

3

DENSITY-FUNCTIONAL THEORY

3.1 The original idea: the Thomas–Fermi model

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 $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ 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 assumptions stated by Thomas (1927) are that: “Electrons are distributed uniformly in 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. We here give a slightly different, but equivalent, derivation of the Thomas–Fermi theory; see Chapter 6 for additional viewpoints.

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 ΔN (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

$$\begin{aligned}\varepsilon(n_x, n_y, n_z) &= \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2) \\ &= \frac{h^2}{8ml^2} R^2\end{aligned}\tag{3.1.1}$$

where $n_x, n_y, n_z = 1, 2, 3, \dots$, and the second equality defines the quantity R . For high quantum numbers, that is, for large R , the number

of distinct energy levels with energy smaller than ε 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

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

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

$$\begin{aligned} g(\varepsilon) \Delta\varepsilon &= \Phi(\varepsilon + \delta\varepsilon) - \Phi(\varepsilon) \\ &= \frac{\pi}{4} \left(\frac{8ml^2}{h^2} \right)^{3/2} \varepsilon^{1/2} \delta\varepsilon + O((\delta\varepsilon)^2) \end{aligned} \quad (3.1.3)$$

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

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

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

which at 0 K reduces to a step function:

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

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

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

$$\begin{aligned} \Delta E &= 2 \int \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon \\ &= 4\pi \left(\frac{2m}{h^2} \right)^{3/2} l^3 \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon \\ &= \frac{8\pi}{5} \left(\frac{2m}{h^2} \right)^{3/2} l^3 \varepsilon_F^{5/2} \end{aligned} \quad (3.1.6)$$

where the factor 2 enters because each energy level is doubly occupied, by one electron with spin α and another with spin β . The Fermi energy ε_F

is related to the number of electrons ΔN in the cell, through the formula

$$\begin{aligned}\Delta N &= 2 \int f(\varepsilon)g(\varepsilon) d\varepsilon \\ &= \frac{8\pi}{3} \left(\frac{2m}{h^2}\right)^{3/2} l^3 \varepsilon_F^{3/2}\end{aligned}\quad (3.1.7)$$

Eliminating ε_F from (3.1.6) by (3.1.7), we obtain

$$\begin{aligned}\Delta E &= \frac{3}{5} \Delta N \varepsilon_F \\ &= \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{2/3} l^3 \left(\frac{\Delta N}{l^3}\right)^{5/3}\end{aligned}\quad (3.1.8)$$

This derivation can be found, for example, in McQuarrie (1976, pp. 164–166).

Equation (3.1.8) is a relation between total kinetic energy and the electron density $\rho = \Delta N/l^3 = \Delta N/\Delta V$ for each cell in the space. (Note that different cells can have different values of ρ .) Adding the contributions from all cells, we find the total kinetic energy to be, now reverting to atomic units,

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}, \quad C_F = \frac{3}{10}(3\pi^2)^{2/3} = 2.871 \quad (3.1.9)$$

where the limit $\Delta V \rightarrow 0$, with $\rho = \Delta N/\Delta V = \rho(\mathbf{r})$ finite, has been taken to give an integration instead of a summation. This is the famous Thomas–Fermi kinetic energy functional, which Thomas and Fermi dared to apply to electrons in atoms, in the manner we are about to describe. [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. In later chapters the LDA is employed for properties other than the kinetic energy.]

What (3.1.9) accomplishes is approximation of the electronic kinetic energy in terms of the density $\rho(\mathbf{r})$, whereas the rigorous energy formula of (2.4.9) gives the kinetic energy in terms of the first-order density matrix. If we further neglect the exchange and correlation terms in (2.4.9), thus only taking into consideration the classical electrostatic energies of electron–nucleus attraction and electron–electron repulsion, we get, using (2.4.10), an energy formula for an atom in terms of electron density alone:

$$E_{TF}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{\mathbf{r}} d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.1.10)$$

This is the energy functional of the Thomas–Fermi theory of atoms. For molecules, the second term is modified appropriately.

We now *assume* that for the ground state of an atom of interest the electron density minimizes the energy functional $E_{\text{TF}}[\rho(\mathbf{r})]$, under the constraint

$$N = N[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) d\mathbf{r} \quad (3.1.11)$$

where N is the total number of electrons in the atom. One may incorporate this constraint by the method of Lagrange multipliers (see Appendix A). The ground-state electron density must satisfy the variational principle

$$\delta \left\{ E_{\text{TF}}[\rho] - \mu_{\text{TF}} \left(\int \rho(\mathbf{r}) d\mathbf{r} - N \right) \right\} = 0 \quad (3.1.12)$$

which yields the Euler–Lagrange equation

$$\mu_{\text{TF}} = \frac{\delta E_{\text{TF}}[\rho]}{\delta \rho(\mathbf{r})} = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r}) \quad (3.1.13)$$

where $\phi(\mathbf{r})$ is the *electrostatic potential* at point \mathbf{r} due to the nucleus and the entire electron distribution:

$$\phi(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \quad (3.1.14)$$

Equation (3.1.13) can be solved in conjunction with the constraint (3.1.11), and the resulting electron density then inserted in (3.1.10) to give the total energy. This is the Thomas–Fermi theory of the atom, an exquisitely simple model.

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*. There exists an exact energy functional $E[\rho]$, and there

exists also an exact variational principle of the form of (3.1–12). This exact theory will now be described, first in its original form, then in more mature versions.

3.2 The Hohenberg–Kohn theorems

Recall that for an electronic system described by the Hamiltonian (1.1.2), both the ground-state energy and the ground-state wave function are determined by the minimization of the energy functional $E[\Psi]$ of (1.2.1) and (1.2.3). But for an N -electron system, the external potential $v(\mathbf{r})$ completely fixes the Hamiltonian; thus N and $v(\mathbf{r})$ determine all properties for the ground state. (Only nondegenerate ground states are considered in this section; degeneracy presents no difficulty, as will be discussed in §3.4.) This of course is not surprising since $v(\mathbf{r})$ defines the whole nuclear frame for a molecule, which together with the number of electrons determines all the electronic properties.

In place of N and $v(\mathbf{r})$, 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 $\rho(\mathbf{r})$.* Since ρ determines the number of electrons, it follows that $\rho(\mathbf{r})$ also determines the ground-state wave function Ψ and all other electronic properties of the system. Note that $v(\mathbf{r})$ is not restricted to Coulomb potentials.

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 ρ for its ground state, we would have two Hamiltonians H and H' whose ground-state densities were the same although the normalized wave functions Ψ and Ψ' would be different. Taking Ψ' as a trial function for the \hat{H} problem, we would then have, using (1.2.3),

$$\begin{aligned} E_0 \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &= E'_0 + \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (3.2.1)$$

where E_0 and E'_0 are the ground-state energies for \hat{H} and \hat{H}' , respectively. Similarly, taking Ψ as a trial function for the \hat{H}' problem,

$$\begin{aligned} E'_0 \langle \Psi | \hat{H}' | \Psi \rangle &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\ &= E_0 - \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r}. \end{aligned} \quad (3.2.2)$$

Adding (3.2.1) and (3.2.2), we would obtain $E_0 + E'_0 < E'_0 + E_0$, a contradiction, and so there cannot be two different v that give the same ρ for their ground states.

Thus, ρ 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 ,

$$\begin{aligned} E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \\ &= \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + F_{\text{HK}}[\rho] \end{aligned} \quad (3.2.3)$$

where

$$F_{\text{HK}}[\rho] = T[\rho] + V_{ee}[\rho] \quad (3.2.4)$$

We may write

$$V_{ee}[\rho] = J[\rho] + \text{nonclassical term} \quad (3.2.5)$$

where $J[\rho]$ is the classical repulsion of (2.4.10). The nonclassical term is a very elusive, very important quantity; it is the major part of the “exchange-correlation energy” defined and discussed at length in Chapters 7 and 8 below.

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 $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$,*

$$E_0 \leq E_v[\tilde{\rho}] \quad (3.2.6)$$

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 $E_{\text{TF}}[\rho]$ is an approximation to $E[\rho]$. To prove this theorem, note that the previous theorem assures that $\tilde{\rho}$ determines its own \tilde{v} , Hamiltonian \hat{H} , and wave $\tilde{\Psi}$, which can be taken as a trial function for the problem of interest having external potential v . Thus,

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + F_{\text{HK}}[\tilde{\rho}] = E_v[\tilde{\rho}] \geq E_v[\rho] \quad (3.2.7)$$

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

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

which gives the Euler–Lagrange equation

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

The quantity μ is the *chemical potential*; it is discussed in detail in Chapters 4 and 5.

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

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.

Various mathematical questions can be put to the derivation just given of density-functional theory; the theory stands up very well. We go into these questions in some detail in the next section. In later sections, we develop the whole theory, and its extensions to variable N and finite temperature, from scratch, by methods that are more transparent and more helpful for subsequent development.

3.3 The v - and N -representability of an electron density

It is extraordinary that, as shown in the previous section, the ground-state electron density uniquely determines the properties of a ground state, particularly the ground-state energy. We now discuss some subtle aspects of this relationship.

Noting the close association of electron density with ground state in the Hohenberg–Kohn theorems, we define a density to be *v -representable* if it is the density associated with the antisymmetric ground-state wave function of a Hamiltonian of the form (1.1.2) with *some* external potential $v(\mathbf{r})$ (not necessarily a Coulomb potential). A given density may or may not be v -representable. We then can restate the first Hohenberg–Kohn theorem as the fact that there is a one-to-one mapping between ground-state wave functions and v -representable electron densities. It is through this unique mapping that a v -representable density determines the properties of its associated ground state. Thus, when we say that all ground-state properties are functionals of the electron density, we need