.e., } v'(\underline{r}) = v(\underline{r}) + \int \frac{n'(\underline{r}') d\underline{r}'}{|\underline{r} - \underline{r}'|} + \frac{\delta E_{xc}}{\delta n'(\underline{r})}$$

to make progress, use:-

### Kohn-Sham Formalism

solve Schrödinger eqn:-

$$\left[ -\frac{1}{2} \nabla^2 + v(\underline{r}) + \int \frac{n(\underline{r}') d\underline{r}'}{|\underline{r} - \underline{r}'|} + \frac{\delta E_{xc}}{\delta n(\underline{r})} \right] \Phi_i = \epsilon_i \Phi_i(\underline{r})$$

with the condition  $n(\underline{r}) = \sum_i |\Phi_i|^2$

usually write  $\frac{\delta E_{xc}}{\delta n(\underline{r})} = \mu_{xc}[n; \underline{r}]$

N.B. ① formally exact!

②  $\mu_{xc}[n](\underline{r})$  is local (its not an integral operator)

Comments :-

- ① Rigorously,  $\epsilon_i$  are just parameters + are NOT strictly related to the electron excitation energies
- ②  $\phi_i$  are single-particle wavefn. which are meaningful only for determination of  $n(\epsilon)$
- ③ It can be shown that

$$\epsilon_i = \frac{\partial E}{\partial n_i}$$

↑ occupation # of  $i$ th orbital



# HOW TO CALCULATE $E_{xc}$ : THE LOCAL DENSITY APPROXIMATION (LDA)

## Approximations:-

① a local approx<sup>n</sup>

assume 
$$E_{xc}[n] = \int n(r) E_{xc}(n(r)) dr$$

②

assume  $E_{xc}(n(r))$  is the exchange-correlation energy per electron of a uniform interacting electron gas of the same density.

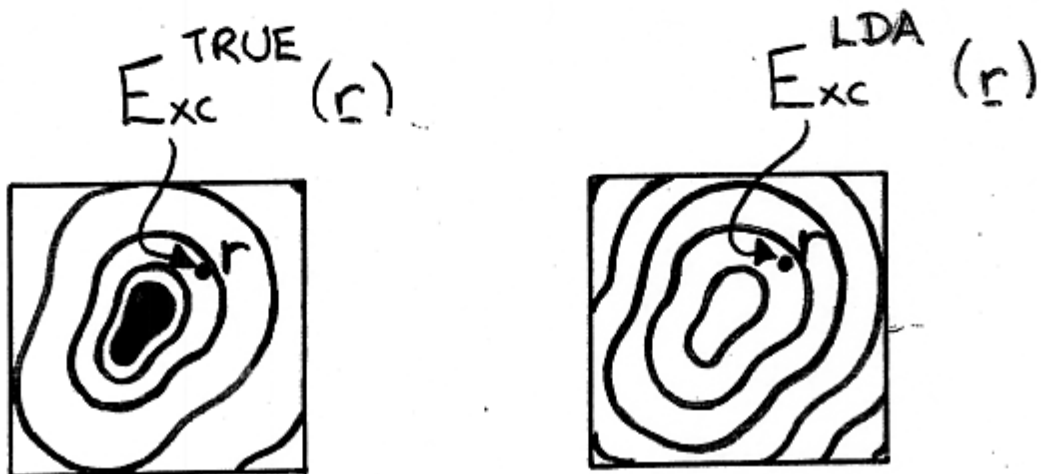
then 
$$V_{eff} = v(r) + \int \frac{n(r')}{|r-r'|} dr' + \mu_{xc}(n(r))$$

depends only on the density at the pt. we're looking at

and 
$$\mu_{xc}(n(r)) = \frac{d}{dn} (n E_{xc}(n))$$

# The Local Density Approximation (LDA)

- assumes that the exchange-correlation energy per electron at a point  $r$  in the electron gas is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as the electron gas at point  $r$ .



There are many ways of parameterizing the LDA exchange-correl<sup>n</sup> functional.

The Perdew-Zunger<sup>\*</sup> parameterization of the Ceperley-Alder<sup>†</sup> functional is widely used.

<sup>\*</sup> J.P. Perdew + A. Zunger, PRB 23, 5048 (1981).

<sup>†</sup> D.M. Ceperley + B.J. Alder, PRL 45, 566 (1980).

Ceperley + Alder calculated the "TRUE" energy of a uniform electron gas over a wide range of densities using quantum Monte Carlo. P+Z then provided a convenient parameterization which is easy to include in computer programs.

# Self-Consistent Equations Including Exchange and Correlation Effects\*

W. KOHN AND L. J. SHAM

*University of California, San Diego, La Jolla, California*

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of  $\frac{2}{3}$ .) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

## I. INTRODUCTION

IN recent years a great deal of attention has been given to the problem of a homogeneous gas of interacting electrons and its properties have been established with a considerable degree of confidence over a wide range of densities. Of course, such a homogeneous gas represents only a mathematical model, since in all real systems (atoms, molecules, solids, etc.) the electronic density is nonuniform.

It is then a matter of interest to see how properties of the homogeneous gas can be utilized in theoretical studies of inhomogeneous systems. The well-known methods of Thomas-Fermi<sup>1</sup> and the Slater<sup>2</sup> exchange hole are in this spirit. In the present paper we use the formalism of Hohenberg and Kohn<sup>3</sup> to carry this approach further and we obtain a set of self-consistent equations which include, in an approximate way, exchange and correlation effects. They require only a knowledge of the true chemical potential,  $\mu_h(n)$ , of a homogeneous interacting electron gas as a function of the density  $n$ .

We derive two alternative sets of equations [Eqs. (2.8) and (2.22)] which are analogous, respectively, to the conventional Hartree and Hartree-Fock equations, and, although they also include correlation effects, they are no more difficult to solve.

The local effective potentials in these equations are unique in a sense which is described in Sec. II. In particular, we find that the Slater exchange-hole potential, besides its omission of correlation effects, is too large by a factor of  $\frac{3}{2}$ .

Apart from work on the correlation energy of the homogeneous electron gas, most theoretical many-body studies have been concerned with elementary excitations and as a result there has been little recent progress in the theory of cohesive energies, elastic constants, etc., of real (i.e., inhomogeneous) metals and alloys. The methods proposed here offer the hope of new progress in this latter area.

\* Supported in part by the U. S. Office of Naval Research.

<sup>1</sup> L. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927); E. Fermi, Z. Physik 48, 73 (1928).

<sup>2</sup> J. C. Slater, Phys. Rev. 81, 385 (1951).

<sup>3</sup> P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); referred to hereafter as HK.

In Secs. III and IV, we describe the necessary modifications to deal with the finite-temperature properties and with the spin paramagnetism of an inhomogeneous electron gas.

Of course, the simple methods which are here proposed in general involve errors. These are of two general origins<sup>4</sup>: a too rapid variation of density and, for finite systems, boundary effects. Refinements aimed at reducing the first type of error are briefly discussed in Appendix II.

## II. THE GROUND STATE

### A. Local Effective Potential

It has been shown<sup>3</sup> that the ground-state energy of an interacting inhomogeneous electron gas in a static potential  $v(\mathbf{r})$  can be written in the form

$$E = \int v(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[n], \quad (2.1)$$

where  $n(\mathbf{r})$  is the density and  $G[n]$  is a universal functional of the density. This expression, furthermore, is a minimum for the correct density function  $n(\mathbf{r})$ . In this section we propose first an approximation for  $G[n]$ , which leads to a scheme analogous to Hartree's method but contains the major part of the effects of exchange and correlation.

We first write

$$G[n] \equiv T_s[n] + E_{xc}[n], \quad (2.2)$$

where  $T_s[n]$  is the kinetic energy of a system of non-interacting electrons with density<sup>5</sup>  $n(\mathbf{r})$  and  $E_{xc}[n]$  is, by our definition, the exchange and correlation energy of an interacting system with density  $n(\mathbf{r})$ . For an arbitrary  $n(\mathbf{r})$ , of course, one can give no simple exact expression for  $E_{xc}[n]$ . However, if  $n(\mathbf{r})$  is sufficiently slowly varying, one can show<sup>3</sup> that

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad (2.3)$$

<sup>4</sup> W. Kohn and L. J. Sham, Phys. Rev. 137, A1697 (1965).

<sup>5</sup> For such a system it follows from HK that the kinetic energy is in fact a unique functional of the density.

## Inhomogeneous Electron Gas\*

P. HOHENBERG†

*École Normale Supérieure, Paris, France*

AND

W. KOHN‡

*École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France*  
and

*University of California at San Diego, La Jolla, California*

(Received 18 June 1964)

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  $E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$  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)  $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$ ,  $\tilde{n}/n_0 \ll 1$ , and (2)  $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$  with  $\varphi$  arbitrary and  $r_0 \rightarrow \infty$ . 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

**D**URING the last decade there has been considerable progress in understanding the properties of a homogeneous interacting electron gas.<sup>1</sup> 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<sup>2</sup> 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,<sup>3</sup> Kirzhnits,<sup>4</sup> Lewis,<sup>5</sup> Baraff and Borowitz,<sup>6</sup> Baraff,<sup>7</sup> and DuBois and Kivelson.<sup>8</sup> 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  $\tilde{n}/n_0 \rightarrow 0$ . 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<sup>9</sup> 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,  $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ ,  $r_0 \rightarrow \infty$ . For this case we derive an expansion of  $F[n]$  in successive orders of  $r_0^{-1}$  or, equivalently of the gradient operator  $\nabla$  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

<sup>9</sup> J. Friedel, *Phil. Mag.* **43**, 153 (1952).

\* Supported in part by the U. S. Office of Naval Research.

† NATO Post Doctoral Fellow.

‡ Guggenheim Fellow.

<sup>1</sup> For a review see, for example, D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin Inc., New York, 1963).

<sup>2</sup> For a review of work up to 1956, see N. H. March, *Advan. Phys.* **6**, 1 (1957).

<sup>3</sup> A. S. Kompaneets and E. S. Pavlovskii, *Zh. Eksperim. i. Teor. Fiz.* **31**, 427 (1956) [English transl.: *Soviet Phys.—JETP* **4**, 328 (1957)].

<sup>4</sup> D. A. Kirzhnits, *Zh. Eksperim. i. Teor. Fiz.* **32**, 115 (1957) [English transl.: *Soviet Phys.—JETP* **5**, 64 (1957)].

<sup>5</sup> H. W. Lewis, *Phys. Rev.* **111**, 1554 (1958).

<sup>6</sup> G. A. Baraff and S. Borowitz, *Phys. Rev.* **121**, 1704 (1961).

<sup>7</sup> G. A. Baraff, *Phys. Rev.* **123**, 2087 (1961).

<sup>8</sup> D. F. Du Bois and M. G. Kivelson, *Phys. Rev.* **127**, 1182 (1962).

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

$$H = T + V + U, \quad (1)$$

where<sup>10</sup>

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

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

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

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  $\Psi$  by

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

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  $\Psi'$  gives rise to the *same* density  $n(\mathbf{r})$ . Now clearly [unless  $v'(\mathbf{r}) - v(\mathbf{r}) = \text{const}$ ]  $\Psi'$  cannot be equal to  $\Psi$  since they satisfy different Schrödinger equations. Hence, if we denote the Hamiltonian and ground-state energies associated with  $\Psi$  and  $\Psi'$  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

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

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

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

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

$$E + E' < E + E'. \quad (8)$$

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

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

<sup>10</sup> Atomic units are used.

where  $F[n]$  is a universal functional, valid for any number of particles<sup>11</sup> 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

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

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

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

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

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

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

$$\mathcal{E}_v[\Psi'] = \int v(\mathbf{r}) n'(\mathbf{r}) d\mathbf{r} + F[n'], \quad (13)$$

$$> \mathcal{E}_v[\Psi] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F[n].$$

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

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

<sup>11</sup> This is obvious since the number of particles is itself a simple functional of  $n(\mathbf{r})$ .

<sup>12</sup> 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  $\bar{n}(\mathbf{r})$ , any distribution of the form  $n'(\mathbf{r}) = n_0 + \bar{n}(\mathbf{r})$  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

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

so that  $E_v[n]$  becomes

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

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

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

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

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

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

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

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

such that

$$G[n] = \int g_r[n] d\mathbf{r}. \quad (19)$$

The fact that  $g_r[n]$  is a functional of  $n$  follows of course from the fact that  $\Psi$  and hence  $n_1$  and  $n_2$  are.

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

$$\bar{g}_r[n] = g_r[n] + \sum_{i=1}^3 \frac{\partial}{\partial x_i} h_r^{(i)}[n], \quad (20)$$

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

The following sections deal with  $G[n]$  and  $g_r[n]$  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

$$n(\mathbf{r}) = n_0 + \bar{n}(\mathbf{r}), \quad (21)$$

with

$$\bar{n}(\mathbf{r})/n_0 \ll 1 \quad (22)$$

and

$$\int \bar{n}(\mathbf{r}) d\mathbf{r} = 0. \quad (23)$$

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

$$G[n] = G[n_0] + \int K(\mathbf{r}-\mathbf{r}') \bar{n}(\mathbf{r}) \bar{n}(\mathbf{r}') d\mathbf{r}d\mathbf{r}' + \int L(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \bar{n}(\mathbf{r}) \bar{n}(\mathbf{r}') \bar{n}(\mathbf{r}'') d\mathbf{r}d\mathbf{r}'d\mathbf{r}'' + \dots \quad (24)$$

In this equation there is no term linear in  $\bar{n}(\mathbf{r})$  since by translational invariance the coefficient of  $\bar{n}(\mathbf{r})$  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

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

The higher order terms will not be further discussed here.

One may also quite trivially introduce a density function

$$\bar{g}_r[n] = g_0(n_0) + \int K(\mathbf{r}') \bar{n}(\mathbf{r} + \frac{1}{2}\mathbf{r}') \bar{n}(\mathbf{r} - \frac{1}{2}\mathbf{r}') d\mathbf{r}' + \dots, \quad (26)$$

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  $\alpha(\mathbf{q})$ . 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

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

Write the electronic density, to first order in  $\lambda$ , as

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

Then

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

Let us now define the operator

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

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

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

so that

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

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

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

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

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

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

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

Equivalently, in terms of the dielectric constant,

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

we may write

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

### 3. The Nature of the Kernel $K$

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

$$q \rightarrow 0: \quad \alpha(q) = 1 + c_2 q^2 + c_4 q^4 + \dots; \quad (38)$$

$$q \rightarrow 2k_F: \quad d\alpha/dq \rightarrow -\infty; \quad (39)$$

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

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

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

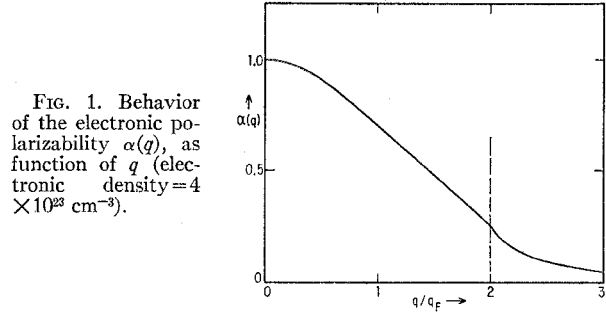


FIG. 1. Behavior of the electronic polarizability  $\alpha(q)$ , as function of  $q$  (electronic density =  $4 \times 10^{23} \text{ cm}^{-3}$ ).

where  $k_T$  is the Thomas-Fermi screening constant,

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

and

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

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

$$q \rightarrow 0: \quad K(q) = 2\pi[-c_2 + (c_2^2 - c_4)q^2 + \dots]; \quad (44)$$

$$q \rightarrow 2k_F: \quad dK/dq \rightarrow +\infty; \quad (45)$$

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

(See Fig. 2.)

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

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

which in turn gives

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

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<sup>13</sup> in  $K(\mathbf{r})$ ,

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

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.

<sup>13</sup> J. S. Langer and S. H. Vosko, Phys. Chem. Solids 12, 196 (1960).



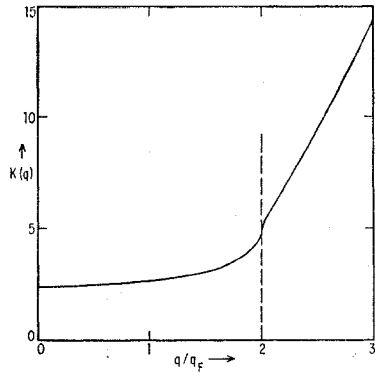


FIG. 2. Behavior of the kernel  $K(q)$ , as a function of  $q$  (electronic density =  $4 \times 10^{23}$  cm $^{-3}$ ).

### 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.,

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

where the Fermi momentum  $k_F$  is given by

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

This results in

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

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  $\mu$  is a Lagrange parameter. This results in the equation

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

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

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

It is obvious that this is quite a different class of systems than that considered in Part II ( $n = n_0 + \tilde{n}$ ,  $\tilde{n}/n_0 \ll 1$ ), since now we shall allow  $\varphi$  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  $g_T[n]$  may be expanded in the form

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

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  $g_T[n]$  is a universal functional of  $n$ , independent of  $v(\mathbf{r})$ . This requires  $g_T[n]$  to be invariant under rotations about  $\mathbf{r}$ . The coefficients  $g_{i,j}, \dots (n(\mathbf{r}))$ , being functions of the scalar  $n$ , are of course invariant under rotations. Hence one finds by elementary considerations that  $g_T[n]$  must have the form

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

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

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

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

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

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

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

Now let us set

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

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

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

Collecting terms of order  $\lambda^0, \lambda^1, \lambda^2$ , we find

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

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

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

giving

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

Also clearly

$$\mu_1 = 0.$$

Similarly, we obtain

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

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

$$\alpha(q) = 1 + c_2 q^2 + c_4 q^4 + \dots \tag{76}$$

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

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

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

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

$$g_4^{(2)}/4\pi = \frac{1}{2}(-c_6 + 2c_2 c_4 - c_2^3). \tag{80}$$

Similarly all other coefficients  $g_\mu^{(\nu)}(n)$  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  $\alpha(\mathbf{q}_1), \dots, \alpha(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{\mu-1})$ .

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  $c_s$  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

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

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

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

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<sup>14</sup>;

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

<sup>14</sup> M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

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

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

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<sup>15</sup>

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

Other approximations are due to Hubbard,<sup>16</sup> Nozières and Pines,<sup>17</sup> and Gaskell.<sup>18</sup>

##### 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

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

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

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.<sup>3</sup>

An expression for  $\alpha(q)$ , allowing in an approximate manner for exchange effects has been proposed by Hubbard.<sup>16</sup> 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

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

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,  $\alpha(q)$ .

<sup>15</sup> E. P. Wigner, Phys. Rev. **40**, 1002 (1934).

<sup>16</sup> J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1957).

<sup>17</sup> P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

<sup>18</sup> T. Gaskell, Proc. Phys. Soc. (London) **77**, 1182 (1961); **80**, 1091 (1962).

## 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 ( $n = n_0 + \bar{n}(r)$ ,  $\bar{n}(r)/n_0 \ll 1$ ) 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.

## ACKNOWLEDGMENTS

This work was begun and, to a considerable extent, carried out at the University of Paris. One of the authors (P. Hohenberg) acknowledges with thanks a NATO Postdoctoral Fellowship; the other author (W. Kohn) a Guggenheim Fellowship. Both authors wish to thank the faculties of the École Normale Supérieure, Paris, and the Service de Physique des Solides, Orsay, for their hospitality, and Professor A. Blandin, Professor J. Friedel, Dr. R. Balian, and Dr. C. De Dominicis for valuable discussions.

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

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

ZOLTAN FRIED†

*U. S. Naval Ordnance Laboratory, Silver Spring, Maryland  
and University of California, Santa Barbara, California*

AND

JOSEPH H. EBERLY‡

*U. S. Naval Ordnance Laboratory, Silver Spring, Maryland  
(Received 15 June 1964)*

“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.<sup>1</sup> 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.<sup>2</sup> And finally, the problem of interaction of laser light with matter has attracted considerable interest.<sup>3</sup> 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

\* A preliminary version of this work was presented at the Pasadena Meeting of the American Physical Society, Bull. Am. Phys. Soc. 8, 615 (1963).

† Present address: Lowell Technological Institute, Lowell, Massachusetts; on leave from the U. S. Naval Ordnance Laboratory.

‡ National Academy of Sciences—National Research Council Postdoctoral Research Associate, 1962–64.

<sup>1</sup> J. R. Singer, *Masers* (John Wiley & Sons, Inc., New York, 1960); F. Schwabl and W. Thirring (to be published); W. E. Lamb, Jr., Lecture Notes, Enrico Fermi International School of Physics, Varenna, 1963 (unpublished).

<sup>2</sup> R. Glauber, Phys. Rev. 130, 2529 (1963); E. C. G. Sudarshan, Phys. Rev. Letters 10, 277 (1963); E. Wolf, Proc. Phys. Soc. (London) 80, 1269 (1962).

<sup>3</sup> J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962); Z. Fried and W. M. Frank, Nuovo Cimento 27, 218 (1963).

where  $\epsilon_{xc}(n)$  is the exchange and correlation energy per electron of a uniform electron gas of density  $n$ . Our sole approximation consists of assuming that (2.3) constitutes an adequate representation of exchange and correlation effects in the systems under consideration. We shall regard  $\epsilon_{xc}$  as known from theories of the homogeneous electron gas.<sup>6</sup>

From the stationary property of Eq. (2.1) we now obtain, subject to the condition

$$\int \delta n(\mathbf{r}) d\mathbf{r} = 0, \quad (2.4)$$

the equation

$$\int \delta n(\mathbf{r}) \left\{ \varphi(\mathbf{r}) + \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \mu_{xc}(n(\mathbf{r})) \right\} d\mathbf{r} = 0; \quad (2.5)$$

here

$$\varphi(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \quad (2.6)$$

and

$$\mu_{xc}(n) = d(n\epsilon_{xc}(n))/dn \quad (2.7)$$

is the exchange and correlation contribution to the chemical potential of a uniform gas of density  $n$ .

Equations (2.4) and (2.5) are precisely the same as one obtains from the theory of Ref. 3 when applied to a system of noninteracting electrons, moving in the given potential  $\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))$ . Therefore, for given  $\varphi$  and  $\mu$ , one obtains the  $n(\mathbf{r})$  which satisfies these equations simply by solving the one-particle Schrödinger equation

$$\left\{ -\frac{1}{2}\nabla^2 + [\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))] \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.8)$$

and setting

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2, \quad (2.9)$$

where  $N$  is the number of electrons.

It is physically very satisfactory that  $\mu_{xc}$  appears in Eq. (2.8) as an additional effective potential so that gradients of  $\mu_{xc}$  lead to forces on the electron fluid in a manner familiar from thermodynamics.

Equations (2.6)–(2.9) have to be solved self-consistently: One begins with an assumed  $n(\mathbf{r})$ , constructs  $\varphi(\mathbf{r})$  from (2.6) and  $\mu_{xc}$  from (2.7), and finds a new  $n(\mathbf{r})$  from (2.8) and (2.9). The energy is given by

$$E = \sum_1^N \epsilon_i - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r}) [\epsilon_{xc}(n(\mathbf{r})) - \mu_{xc}(n(\mathbf{r}))] d\mathbf{r}. \quad (2.10)$$

The results of our procedure are exact in two limiting cases:

(a) *Slowly varying density.* This regime is characterized by the condition  $r_s/r_0 \ll 1$ , where  $r_s$  is the Wigner-

<sup>6</sup> For a review see D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963).

Seitz radius and  $r_0$  is a typical length over which there is an appreciable change in density. In this case, as shown in HK, we can expand the true exchange and correlation energy as follows:

$$E_{xc}[n] = \int \epsilon_{xc}(n) n d\mathbf{r} + \int \epsilon_{xc}^{(2)}(n) |\nabla n|^2 d\mathbf{r} + \dots, \quad (2.11)$$

where  $\epsilon_{xc}^{(2)}$  is the exchange and correlation portion of the second term in the energy expansion in powers of the gradient operator. In this regime we may similarly expand  $T_s[n]$  in the form

$$T_s[n] = \int \frac{3}{10} (3\pi^2 n)^{2/3} n d\mathbf{r} + \int t^{(2)}(n) |\nabla n|^2 d\mathbf{r} + \dots. \quad (2.12)$$

From HK, especially Sec. III 2, we have the following expression for the energy:

$$E_v[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int g_0(n) d\mathbf{r} + \int g_2^{(2)}(n) |\nabla n|^2 d\mathbf{r} + \dots, \quad (2.13)$$

where

$$g_0(n) = \left\{ \frac{3}{10} (3\pi^2 n)^{2/3} + \epsilon_{xc}(n) \right\} n, \quad (2.14)$$

and

$$g_2^{(2)}(n) = \{ \epsilon_{xc}^{(2)}(n) + t^{(2)}(n) \} n. \quad (2.15)$$

Since in our approximation (2.3), the  $|\nabla|^2$  term of Eq. (2.11) is neglected, it is clear that for a gas of slowly varying density our expression (2.10) for the energy has errors of the order  $|\nabla|^2$ , or equivalently, of the order  $r_0^{-2}$ .

Surprisingly, our procedure determines the density with greater accuracy, the errors being of order  $|\nabla|^4$ . This is shown in Appendix I.

At this point a comparison of our procedure and that of Slater<sup>2</sup> may be appropriate. For one thing, Slater's original work does not include correlation effects.<sup>7</sup> But even the exchange correction is different from ours. To obtain Slater's exchange correction, one may begin by writing the Hartree-Fock exchange operator in the form of an equivalent potential acting on the  $k$ th wave function

$$v_{xk}(\mathbf{r}) = - \sum_{k'=1}^N \int \frac{\psi_k^*(\mathbf{r}) \psi_{k'}^*(\mathbf{r}') \psi_{k'}(\mathbf{r}) \psi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' / \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}), \quad (2.16)$$

<sup>7</sup> Subsequent to the original paper by Slater, there have been several attempts to add correlation corrections: S. Olszewski, Phys. Rev. 121, 42 (1961); J. E. Robinson, F. Bassani, B. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters 9, 215 (1962); W. A. Harrison, Phys. Rev. 136, A1107 (1964); S. Lundqvist and C. W. Ufford, Phys. Rev. 139, A1 (1965).

where the symbols  $\mathbf{r}$  and  $\mathbf{r}'$  are understood to include electron spin coordinates and integration is understood to include summation over spin coordinates. One next assumes that the wave functions can be approximated by plane waves which results in

$$v_{xk}(\mathbf{r}) = -\frac{k_F(\mathbf{r})}{\pi} \left[ 1 + \frac{k_F^2(\mathbf{r}) - k^2}{2kk_F(\mathbf{r})} \ln \left| \frac{k + k_F(\mathbf{r})}{k - k_F(\mathbf{r})} \right| \right], \quad (2.17)$$

where  $k_F(\mathbf{r}) \equiv \{3\pi^2 n(\mathbf{r})\}^{1/3}$ . Finally, one averages  $v_{xk}$  over the occupied state  $k$ , which results in

$$v_x(\mathbf{r}) = -(3/2\pi)\{3\pi^2 n(\mathbf{r})\}^{1/3}. \quad (2.18)$$

In our procedure (neglecting correlation) we obtain, in place of Slater's  $v_x$

$$\mu_x(\mathbf{r}) = -(1/\pi)\{3\pi^2 n(\mathbf{r})\}^{1/3}, \quad (2.19)$$

smaller by a factor of  $\frac{2}{3}$ . From the discussion in Appendix I, it follows that while  $\mu_x$  gives the exchange correction of the density correct to order  $|\nabla|^2$ , inclusive,  $v_x$  [as indeed any other function of  $n(\mathbf{r})$ ] leads to errors of order  $|\nabla|^2$ . The same comment applies to any extension of Slater's exchange to include correlation in the self-consistent potential.

We may note that our result is equivalent to taking, not the average of (2.17), but rather its value at  $k = k_F(\mathbf{r})$ ; i.e., the effective exchange potential for a state at the top of the Fermi distributions. This is physically understandable since density adjustments come about by redistribution of the electrons near the Fermi level.

(b) *High density.* This regime is characterized by the condition  $r_s/a_0 \ll 1$ , where  $a_0$  is the Bohr radius. In this case, the entire exchange and correlation energy is smaller than the kinetic energy by a factor of order  $(r_s/a_0)$  and hence our inaccuracy in representing these portions becomes negligible.

The reader will have noticed that while in Eq. (2.3) we approximate the exchange and correlation energy by the expression valid for a slowly varying density, we made no approximation for the kinetic-energy functional  $T_s[n]$  of Eq. (2.2). This procedure is responsible for the exactness of the high-density limit, even when the density is rapidly varying, such as in the vicinity of an atomic nucleus.

We now make a few further remarks about our approximation. If in Eq. (2.2), we had approximated  $T_s[n]$  by its form appropriate to a system of slowly varying density,

$$T_s[n] \rightarrow \int \frac{3}{10} (3\pi^2 n)^{2/3} n \, d\mathbf{r}, \quad (2.20)$$

we would have been led to the generalization of the Thomas-Fermi method suggested by Lewis.<sup>8</sup> This method shares with the Thomas-Fermi method two shortcomings: (1) It leads to an infinite density near

<sup>8</sup> H. W. Lewis, Phys. Rev. **111**, 1554 (1958).

an atomic nucleus, and (2) it does not lead to quantum density oscillations,<sup>4</sup> such as the density fluctuations due to atomic shell structures. By not making the replacement (2.20), we avoid both of these shortcomings.

Let us now qualitatively discuss the appropriateness of our procedure for various classes of electronic systems.

In atoms and molecules one can distinguish three regions: (1) A region near the atomic nucleus, where the electronic density is high and therefore, in view of case (b) above, we expect our procedure to be satisfactory. (2) The main "body" of the charge distribution where the electronic density  $n(\mathbf{r})$  is relatively slowly varying, so that our approximation (2.3) for  $\epsilon_{xc}$  is expected to be satisfactory as discussed in case (a) above. (3) The "surface" of atoms and the overlap regions in molecules. Here our approximation (2.3) has no validity and therefore we expect this region to be the main source of error. We do not expect an accurate description of chemical binding. In large atoms, of course, this "surface" region becomes of less importance. (The surface is more satisfactorily handled in the nonlocal method described under *B* below.)

For metals, alloys, and small-gap insulators we have, of course, no surface problem and we expect our approximation (2.3) to give a good representation of exchange and correlation effects. In large-gap insulators, however, the actual correlation energy will be considerably reduced compared to that of a homogeneous electron gas of the same density.

## B. Nonlocal Effective Potential

Instead of the Hartree-type procedure discussed in Sec. IIA it is also possible to obtain a scheme which includes exchange effects exactly. We write in place of Eq. (2.3)

$$E_{xc}[n] = E_x[n] + \int n(\mathbf{r}) \epsilon_c(n(\mathbf{r})) \, d\mathbf{r} \quad (2.21)$$

where  $E_x[n]$  is the exchange energy of a Hartree-Fock system of density  $n(\mathbf{r})$  and  $\epsilon_c(n)$  is the correlation energy per particle of a homogeneous electron gas. Applying this ansatz in conjunction with Eq. (2.2) and the stationary property of (2.1) leads to the following system of equations:

$$\left\{ -\frac{1}{2}\nabla^2 + \varphi(\mathbf{r}) + \mu_c(\mathbf{r}) \right\} \psi_i(\mathbf{r}) - \int \frac{n_1(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}') \, d\mathbf{r}' = \epsilon_i \psi_i(\mathbf{r}), \quad (2.22)$$

where

$$\mu_c = d(n\epsilon_c)/dn, \quad (2.23)$$

$$n_1(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^N \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}'), \quad (2.24)$$

and  $\varphi(\mathbf{r})$ ,  $n(\mathbf{r})$  are defined as before, Eqs. (2.6) and (2.9).

The energy is now

$$E = \sum_1^N \epsilon_i - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \iint \frac{n_1(\mathbf{r},\mathbf{r}')n_1(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int n(\mathbf{r})\{\epsilon_c(n(\mathbf{r})) - \mu_c(n(\mathbf{r}))\} d\mathbf{r}. \quad (2.25)$$

This procedure may be regarded as a Hartree-Fock method corrected for correlation effects. It is no more complicated than the uncorrected Hartree-Fock method but, because of the nonlocal operator appearing in Eq. (2.22), very much more complicated than the method described in Sec. IIA. Since at least exchange effects are now treated exactly we must expect, in general, more accurate results than from the method of Sec. IIA. In particular, near the surface of an atom the effective potential now is correctly  $(-1/r)$  whereas in Sec. IIA it approaches zero much faster. Even here, however, correlation effects are not correctly described near the surface.

### III. FREE ENERGY; SPECIFIC HEAT

We can generalize the consideration of the ground state to finite temperature ensembles by using the finite temperature generalization of Eq. (2.1) given by Mermin.<sup>9</sup> He has shown that the grand canonical potential can be written in the form

$$\Omega = \int v(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[n] - \mu \int n(\mathbf{r}) d\mathbf{r}, \quad (3.1)$$

where  $G[n]$  is a unique functional of the density at a given temperature  $\tau$  and  $\mu$  is the chemical potential. For the correct  $n$  this quantity is a minimum.

In analogy with (2.2) we now write

$$G[n] = G_s[n] + F_{xc}[n]; \quad (3.2)$$

here

$$G_s[n] \equiv T_s[n] - \tau S_s[n], \quad (3.3)$$

where  $T_s[n]$  and  $S_s[n]$  are, respectively, the kinetic energy and entropy of noninteracting electrons with density  $n(\mathbf{r})$  at a temperature  $\tau$ ; and  $F_{xc}[n]$  is, by definition, the exchange and correlation contribution to the free energy. For the latter quantity, we make the approximation

$$F_{xc}[n] = \int n(\mathbf{r})f_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad (3.4)$$

where  $f_{xc}(n)$  is the exchange and correlation contribution to the free energy per electron of a uniform electron

gas of density  $n$ ; i.e.,

$$f_{xc}(n) \equiv f(n) - f_0(n), \quad (3.5)$$

where  $f$  and  $f_0$  are the free energies per electron of an interacting and noninteracting gas, respectively.

$$0 = \varphi(\mathbf{r}) + (\delta G_s[n]/\delta n(\mathbf{r})) + \mu_{xc}(n(\mathbf{r})) - \mu, \quad (3.6)$$

where  $\varphi(\mathbf{r})$  is given, as before, by Eq. (2.6) and

$$\mu_{xc}(n) \equiv d(n f_{xc}(n))/dn. \quad (3.7)$$

Equation (3.6) is identical to the corresponding equation for a system of noninteracting electrons in the effective potential  $\varphi + \mu_{xc}$ . Its solution is therefore determined by the following system of equations:

$$\{-\frac{1}{2}\nabla^2 + \varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))\}\psi_i = \epsilon_i\psi_i, \quad (3.8)$$

and

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 / \{e^{\epsilon_i - \mu}/k\tau + 1\}. \quad (3.9)$$

$\mu$  is determined as usual by the total number of particles from Eq. (3.9). This value also represents our approximation for the chemical potential of the interacting system.

Of special interest for metals and alloys is the low-temperature heat capacity. This may be obtained by making an expansion, in powers of  $\tau$ , of the above system of equations. An equivalent, but more convenient, method is as follows: From thermodynamics and Eq. (3.1) we have

$$S[n] \equiv -\frac{\partial}{\partial \tau}(\Omega + \mu N)_V = -\int \left\{ \varphi(\mathbf{r}) + \frac{\delta G}{\delta n(\mathbf{r})} \right\} \times \left( \frac{\partial n(\mathbf{r})}{\partial \tau} \right)_V d\mathbf{r} - \left( \frac{\partial G[n]}{\partial \tau} \right)_{n(\mathbf{r}), V}. \quad (3.10)$$

The integral vanishes because of the stationary property of  $\Omega$ , so that

$$S[n] = -(\partial G[n]/\partial \tau)_{n(\mathbf{r}), V}. \quad (3.11)$$

The same argument, applied to a system of noninteracting electrons of density  $n(\mathbf{r})$ , gives

$$S_s[n] = -(\partial G_s[n]/\partial \tau)_{n(\mathbf{r}), V}. \quad (3.12)$$

Combining Eqs. (3.11), (3.12), (3.2), and (3.4), we obtain

$$S[n] = S_s[n] + \int n(\mathbf{r})(\partial f_{xc}(n)/\partial \tau)_{n(\mathbf{r}), V} d\mathbf{r}. \quad (3.13)$$

For small  $\tau$  it is well known that  $S_s$  is given by

$$S_s[n] = N \frac{1}{3} \pi^2 k^2 \tau g_s(\mu), \quad (3.14)$$

where  $g_s$  is the single-particle density of states in the effective potential  $\varphi + \mu_{xc}$  at zero temperature; further,

$$(\partial f_{xc}(n)/\partial \tau)_{n(\mathbf{r}), V} = \frac{1}{3} \pi^2 k^2 \tau [g(\mu_h(n)) - g_0(\mu_0(n))], \quad (3.15)$$

<sup>9</sup> N. D. Mermin, Phys. Rev. 137, A1441 (1965).

where  $\mu_h(n)$  and  $\mu_0(n)$  are, respectively, the chemical potentials of an interacting and a noninteracting homogeneous gas of density  $n$ , and  $g$  and  $g_0$  are the respective densities of states.<sup>10</sup>

It follows immediately that the low-temperature heat capacity is given by

$$C_v = \gamma \tau, \quad (3.16)$$

where

$$\gamma = \frac{1}{3} \pi^2 k^2 \left[ N g_s(\mu) + \int n(\mathbf{r}) \{ g(\mu_h(n)) - g_0(\mu_0(n)) \} d\mathbf{r} \right]. \quad (3.17)$$

We shall not present a treatment, analogous to Sec. IIB, in which exchange effects are included exactly. The development is straightforward but leads to a well-known divergence in the low-temperature specific heat.

#### IV. SPIN SUSCEPTIBILITY

To obtain a theory of the spin susceptibility of an electron gas, we first extend the theory of HK to include the effects of spin interaction with an external magnetic field. The result is that if we take the field in the  $z$  direction and write the magnetic-moment density as

$$m(\mathbf{r}) = - (1/2c) \langle 0 | \psi_{\uparrow}^*(\mathbf{r}) \psi_{\uparrow}(\mathbf{r}) - \psi_{\downarrow}^*(\mathbf{r}) \psi_{\downarrow}(\mathbf{r}) | 0 \rangle, \quad (4.1)$$

the ground-state energy can be written in the form

$$E_{v,H} = \int \{ v(\mathbf{r}) n(\mathbf{r}) - H(\mathbf{r}) m(\mathbf{r}) \} d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[n(\mathbf{r}), m(\mathbf{r})], \quad (4.2)$$

where  $G$  is a universal functional of  $n$  and  $m$ , and the correct  $m(\mathbf{r})$ ,  $n(\mathbf{r})$  make (4.2) a minimum.

For small  $m$  we expand  $G$  in the form

$$G = G[n] + \frac{1}{2} \int G(\mathbf{r}, \mathbf{r}'; [n]) m(\mathbf{r}) m(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots; \quad (4.3)$$

the linear term vanishes for a paramagnetic system in which  $m \equiv 0$  when  $H \equiv 0$ . From the stationary property of (4.2) we find, for small  $H$ , that  $n$  is unchanged to first order and that

$$-H(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}'; [n]) m(\mathbf{r}') d\mathbf{r}' = 0, \quad (4.4)$$

where  $n$  is the zero-field density. We now formally invert this equation, which gives

$$m(\mathbf{r}) = \int G^{-1}(\mathbf{r}, \mathbf{r}'; [n]) H(\mathbf{r}') d\mathbf{r}'. \quad (4.5)$$

For a uniform field this gives for the susceptibility

$$\chi[n] = \frac{1}{V} \frac{\partial}{\partial H} \int m(\mathbf{r}) d\mathbf{r} = \int G^{-1}(\mathbf{r}, \mathbf{r}'; [n]) d\mathbf{r} d\mathbf{r}'. \quad (4.6)$$

<sup>10</sup> J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).

So far everything is formal and exact. We now write, in the spirit of the previous sections,

$$G^{-1}(\mathbf{r}, \mathbf{r}'; [n]) \equiv G_s^{-1}(\mathbf{r}, \mathbf{r}'; [n]) + G_{xc}^{-1}(\mathbf{r}, \mathbf{r}'; [n]). \quad (4.7)$$

The second term we approximate as for a slowly varying gas, which gives

$$\chi[n] = \chi_s[n] + \frac{1}{V} \int [\chi(n(\mathbf{r})) - \chi_0(n(\mathbf{r}))] d\mathbf{r}, \quad (4.8)$$

where

$$\chi_s[n] = (1/2c)^2 (N/V) \times g_s(\mu), \quad (4.9)$$

and  $\chi(n)$ ,  $\chi_0(n)$  are, respectively, the susceptibilities for uniform systems with and without interactions.

#### APPENDIX I: GRADIENT EXPANSION OF THE DENSITY

In this Appendix we show that for a system of slowly varying density our procedure gives the density correct to order  $|\nabla|^2$  inclusive. When dealing with such a system we may proceed in two entirely equivalent ways: (1) We can solve the self-consistent equations, Eqs. (2.8) and (2.9), for  $n(\mathbf{r})$ , and (2) we can go back to the underlying variational principle (2.5), make a gradient expansion and determine  $n(\mathbf{r})$  directly. We shall here follow the second route to estimate the errors in  $n(\mathbf{r})$ .

From (2.5) and the expansion (2.12) of  $T_s[n]$ , we obtain

$$\mu = \varphi(\mathbf{r}) + \mu_h(n) - i^{(2)'}(n) |\nabla n|^2 - 2i^{(2)''}(n) \nabla^2 n + O(\nabla^4), \quad (A1.1)$$

where  $\mu$  is the chemical potential [cf. HK, Eq. (68)]. Note however that because of our approximation of keeping only the first term in (2.11), some other contributions of order  $|\nabla|^2$  are missing in (A1.1).

To solve (A1.1), let us write the external charge density as

$$n_{\text{ext}}(\mathbf{r}) \equiv f_0(\mathbf{r}/r_0), \quad (A1.2)$$

where  $r_0 \rightarrow \infty$  (slow spatial variation), and try the ansatz

$$n(\mathbf{r}) = n_0(\mathbf{r}) + n_1(\mathbf{r}), \quad (A1.3)$$

where

$$n_0(\mathbf{r}) = f_0(\mathbf{r}/r_0) \quad (A1.4)$$

exactly neutralizes the external charge and  $n_1$  is assumed to approach zero as  $r_0 \rightarrow \infty$ . Neglecting, for the moment, the terms of order  $|\nabla|^2$  in (A1.1) and substituting (A1.3) into (A1.1), we obtain

$$\mu = \int \frac{n_1(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_h(n_0) + n_1(\mathbf{r}) \mu_h'(n_0) + O(n_1^2). \quad (A1.5)$$

Now define

$$\mathbf{R} \equiv \mathbf{r}/r_0, \quad (A1.6)$$

and write

$$n_1(\mathbf{r}) \equiv f_1(\mathbf{R}). \quad (A1.7)$$



With this notation, (A1.5) becomes

$$\mu = r_0^2 \int \frac{f_1(\mathbf{R}')}{|\mathbf{R}-\mathbf{R}'|} d\mathbf{R}' + \mu_h(f_0(\mathbf{R})) + f_1(\mathbf{R})\mu_h'(f_0(\mathbf{R})) + O(f_1^2). \quad (\text{A1.8})$$

We may now write

$$f_1(\mathbf{R}) = (1/r_0^2)f_1^{(2)}(\mathbf{R}) + (1/r_0^4)f_1^{(4)}(\mathbf{R}) + \dots, \quad (\text{A1.9})$$

and

$$\mu = \mu^{(0)} + (1/r_0^2)\mu^{(2)} + \dots. \quad (\text{A1.10})$$

The first term of Eq. (A1.9) is correctly determined by Eq. (A1.8) and not affected either by the inclusion of terms of order  $\nabla^2$  in (A1.5) or by the terms of order  $f_1^2$  in (A1.8). Hence, in spite of the errors of order  $\nabla^2$  in (A1.1), the density given by our procedure is correct to order  $1/r_0^2$  or  $|\nabla|^2$ , inclusive. Equation (A1.8) shows that this curious result stems from the infinite range of the Coulomb interaction.

## APPENDIX II: EFFECT OF RAPID DENSITY OSCILLATION ON EXCHANGE AND CORRELATION

In Eq. (2.3), we approximated  $E_{xc}[n]$  by the first term in the gradient expansion. In actual physical systems, there are quantum density oscillations<sup>4</sup> whose effects on exchange and correlation are not included in the approximation (2.3). Now we put forward a correction to (2.3) to include such effects.

In HK, the gradient expression for the energy functional is partially summed such that it is also correct for a system of almost constant density<sup>1</sup> even when the density fluctuations are of short wavelength<sup>11</sup>:

$$G[n] = \int g_0(n(\mathbf{r})) d\mathbf{r} - \frac{1}{2} \int K(\mathbf{r}-\mathbf{r}'; n(\bar{\mathbf{r}})) \times \{n(\mathbf{r}) - n(\mathbf{r}')\}^2 d\mathbf{r} d\mathbf{r}', \quad (\text{A2.1})$$

where  $K(\mathbf{r}-\mathbf{r}'; n)$  is determined by the polarizability of a homogeneous electron gas at density  $n$ , and  $\bar{\mathbf{r}} = \frac{1}{2}(\mathbf{r} + \mathbf{r}')$ . To the same approximation,

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r})) d\mathbf{r} - \frac{1}{2} \int K_{xc}(\mathbf{r}-\mathbf{r}'; n(\bar{\mathbf{r}})) \times \{n(\mathbf{r}) - n(\mathbf{r}')\}^2 d\mathbf{r} d\mathbf{r}' \quad (\text{A2.2})$$

where  $K_{xc}$  is the difference between  $K$  of the interacting homogeneous gas and that of the noninteracting gas at the same density. We believe that for an infinite system,

<sup>11</sup> The second term of HK, Eq. (83) is in error; it should be

$$-\frac{1}{2} \int K(\mathbf{r}'; n(\mathbf{r})) \{n(\mathbf{r} + \frac{1}{2}\mathbf{r}') - n(\mathbf{r} - \frac{1}{2}\mathbf{r}')\}^2 d\mathbf{r}'.$$

The kernel  $K$  has the same meaning as in HK.

such as a metal or an alloy, the second term on the right-hand side of (A2.2) accounts adequately for the effect of rapid density change on exchange and correlation.

This  $E_{xc}[n]$  again leads to a set of Hartree-type equations like Eq. (2.8), with an addition to the effective potential given by

$$-\frac{1}{2} \int \{\partial K_{xc}(\mathbf{r}'; n(\mathbf{r})) / \partial n(\mathbf{r})\} \times \{n(\mathbf{r} + \frac{1}{2}\mathbf{r}') - n(\mathbf{r} - \frac{1}{2}\mathbf{r}')\}^2 d\mathbf{r}' - 2 \int K_{xc}(\mathbf{r}-\mathbf{r}'; n(\bar{\mathbf{r}})) \{n(\mathbf{r}) - n(\mathbf{r}')\} d\mathbf{r}'. \quad (\text{A2.3})$$

Note that in the random-phase approximation  $K_{xc}$  vanishes. Hence, in a calculation which includes the effective potential (A2.3), we need reliable estimates of  $K_{xc}$ , calculated beyond the random-phase approximation, which are not available at present.

The addition of (A2.3) to the effective potential obviously makes the solution of the self-consistent equations much more difficult. However, assuming that the modification of  $n(\mathbf{r})$  produced by this term is small, one may calculate  $n(\mathbf{r})$  and  $E$  first without including it, and then, because of the stationary property, Eq. (2.5), one can obtain the correction to the energy by evaluating the second term in (A2.2) with the unmodified density.

*Note added in proof.* We should like to point out that it is possible, formally, to replace the many-electron problem by an *exactly* equivalent set of self-consistent one-electron equations. This is accomplished quite simply by using the expression (2.2) [without the approximation (2.3)] in the energy variational principle. This leads to a set of equations, analogous to Eqs. (2.4)–(2.9), but with  $\mu_{xc}(n)$  replaced by an effective one-particle potential  $v_{xc}$ , defined formally as

$$v_{xc}(\mathbf{r}) \equiv \delta E_{xc}[n] / \delta n(\mathbf{r}).$$

Of course, an explicit form of  $v_{xc}$  can be obtained only if the functional  $E_{xc}[n]$ , which includes all many-body effects, is known. This effective potential will reproduce the exact density and the exact total energy is then given by

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n] - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}.$$

Of course, if we make the approximation (2.3) for  $E_{xc}$  the above exact formulation reverts to the approximate theory of Sec. II.