
 FIP10601 – Text 9

Ground state of interacting electrons

The first part of this course (Unit 1) focused on the *independent-electron approximation*, in which electrons do not explicitly interact with each other, their interaction being implicitly included in the periodic potential due to the lattice. In contrast, from here on we will turn our attention to the electron-electron (e-e) interaction.

Keeping the rigid-lattice approximation, we write the electronic Hamiltonian as

$$\mathcal{H} = \sum_l \mathcal{H}_l^0 + \frac{1}{2} \sum_{l \neq l'} U(\mathbf{r}_l - \mathbf{r}_{l'}), \quad (1)$$

where the primed sum indicates exclusion of equal subscripts,

$$\mathcal{H}_l^0 \equiv \frac{p_l^2}{2m} + V(\mathbf{r}_l) \quad (2)$$

is the single-particle Hamiltonian, including kinetic energy and lattice potential, while $U(\mathbf{r}_l - \mathbf{r}_{l'})$ explicitly describes the Coulomb interaction between electrons, given by

$$U(\mathbf{r}_l - \mathbf{r}_{l'}) \equiv \frac{\kappa e^2}{|\mathbf{r}_l - \mathbf{r}_{l'}|}, \quad \text{with } \kappa \equiv \frac{1}{4\pi\epsilon_0}. \quad (3)$$

Note that we keep our convention of calling *electrons* only those that are involved in the band structure, assuming that the effect of core electrons is taken into account in the lattice potential $V(\mathbf{r})$.

The e-e interaction term prevents separation of variables in the eigenvalue equation for \mathcal{H} in coordinate representation. Therefore, reduction to a single-electron problem is no longer possible, and it is necessary to work with a many-body system. In this context, the notion of energy eigenvalues of individual electrons does not make sense. Only the total-energy eigenvalues are physically meaningful.

In principle, we want to determine the ground-state energy and the spectrum of *elementary excitations*, that is, energies of the lowest-lying excited states measured from the ground state. Particularly relevant are *single-particle excitations*, which correspond to changes in the system energy when a single electron is added or removed. Although such excitations are artificial as real processes in the system, they are interesting because their energies must reproduce the noninteracting electron spectrum if the e-e interaction is reduced to zero, thus providing a point of contact with the independent-electron approximation.

Ground-state energy

Formally, the eigenvalue problem of the complete Hamiltonian is

$$\mathcal{H}\Psi = E\Psi , \quad (4)$$

where Ψ is a function of the coordinates of **all** electrons present in the system. Given the complexity of the Hamiltonian (1), this generic problem has no exact solution.

If we knew the (normalized) **ground-state** wavefunction Ψ_0 , the corresponding energy would be exactly given by

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle . \quad (5)$$

Because the exact form of this wavefunction cannot be known, one of the possible approaches is to resort to a *variational method*. It is based on the fact that the ground-state energy satisfies the relationship

$$E_0 \leq E_\Phi \equiv \langle \Phi | \mathcal{H} | \Phi \rangle , \quad (6)$$

where Φ is an arbitrary normalized function of the same coordinates, which is viewed as a *trial wavefunction*. It should contain a certain number of *variational parameters* whose values are adjusted to **minimize** E_Φ . This minimum value provides an approximation (upper bound) for E_0 . The main difficulty of this method lies in an appropriate choice of trial function, since the better Φ “resembles” Ψ_0 the more accurate is the estimated E_0 .

Hartree approximation

The simplest choice of trial function is of the independent-electron type, i.e., a simple product of single-particle wavefunctions,

$$\Phi_H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots) = \psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2)\psi_{\nu_3}(\mathbf{r}_3)\dots , \quad (7)$$

which is known as *Hartree approximation*. The numerical subscripts on \mathbf{r} vectors run over all the electrons in the system, while each ν_i subscript represents the set of quantum numbers associated to a single-particle wavefunction. An *ad hoc* constraint is that all ν_i 's in the above product must be distinct due to Pauli's Exclusion Principle, even though the total wavefunction Φ_H is not antisymmetric under pair exchanges.

Using Φ_H as trial function, and introducing the corresponding vectors in abstract Hilbert space, we have

$$E_{\Phi_H} = \sum_{\mu} \langle \psi_{\mu} | \mathcal{H}_0 | \psi_{\mu} \rangle + \frac{1}{2} \sum_{\mu\nu} \langle \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\nu} \rangle | \psi_{\mu} \rangle , \quad (8)$$

where, in coordinate representation,

$$\begin{aligned} \langle \psi_{\mu} | \mathcal{H}_0 | \psi_{\mu} \rangle &\equiv \int d^3r \psi_{\mu}^*(\mathbf{r}) \mathcal{H}_0(\mathbf{r}) \psi_{\mu}(\mathbf{r}) \\ \langle \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\nu} \rangle | \psi_{\mu} \rangle &\equiv \int d^3r \int d^3r' \psi_{\mu}^*(\mathbf{r}) \psi_{\nu}^*(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') \psi_{\nu}(\mathbf{r}') \psi_{\mu}(\mathbf{r}) \\ &= \int d^3r \int d^3r' |\psi_{\mu}(\mathbf{r})|^2 |\psi_{\nu}(\mathbf{r}')|^2 U(\mathbf{r} - \mathbf{r}') . \end{aligned} \quad (9)$$

The process of minimizing E_{Φ_H} must keep the functions ψ_μ normalized. Introduction of this constraint into the variational procedure implies that

$$\delta \left[E_{\Phi_H} - \sum_{\mu} \varepsilon_{\mu} (\langle \psi_{\mu} | \psi_{\mu} \rangle - 1) \right] = 0 , \quad (10)$$

where the ε_{μ} are Lagrange multipliers (with physical dimension of energy). Using Eq. (8) for E_{Φ_H} , and *varying* ψ_{μ}^* (i.e., $\langle \psi_{\mu} |$), we have

$$\langle \delta \psi_{\mu} | \mathcal{H}_0 | \psi_{\mu} \rangle + \sum_{\nu (\neq \mu)} \langle \delta \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\nu} \rangle | \psi_{\mu} \rangle - \varepsilon_{\mu} \langle \delta \psi_{\mu} | \psi_{\mu} \rangle = 0 , \quad (11)$$

or

$$\langle \delta \psi_{\mu} | \left[\mathcal{H}_0 + \sum_{\nu (\neq \mu)} \langle \psi_{\nu} | U | \psi_{\nu} \rangle - \varepsilon_{\mu} \right] | \psi_{\mu} \rangle = 0 . \quad (12)$$

As $\langle \delta \psi_{\mu} |$ is arbitrary, it follows that

$$\left[\mathcal{H}_0 + \sum_{\nu (\neq \mu)} \langle \psi_{\nu} | U | \psi_{\nu} \rangle \right] | \psi_{\mu} \rangle = \varepsilon_{\mu} | \psi_{\mu} \rangle . \quad (13)$$

This is the **Hartree equation**, written in coordinate representation as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \kappa e^2 \sum_{\nu (\neq \mu)} \int d^3 r' \frac{|\psi_{\nu}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_{\mu}(\mathbf{r}) = \varepsilon_{\mu} \psi_{\mu}(\mathbf{r}) . \quad (14)$$

The last term inside the brackets describes the interaction of one electron with the charge density of the others. If we neglect the difference between this density and that of the complete system, i.e.,

$$\sum_{\nu (\neq \mu)} |\psi_{\nu}(\mathbf{r})|^2 \simeq \sum_{\nu} |\psi_{\nu}(\mathbf{r})|^2 \equiv \rho(\mathbf{r}) , \quad (15)$$

then Eq. (14) can be written as a Schrödinger equation for a single electron in the presence of an effective potential,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\mathbf{r}) \right] \psi_{\mu}(\mathbf{r}) = \varepsilon_{\mu} \psi_{\mu}(\mathbf{r}) , \quad (16)$$

where

$$V^{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \kappa e^2 \int d^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} . \quad (17)$$

Despite the appeal of this formulation, since it recovers a single-electron problem, it should be noticed that the solution must be **self-consistent**. This is due to the effective potential dependence on the electron density, which is determined from Eq. (15), i.e., by the very wave functions that must be found by solving Eq. (16).

The ground-state energy obtained by this method is, in compact notation,

$$E_0^{\text{H}} = \sum_{\mu} \varepsilon_{\mu} - \frac{1}{2} \sum_{\mu\nu} \langle \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\nu} \rangle | \psi_{\mu} \rangle . \quad (18)$$

This shows that the total energy **is not** simply the sum of “energies” ε_{μ} , which therefore **cannot** be interpreted as individual energies. Another point to emphasize is that the resulting set of functions $\{\psi_{\mu}\}$ is optimized to evaluate the **ground-state** energy, with no justification to use the same set to describe excited states.

Hartree-Fock approximation

Still using an independent-electron trial wavefunction, the Hartree-Fock approximation makes this function explicitly antisymmetric with respect to exchange of two electrons. After choosing a single-particle basis $\{\psi_{\mu}\}$, the trial function Φ_{HF} is written as a *Slater determinant* of individual functions. This determinant has dimension $N \times N$ for a system with N electrons. Taking this into account, the same procedure as in the Hartree approximation is employed, and we obtain

$$E_{\Phi_{\text{HF}}} = \sum_{\mu} \langle \psi_{\mu} | \mathcal{H}_0 | \psi_{\mu} \rangle + \frac{1}{2} \sum_{\mu\nu} [\langle \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\nu} \rangle | \psi_{\mu} \rangle - \langle \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\mu} \rangle | \psi_{\nu} \rangle] . \quad (19)$$

In coordinate representation, the last term, known as **exchange term**, is written as

$$\langle \psi_{\mu} | \langle \psi_{\nu} | U | \psi_{\mu} \rangle | \psi_{\nu} \rangle = \int d^3r \int d^3r' \psi_{\mu}^*(\mathbf{r}) \psi_{\nu}^*(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') \psi_{\mu}(\mathbf{r}') \psi_{\nu}(\mathbf{r}) . \quad (20)$$

Note that the subscripts of single-electron functions must contain information on the spin. Then, since the Coulomb interaction does not depend on spin, the exchange term is nonzero only if the spin states associated with μ and ν are the same.

Repeating the previous variational development, we obtain the equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + \kappa e^2 \sum_{\nu} \int d^3r' \frac{|\psi_{\nu}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_{\mu}(\mathbf{r}) - \kappa e^2 \sum_{\nu} \int d^3r' \frac{\psi_{\nu}^*(\mathbf{r}') \psi_{\nu}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \psi_{\mu}(\mathbf{r}') = \varepsilon_{\mu} \psi_{\mu}(\mathbf{r}) . \quad (21)$$

Here the restriction $\nu \neq \mu$ in the sums is automatically fulfilled since the contributions of terms with $\nu = \mu$ cancel exactly.

Equation (21), which characterizes the **Hartree-Fock approximation**, can be written as a Schrödinger equation for an electron subjected to a **nonlocal** effective potential:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_{\mu}(\mathbf{r}) + \int d^3r' \tilde{V}^{\text{eff}}(\mathbf{r}, \mathbf{r}') \psi_{\mu}(\mathbf{r}') = \varepsilon_{\mu} \psi_{\mu}(\mathbf{r}) . \quad (22)$$

One can recover an equation with a local potential. To do this we multiply both numerator and denominator in the exchange term of Eq. (21) by the same quantity, but written as $|\psi_\mu(\mathbf{r})|^2$ in the denominator and as $\psi_\mu^*(\mathbf{r})\psi_\mu(\mathbf{r})$ in the numerator. We then define

$$\rho_\mu^{\text{HF}}(\mathbf{r}, \mathbf{r}') \equiv \sum_\nu \frac{\psi_\mu^*(\mathbf{r})\psi_\nu(\mathbf{r})\psi_\nu^*(\mathbf{r}')\psi_\mu(\mathbf{r}')}{|\psi_\mu(\mathbf{r})|^2}, \quad (23)$$

in analogy with the electron density, and arrive at the form

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_\mu^{\text{eff}}(\mathbf{r}) \right] \psi_\mu(\mathbf{r}) = \varepsilon_\mu \psi_\mu(\mathbf{r}), \quad (24)$$

where

$$V_\mu^{\text{eff}}(\mathbf{r}) \equiv V(\mathbf{r}) + \kappa e^2 \int d^3r' \frac{\rho(\mathbf{r}') - \rho_\mu^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (25)$$

The effective potential is now local. However, it is not unique but depends on the particular state occupied by the electron. This inconvenience can be avoided through to an additional approximation, known as *Slater approximation*, which consists in the substitution

$$\rho_\mu^{\text{HF}}(\mathbf{r}, \mathbf{r}') \longrightarrow \bar{\rho}^{\text{HF}}(\mathbf{r}, \mathbf{r}') \equiv \frac{\sum_\mu |\psi_\mu(\mathbf{r})|^2 \rho_\mu^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{\sum_\mu |\psi_\mu(\mathbf{r})|^2}. \quad (26)$$

Thus, a unique effective potential is recovered, with the form

$$\bar{V}^{\text{eff}}(\mathbf{r}) \equiv V(\mathbf{r}) + \kappa e^2 \int d^3r' \frac{\rho(\mathbf{r}') - \bar{\rho}^{\text{HF}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (27)$$

It is interesting to observe that the Hartree-Fock(-Slater) effective potential is similar in form to the Hartree one, but with a local **reduction** of the charge density with which an electron interacts. This effect of the exchange term is usually called *exchange hole*.

Once more we find that the set of individual functions $\{\psi_\mu\}$ and corresponding parameters ε_μ are determined by solving an equation which is formally equivalent to a single-electron Schrödinger equation. Using this set of individual functions is only justified to evaluate the ground-state energy, which is now given by

$$E_0^{\text{HF}} = \sum_\mu \varepsilon_\mu - \frac{1}{2} \sum_{\mu\nu} [\langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle - \langle \psi_\mu | \langle \psi_\nu | U | \psi_\mu \rangle | \psi_\nu \rangle]. \quad (28)$$

Here again it is clear that the quantities ε_μ cannot be identified with individual-electron energies.

Density Functional Theory

Evaluation of the ground-state energy of a many-electron system using the solution of a one-electron Schrödinger equation, as done both in Hartree and Hartree-Fock approximations, may be rigorously formulated through the *Density Functional Theory* (DFT). This theory is based on two theorems proposed by P. Hohenberg and W. Kohn [Phys. Rev. **136**, B864 (1964)]. The original theorems are often presented in alternative forms. Here we choose the one stated below.

Theorem 1 - The ground-state energy of a many-electron system subjected to an external potential $V(\mathbf{r})$ is a functional of the electron density $\rho(\mathbf{r})$ which can be written in the form

$$E[\rho] = \int d^3r V(\mathbf{r})\rho(\mathbf{r}) + F[\rho] , \quad (29)$$

where $F[\rho]$ is a **universal** functional of the density (although not known a priori), and is therefore independent of the external potential.

Theorem 2 - The functional $E[\rho]$ is minimized by the density $\rho_0(r)$ corresponding to the ground state.

Demonstration of Theorem 1 - To begin with, given a certain density $\rho(\mathbf{r})$, we suppose that it can be written as

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle , \quad (30)$$

that is, the expectation value of a *density operator*¹ in the many-electron state described by the wave function Ψ . It is assumed that this wave function belongs to a set $S(\rho)$ of a certain number of wavefunctions, all yielding the same density $\rho(\mathbf{r})$. For any operator A , one can define a density-functional $A[\rho]$ as

$$A[\rho] \equiv \min_{|\Psi\rangle \in S(\rho)} \langle \Psi | A | \Psi \rangle . \quad (31)$$

Therefore, we can define

$$F[\rho] \equiv \min_{|\Psi\rangle \in S(\rho)} \langle \Psi | T + U | \Psi \rangle , \quad (32)$$

where T and U are, respectively, the Hamiltonian parts corresponding to kinetic energy and e-e interaction. This last relation is universal in the sense that it does not refer to any particular system, characterized by a given potential $V(\mathbf{r})$. Since $V(\mathbf{r})$ is a purely multiplicative function of \mathbf{r} , the first term in the right-hand side of Eq. (29) can be identified with $V[\rho]$, the Hamiltonian part accounting for the sum of single-particle potential energies.

¹In Unit 2 we will see how one can to define a density operator.

Demonstration of Theorem 2 - Let $|\Psi_0\rangle$ be the ground-state wavefunction and $\rho_0(\mathbf{r})$ the corresponding density. Consider now a density $\rho_1(\mathbf{r})$ and let $|\Psi_1\rangle$ be the wavefunction belonging to the set $S(\rho_1)$ that defines the functional $F[\rho_1]$, i.e.,

$$F[\rho_1] = \langle \Psi_1 | T + U | \Psi_1 \rangle . \quad (33)$$

The inequality

$$\langle \Psi_1 | T + U + V | \Psi_1 \rangle \geq \langle \Psi_0 | T + U + V | \Psi_0 \rangle \quad (34)$$

is obviously true because $|\Psi_0\rangle$ is the ground state. Therefore,

$$E[\rho_1] \geq E_0 = E[\rho_0] . \quad (35)$$

As we mentioned before, although $F[\rho]$ is a unique functional of the density $\rho(\mathbf{r})$, this functional is not known a priori. In practice, applications of the theory involve approximations to this functional. The usual procedure is to write down the functional $F[\rho]$ as

$$F[\rho] = \frac{\kappa e^2}{2} \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + T_0[\rho] + E_{\text{xc}}[\rho] , \quad (36)$$

where part of the e-e interaction term and part of the kinetic-energy term have been separated. The first part is the Hartree term, while the functional $T_0[\rho]$ accounts for the kinetic energy of a **noninteracting** electron system with the **same density** as the interacting one. What remains after these subtractions is represented by the functional $E_{\text{xc}}[\rho]$, which accounts for **exchange and correlation** contributions to the energy.

We have already seen how the exchange energy appears in the Hartree-Fock approximation, that is, for independent (uncorrelated) electrons. Corrections to this type of approximation account for *correlation effects*, which manifest themselves both in interaction and kinetic energies.

Using Eq. (36), minimization of the functional $E[\rho]$, Eq. (29), yields the variational equation

$$\int d^3r \delta\rho(\mathbf{r}) \left\{ V(\mathbf{r}) + \kappa e^2 \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta T_0[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})} \right\} = 0 , \quad (37)$$

while conservation of electron number introduces the subsidiary condition

$$\int d^3r \delta\rho(\mathbf{r}) = 0 . \quad (38)$$

The problem is **formally** equivalent to that of a **noninteracting** electron system subjected to the effective potential

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \kappa e^2 \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r}) . \quad (39)$$

The last term is defined as the *exchange-correlation potential*

$$v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}. \quad (40)$$

One can thus determine $\rho(\mathbf{r})$ by solving a Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_\mu(\mathbf{r}) = \varepsilon_\mu \psi_\mu(\mathbf{r}) \quad (41)$$

and evaluating the electron density as

$$\rho(\mathbf{r}) = \sum_\mu |\psi_\mu(\mathbf{r})|^2. \quad (42)$$

Equations (39)–(42) are known as *Kohn-Sham equations*, as they first appeared in a paper by W. Kohn and L. Sham [Phys. Rev. **140**, A1133 (1965)].

Once more, the solution is self-consistent and the eigenvalues ε_μ cannot be identified with individual-electron energies, as is evident from the ground-state energy, which is

$$E_0 = \sum_\mu \varepsilon_\mu - \frac{\kappa e^2}{2} \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho] - \int d^3r v_{\text{xc}}(\mathbf{r})\rho(\mathbf{r}). \quad (43)$$

In spite of the similarity with the previous approximations, DFT is a **formally exact** approach to the problem of interacting electrons in a solid. In practice, however, the absence of an explicit mathematical definition of the functional $E_{\text{xc}}[\rho]$ leads to approximations. The simplest (and most employed) one is LDA (*Local-Density Approximation*). It starts with a **homogeneous** system of interacting electrons (*jellium model*). The exchange part may then be obtained from a Hartree-Fock calculation, but the correlation part must resort to more sophisticated methods, such as Quantum Monte Carlo simulations in finite-size systems. We will discuss the homogeneous limit of interacting electrons later on.

We have emphasized that Kohn-Sham eigenvalues (like their equivalents in the Hartree and Hartree-Fock approximations) are **not** to be taken as individual-electron energies yielding a band structure. Nevertheless, we must remark that most band-structure calculations for real solids are done in the context of DFT, i.e., they are actually calculations of Kohn-Sham eigenvalues. One should be aware that DFT at this level ceases to be a rigorous many-body theory to become an independent-electron approximation, although a good one in many cases.

A detailed study of DFT is beyond the scope of this course. For those interested in more details, a quite readable review paper (with many references) is “A Bird’s-Eye View of Density-Functional Theory”, by Klaus Capelle [Braz. J. Phys. **36**, 1318 (2006)].