# Condensed Matter Physics

## PHY 5111

### Dr Mohammad Abdur Rashid

# Density Functional Theory

*Density-Functional Theory of Atoms and Molecules*
– Robert G. Parr and Weitao Yang

Chapter 3

# Electron density

In an electronic system, the number of electrons per unit volume in a given state is the *electron density* for that state. This quantity will be of great importance in this book; we designate it by $\rho(\mathbf{r})$. Its formula in terms of $\Psi$ is

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \, ds_1 \, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

This is a nonnegative simple function of three variables, $x$, $y$, and $z$, integrating to the total number of electrons,

$$\int \rho(\mathbf{r}) \, d\mathbf{r} = N$$

# Introduction

We are now ready to begin to expound the density-functional theory of electronic structure, the principal subject of this book. This is a remarkable theory that allows one to replace the complicated $N$-electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ and the associated Schrödinger equation by the much simpler electron density $\rho(\mathbf{r})$ and its associated calculational scheme. Remarkable indeed!

There is a long history of such theories, which until 1964 only had status as models. The history begins with the works of Thomas and Fermi in the 1920s (Thomas 1927; Fermi 1927, 1928a, 1928b; March 1975). What these authors realized was that statistical considerations can be used to approximate the distribution of electrons in an atom.

# The Thomas-Fermi model

The assumptions stated by Thomas (1927) are that: "Electrons are distributed uniformly io the six-dimensional phase space for the motion of an electron at the rate of two for each $h^3$ of volume," and that there is an effective potential field that "is itself determined by the nuclear charge and this distribution of electrons." The Thomas-Fermi formula for electron density can be derived from these assumptions.

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) \, d\mathbf{r}, \qquad C_F = \tfrac{3}{10}(3\pi^2)^{2/3} = 2.871$$

# The Thomas-Fermi model

We divide the space into many small cubes (cells), each of side $l$ and volume $\Delta V = l^3$, each containing some fixed number of electrons $\Delta N$ (which may have different values for different cells), and we assume that the electrons in each cell behave like independent fermions at the temperature 0 K, with the cells independent of one another.

The energy levels of a particle in a three-dimensional infinite well are given by the formula

$$\varepsilon(n_x, n_y, n_z) = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

$$= \frac{h^2}{8ml^2}R^2 \qquad\qquad (3.1.1)$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$

For high quantum numbers, that is, for large $R$, the number of distinct energy levels with energy smaller than $\varepsilon$ can be approximated by the volume of one octant of a sphere with radius $R$ in the space $(n_x, n_y, n_z)$. This number is

$$\Phi(\varepsilon) = \frac{1}{8}\left(\frac{4\pi R^3}{3}\right) = \frac{\pi}{6}\left(\frac{8ml^2\varepsilon}{h^2}\right)^{3/2} \tag{3.1.2}$$

The number of energy levels between $\varepsilon$ and $\varepsilon + \delta\varepsilon$ is accordingly

$$g(\varepsilon)\,\Delta\varepsilon = \Phi(\varepsilon + \delta\varepsilon) - \Phi(\varepsilon)$$

$$= \frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2} \varepsilon^{1/2}\,\delta\varepsilon + O((\delta\varepsilon)^2) \tag{3.1.3}$$

where the function $g(\varepsilon)$ is the *density of states at energy $\varepsilon$.*

To compute the total energy for the cell with $\Delta N$ electrons, we need the probability for the state with energy $\varepsilon$, to be occupied, which we call $f(\varepsilon)$. This is the Fermi–Dirac distribution,

$$f(\varepsilon) = \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} \tag{3.1.4}$$

which at 0 K reduces to a step function:

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases} \quad \text{as } \beta \to \infty \tag{3.1.5}$$

where $\varepsilon_F$ is the so-called Fermi energy. All the states with energy smaller than $\varepsilon_F$ are occupied and those with energy greater than $\varepsilon_F$ are unoccupied. The Fermi energy $\varepsilon_F$ is the zero-temperature limit of the chemical potential $\mu$.

# The Thomas-Fermi model

Now we find the total energy of the electrons in this cell by summing the contributions from the different energy states:

$$\Delta E = 2 \int \varepsilon f(\varepsilon) g(\varepsilon) \, d\varepsilon$$

$$= 4\pi \left(\frac{2m}{h^2}\right)^{3/2} l^3 \int_0^{\varepsilon_F} \varepsilon^{3/2} \, d\varepsilon$$

$$= \frac{8\pi}{5} \left(\frac{2m}{h^2}\right)^{3/2} l^3 \varepsilon_F^{5/2} \qquad\qquad (3.1.6)$$

where the factor 2 enters because each energy level is doubly occupied, by one electron with spin $\alpha$ and another with spin $\beta$.

# The Thomas-Fermi model

The Fermi energy $\varepsilon_F$ is related to the number of electrons $\Delta N$ in the cell, through the formula

$$\Delta N = 2 \int f(\varepsilon) g(\varepsilon)\, d\varepsilon = \frac{8\pi}{3} \left(\frac{2m}{h^2}\right)^{3/2} l^3 \varepsilon_F^{3/2}$$

$$\Delta E = \frac{3}{5} \Delta N\, \varepsilon_F$$

$$= \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3} l^3 \left(\frac{\Delta N}{l^3}\right)^{5/3}$$

$$\rho = \Delta N/l^3 = \Delta N/\Delta V$$

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r},$$

$$C_F = \tfrac{3}{10}(3\pi^2)^{2/3} = 2.871$$

# The Thomas-Fermi model

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r}, \qquad C_F = \tfrac{3}{10}(3\pi^2)^{2/3} = 2.871$$

We here first encounter one of the most important ideas in modern density-functional theory, the local density approximation (LDA). In this approximation, electronic properties are determined as functionals of the electron density by applying locally relations appropriate for a homogeneous electronic system.

$$E_{TF}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{\mathbf{r}}\, d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

Countless modifications and improvements of the Thomas–Fermi theory have been made over the years. Some of them will be discussed in Chapter 6, where the underlying approximations will also be examined in some detail. Unfortunately, the primitive method just described founders when one comes to molecules. As will be shown in Chapter 6, no molecular binding whatever is predicted in the method (Teller 1962). This, plus the fact that the accuracy for atoms is not high as that with other methods, caused the method to come to be viewed as an oversimplified model of not much real importance for quantitative predictions in atomic or molecular or solid-state physics.

However, the situation changed with the publication of the landmark paper by Hohenberg and Kohn (1964). They provided the fundamental theorems showing that for ground states the Thomas–Fermi model may be regarded as an approximation to an exact theory, the *density-functional theory.*

# Inhomogeneous Electron Gas*

P. HOHENBERG†

*École Normale Superieure, Paris, France*

AND

W. KOHN‡

*École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France*
*and*
*University of California at San Diego, La Jolla, California*

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

# The Hohenberg-Kohn theorems

The first Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) legitimizes the use of electron density $\rho(\mathbf{r})$ as basic variable. It states: **The external potential $v(\mathbf{r})$ is determined, within a trivial additive constant, by the electron density $\boldsymbol{\rho}(\mathbf{r})$.** Since $\rho$ determines the number of electrons, it follows that $\rho(\mathbf{r})$ also determines the ground-state wave function $\Psi$ and all other electronic properties of the system. Note that $v(\mathbf{r})$ is not restricted to Coulomb potentials.

# The Hohenberg-Kohn theorems

The proof of this theorem of Hohenberg and Kohn is disarmingly simple. All that is employed is the minimum-energy principle for the ground state. Consider the electron density $\rho(\mathbf{r})$ for the nondegenerate ground state of some $N$-electron system. It determines $N$ by simple quadrature [(1.5.2)]. It also determines $v(\mathbf{r})$, and hence all properties. For if there were two external potentials $v$ and $v'$ differing by more than a constant, each giving the same $\rho$ for its ground state, we would have two Hamiltonians $H$ and $H'$ whose ground-state densities were the same although the normalized wave functions $\Psi$ and $\Psi'$ would be different.

# Variational principle for the ground state

$$E[\Psi] = \frac{\langle \Psi| \hat{H} |\Psi\rangle}{\langle \Psi | \Psi\rangle}$$

$$E[\Psi] \geqslant E_0$$

The energy computed from a guessed $\Psi$ is an upper bound to the true ground-state energy $E_0$. Full minimization of the functional $E[\Psi]$ with respect to all allowed $N$-electron wave functions will give the true ground state $\Psi_0$ and energy $E[\Psi_0] = E_0$; that is,

$$E_0 = \min_{\Psi} E[\Psi]$$

# The Hohenberg-Kohn theorems

Taking $\Psi'$ as a trial function for the $\hat{H}$ problem, we would then have,

$$E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle$$

$$= E_0' + \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})] \, d\mathbf{r}$$

where $E_0$ and $E_0'$ are the ground-state energies for $\hat{H}$ and $\hat{H}'$, respecively. Similarly, taking $\Psi$ as a trial function for the $\hat{H}'$ problem,

$$E_0' < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle$$

$$= E_0 - \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})] \, d\mathbf{r}.$$

$$\boxed{E_0 + E_0' < E_0' + E_0}$$

# The Hohenberg-Kohn theorems

Thus, $\rho$ determines $N$ and $v$ and hence all properties of the ground state, for example the kinetic energy $T[\rho]$, the potential energy $V[\rho]$, and the total energy $E[\rho]$. In place of (3.1.10) we have, writing $E_v$ for $E$ to make explicit the dependence on $v$,

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

$$= \int \rho(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + F_{\mathrm{HK}}[\rho]$$

where

$$F_{\mathrm{HK}}[\rho] = T[\rho] + V_{ee}[\rho]$$

We may write

$$V_{ee}[\rho] = J[\rho] + \text{nonclassical term}$$

$$\boxed{J[\rho] = \frac{1}{2}\int\int \frac{1}{r_{12}}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2}$$

# The Hohenberg-Kohn theorems

The second Hohenberg–Kohn theorem (Hohenberg and Kohn 1964) provides the energy variational principle. It reads: *For a trial density $\tilde{\rho}(\mathbf{r})$, such that $\tilde{\rho}(\mathbf{r}) \geqslant 0$ and $\int \tilde{\rho}(\mathbf{r}) \, d\mathbf{r} = N$,*

$$E_0 \leqslant E_v[\tilde{\rho}] \tag{3.2.6}$$

*where $E_v[\tilde{\rho}]$ is the energy functional of* (3.2.3). This is analogous to the variational principle for wave functions, (1.2.3). It provides the justification for the variational principle in Thomas–Fermi theory in that $E_{\mathrm{TF}}[\rho]$ is an approximation to $E[\rho]$.

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) \, d\mathbf{r} + F_{\mathrm{HK}}[\tilde{\rho}] = E_v[\tilde{\rho}] \geqslant E_v[\rho]$$

# The Hohenberg-Kohn theorems

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r}) v(\mathbf{r}) \, d\mathbf{r} + F_{\text{HK}}[\tilde{\rho}] = E_v[\tilde{\rho}] \geq E_v[\rho]$$

Assuming differentiability of $E_v[\rho]$, the variational principle (3.2.6) requires that the ground-state density satisfy the stationary principle

$$\delta \left\{ E_v[\rho] - \mu \left[ \int \rho(\mathbf{r}) \, d\mathbf{r} - N \right] \right\} = 0 \tag{3.2.8}$$

which gives the Euler–Lagrange equation

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(\mathbf{r})} \tag{3.2.9}$$

# The Hohenberg-Kohn theorems

If we knew the exact $F_{HK}[\rho]$, (3.2.8) would be an exact equation for the ground-state electron density. Note that $F_{HK}[\rho]$ of (3.2.4) is defined independently of the external potential $v(\mathbf{r})$; this means that $F_{HK}[\rho]$ is a *universal functional* of $\rho(\mathbf{r})$. Once we have an explicit form (approximate or accurate) for $F_{HK}[\rho]$, we can apply this method to any system. Equation (3.2.9) is the basic working equation of density-functional theory.

# The Hohenberg-Kohn theorems

Accurate calculational implementations of the density-functional theory are far from easy to achieve, because of the unfortunate (but challenging) fact that the functional $F_{\text{HK}}[\rho]$ is hard to come by in explicit form. We will say a great deal more about these matters in subsequent chapters. Suffice it here to emphasize that the very existence of the exact theory provides impetus both to work to advance the calculational procedures to higher and higher accuracy and also to strive to develop the conceptual consequences. In this reformulation of wave mechanics, the electron density, and only the electron density, plays the key role, and that emphatically bodes well for simple descriptive consequences.

# The *v*- and *N*-representability of an electron density

$$\hat{H} = \sum_{i=1}^{N} \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

A density is *v*-representable if it is the density associated with the antisymmetric ground-state wave function with some external potential $v(\mathbf{r})$ (not necessarily a Coulomb potential).

A density is *N*-representable if it can be obtained from some antisymmetric wave function.

# The *v*- and *N*-representability of an electron density

**The first Hohenberg-Kohn theorem:**

There is a one-to-one mapping between ground-state wave functions and *v*-representable electron densities. It is through this unique mapping a *v*-representable density determines the properties of its associated ground state.

Of particular importance is the functional $F_{\text{HK}}[\rho]$

$$F_{\text{HK}}[\rho] = \langle \Psi | \ \hat{T} + \hat{V}_{ee} \ | \Psi \rangle$$

where $\Psi$ is the ground-state wave function associated with $\rho$, which has to be *v*-representable.

# The $v$- and $N$-representability of an electron density

The second Hohenberg–Kohn theorem simply states that for all $v$-representable densities,

$$E_v[\rho] \equiv F_{HK}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \geqslant E_v[\rho_0] \qquad (3.3.2)$$

where $E_v[\rho_0]$ is the ground-state energy of the Hamiltonian with $v(\mathbf{r})$ as external potential, and $\rho_0$ is its ground-state density.

**What if a trial density is not $v$-representable?**

# The *v*- and *N*-representability of an electron density

The $N$-representability condition is satisfied for any reasonable density. More mathematically stated, a density $\rho(\mathbf{r})$ is $N$-representable if

$$\rho(\mathbf{r}) \geqslant 0, \qquad \int \rho(\mathbf{r})\, d\mathbf{r} = N, \qquad \text{and} \qquad \int |\nabla \rho(\mathbf{r})^{1/2}|^2\, d\mathbf{r} < \infty.$$

This was first shown by Gilbert (1975), who exhibited how one can represent such $\rho$ in terms of $N$ orthonormal orbitals based on a space partitioning (and hence generate $\rho$ from a single-determinantal wave function); see also the proof of Lieb (1982).

# The Levy constrained-search formulation

Having established in the last two sections the one-to-one correspondence between ground-state electron density $\rho_0(\mathbf{r})$ and the ground-state wave function $\Psi_0$, we now proceed to show how one in fact can determine $\Psi_0$ from a given $\rho_0(\mathbf{r})$. (Here subscripts have been given to $\Psi$ and $\rho$ to emphasize their ground-state nature.)

The inverse of this problem is trivial: $\Psi_0$ gives $\rho_0(\mathbf{r})$ by quadrature. But there exist an infinite number of antisymmetric wave functions (not necessarily from ground states) that all give the same density. Given one of these functions that integrates to $\rho_0$, say $\Psi_{\rho_0}$, how do we distinguish it from the true ground-state $\Psi_0$?

The minimum-energy principle for the ground state gives

$$\langle \Psi_{\rho_0} | \hat{H} | \Psi_{\rho_0} \rangle \geqslant \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0$$

where $\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i)$, the Hamiltonian for the $N$-electron system. Since the potential energy due to the external field $v(\mathbf{r})$ is a simple functional of density, we therefore have

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle + \int v(\mathbf{r})\rho_0(\mathbf{r}) \, d\mathbf{r} \geqslant \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle + \int v(\mathbf{r})\rho_0(r) \, d\mathbf{r}$$

Thus,

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle \geqslant \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle \tag{3.4.3}$$

and we conclude that among all the wave functions giving the same ground-state density $\rho_0$, the ground state $\Psi_0$ minimizes the expectation value $\langle \hat{T} + \hat{V}_{ee} \rangle$.
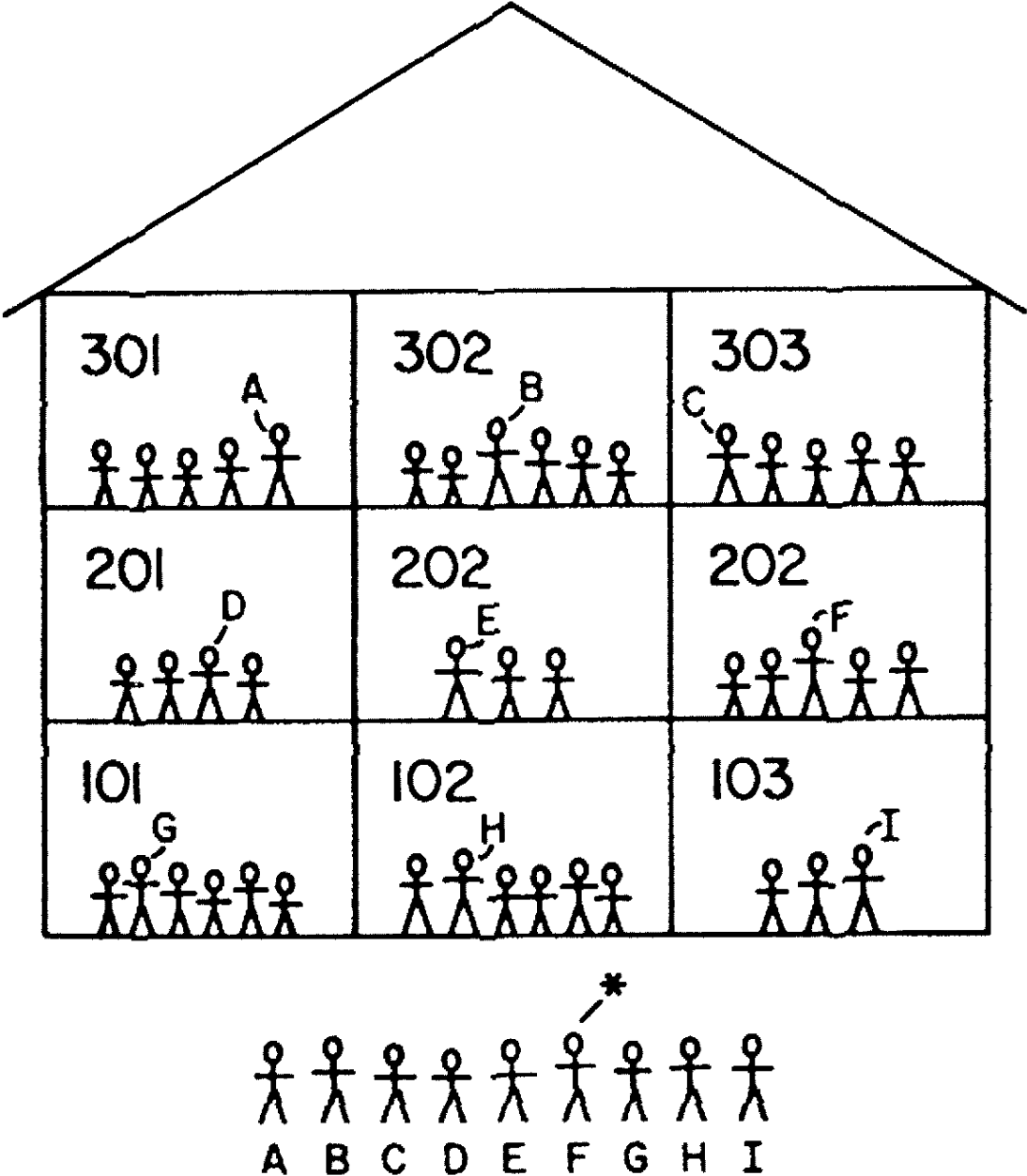
# The Levy constrained-search formulation

$$F_{\mathrm{HK}}[\rho_0] = \langle \Psi_0 | \, \hat{T} + \hat{V}_{ee} \, | \Psi_0 \rangle$$

$$= \underset{\Psi \to \rho_0}{\mathrm{Min}} \, \langle \Psi | \, \hat{T} + \hat{V}_{ee} \, | \Psi \rangle \qquad\qquad (3.4.4)$$

This is a *constrained-search* definition for the density functional $F_{\mathrm{HK}}[\rho_0]$. Searching over all the antisymmetric wave functions that yield the input density $\rho_0$, $F_{\mathrm{HK}}[\rho_0]$ delivers the minimum expectation value of $\langle \hat{T} + \hat{V}_{ee} \rangle$.

Defining $F_{\mathrm{HK}}[\rho_0]$ by (3.4.4) not only provides a new proof for the first theorem of Hohenberg and Kohn, but also eliminates the original Hohenberg–Kohn limitation that there be no degeneracy in the ground state. For in the constrained search, only one of a set of degenerate wave functions is selected, the one corresponding to $\rho_0$.

# Constrained-search formulation

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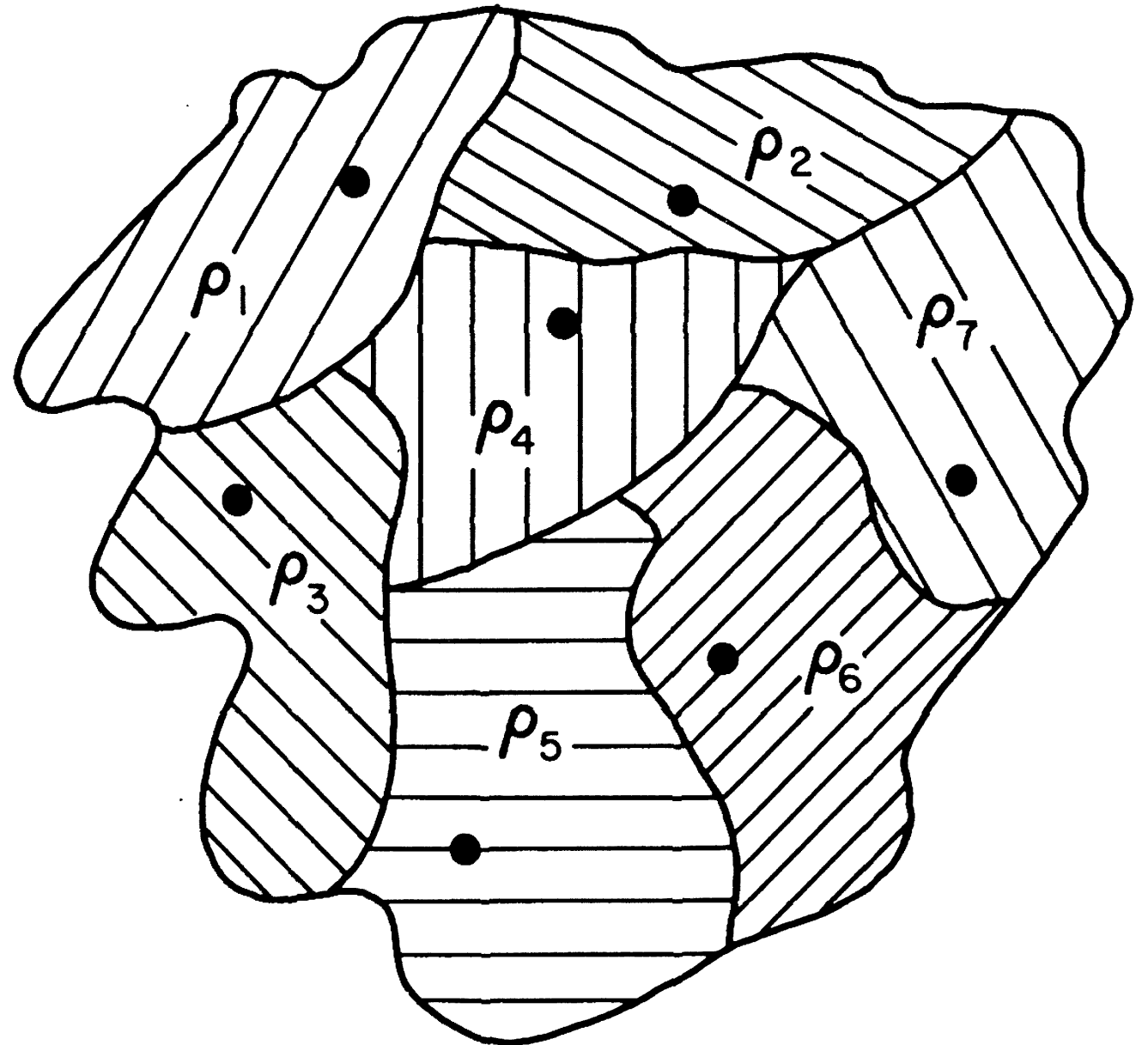
In the constrained-search formula for $F_{\mathrm{HK}}[\rho_0]$, that is, the second equality in (3.4.4), there is no need to make reference to the fact that $\rho_0$ is a $v$-representable ground-state density, so long as it comes from an antisymmetric wave function. This permits one to extend the domain of definition for $F_{\mathrm{HK}}[\rho_0]$ from $v$-representable densities to $N$-representable densities. Define

$$F[\rho] = \underset{\Psi \to \rho}{\mathrm{Min}} \langle \Psi | \, \hat{T} + \hat{V}_{ee} \, | \Psi \rangle \qquad (3.4.5)$$

for any $\rho$ that is $N$-representable. The functional $F[\rho]$ searches all $\Psi$ that yield the input density $\rho(\mathbf{r})$ and then delivers the minimum of $\langle \hat{T} + \hat{V}_{ee} \rangle$. It follows from (3.4.4) and (3.4.5) that

$$F_{\mathrm{HK}}[\rho_0] = F[\rho_0] \qquad (3.4.6)$$

for any $\rho_0$ that is $v$-representable.

# The Levy constrained-search formulation

$$E_0 = \underset{\Psi}{\text{Min}} \; \langle \Psi | \; \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) \; | \Psi \rangle$$

$$= \underset{\rho}{\text{Min}} \left\{ \underset{\Psi \to \rho}{\text{Min}} \; \langle \Psi | \; \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) \; | \Psi \rangle \right\}$$

$$= \underset{\rho}{\text{Min}} \left\{ \underset{\Psi \to \rho}{\text{Min}} \left[ \langle \Psi | \; \hat{T} + \hat{V}_{ee} \; | \Psi \rangle + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \right] \right\}$$
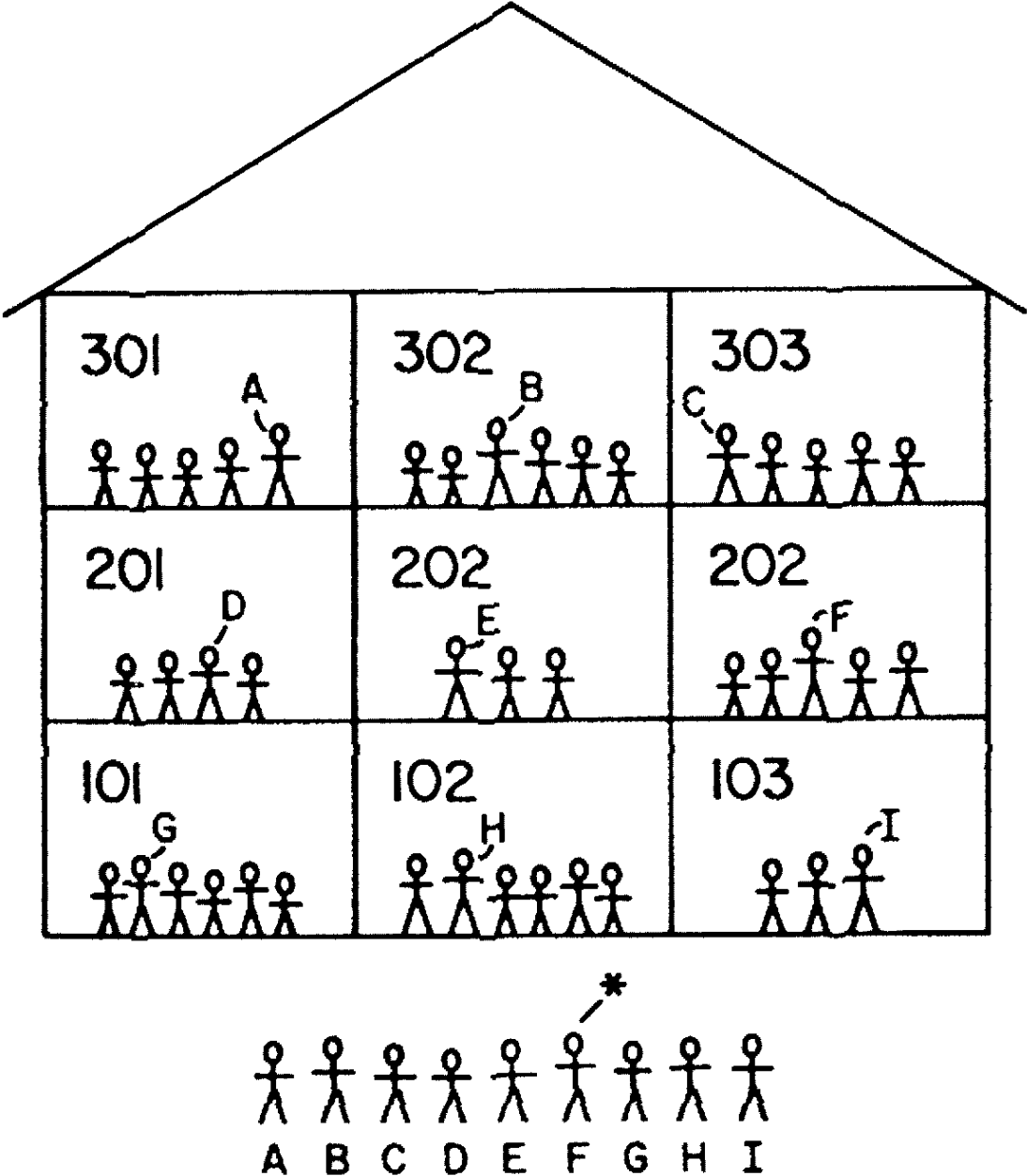
$$= \underset{\rho}{\text{Min}} \left\{ F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} \right\}$$

$$= \underset{\rho}{\text{Min}} \; E[\rho]$$

$$\boxed{E[\rho] = F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r}}$$

# Constrained-search formulation

# The Levy constrained-search formulation

$$E_0 = \underset{\rho}{\text{Min}} \left\{ F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \right\}$$

$$= \underset{\rho}{\text{Min}} \, E[\rho]$$

The variation in (3.4.8) is over all $N$-representable densities; it requires no more than the nonnegativity, proper normalization, and continuity of the trial densities [cf. (3.3.3)]. This makes the minimization in (3.4.7) easier to carry out than the original Hohenberg–Kohn minimization of (3.3.2). The $v$-representability problem in the original approach has been eliminated.

# Inhomogeneous Electron Gas*

P. Hohenberg†

*École Normale Superieure, Paris, France*

AND

W. Kohn‡

*École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California*

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