

CLASSICS



Shobhana Narasimhan's article 'A Tryst With Density' in this issue of *Resonance* describes a remarkable theorem proved by Hohenberg and Kohn in 1964, and its aftermath. These authors considered a system of electrons in an external potential. This is an excellent idealised model of an atom, molecule or solid because the nuclei are so much heavier than the electrons and can be treated as an external potential. The difficulty lies in accounting for the interaction between the electrons – what one electron is doing depends on what all the others are doing. It therefore came as a shock when the ground state energy of this very general and nontrivial system was shown by Hohenberg and Kohn to be the result of minimising an expression which only contained a function of three variables. This function was just the number of electrons per unit volume as a function of position, something which chemists and crystallographers had long dealt with as a very meaningful and measurable quantity. The theorem showed that such an expression exists, but did not provide the form, which could contain nonlinear terms, derivatives, and integrals of the electron density. While approximate theories of this kind had been proposed before, it was unexpected that the idea of using the electron density could be made exact. What a marvellous turn of events that an existence theorem, proved by contradiction in a modestly written paper would revolutionise the modeling of materials half a century later and win a Nobel Prize in Chemistry for one of the authors!

Even more surprising was that this proof needed no fireworks of many-body theory, which was just beginning to bloom in 1964 (and of which Kohn himself was a leading exponent). A second course on quantum mechanics is all that is needed – in particular, the variational principle for the ground state energy of a system. This simply states that if we evaluate the expectation of the energy with the 'wrong' wave function – that is, any wave function except the true, (assumed nondegenerate) ground state wave function, one will get an answer higher than the true ground state energy. Readers armed with this can enjoy the terse, elegant proof. They need not be put-off by the use of quantum field operators (which usually belong to a third course in quantum theory), they only play the role of a concise language to express the kinetic energy, energy in the external potential, and interaction between the electrons. The proof can be followed from equations 6, 7, and 8 of Section I of the paper reproduced here.

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

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 method² 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., $n(\mathbf{r}) = n_0 + \bar{n}(\mathbf{r})$, with $\bar{n}/n_0 \rightarrow 0$. 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 oscillations⁹ 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 ∇ 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

⁹ J. Friedel, *Phil. Mag.* **43**, 153 (1952).

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

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

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

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

⁵ H. W. Lewis, *Phys. Rev.* **111**, 1554 (1958).

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

⁷ G. A. Baraff, *Phys. Rev.* **123**, 2087 (1961).

⁸ 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

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

where¹⁰

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

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

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

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

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

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

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

¹⁰ Atomic units are used.

where $F[n]$ is a universal functional, valid for any number of particles¹¹ 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

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

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

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

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

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

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)

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

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

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

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 $n(\mathbf{r})$, any distribution of the form $n'(\mathbf{r}) = n_0 + \delta n(\mathbf{r})$ can be so realized and we believe that in fact all, except some pathological distributions, can be realized.