

Density Functional Theory

Density-Functional Theory of Atoms and Molecules
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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 Ψ is

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

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 $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ 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 Thomas-Fermi model

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.

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



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 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 $n_x, n_y, n_z = 1, 2, 3, \dots$



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 .



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:

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

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



The Thomas-Fermi model

The Fermi energy ε_F is related to the number of electrons ΔN in the cell, through the formula

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

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

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

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

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



The Thomas-Fermi model

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

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.

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



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*

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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 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.



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 $\rho(\mathbf{r})$.** 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 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 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.



Variational principle for the ground state

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

$$E[\Psi] \geq E_0$$

The energy computed from a guessed Ψ 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 Ψ_0 and energy $E[\Psi_0] = E_0$; that is,

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



The Hohenberg-Kohn theorems

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

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

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,

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

$$E_0 + E'_0 < E'_0 + E_0$$



The Hohenberg-Kohn theorems

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 ,

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

where

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

We may write

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

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



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 $\tilde{\rho}(\mathbf{r}) \geq 0$ 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 $E[\rho]$.

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



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

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

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 Hohenberg-Kohn theorems

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.



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 $E_{\text{HK}}[\rho]$ 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.

