Unit 1 of this course was based 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 (for now) the rigid-lattice approximation, we write the electronic Hamiltonian as

$$\mathcal{H} = \sum_l \mathcal{H}_l^0 + \frac{1}{2} \sum_{ll'} U(l, l') ,$$

where the primed sum indicates exclusion of equal subscripts,

$$\mathcal{H}_l^0 \equiv \frac{\mathbf{p}_l^2}{2m} + V(r_l)$$

is the single-particle Hamiltonian, including kinetic energy and lattice potential, while \(U(l, l')\) explicitly describes the Coulomb interaction between electrons, being given by

$$U(l, l') \equiv \kappa e^2 \frac{1}{|r_l - r_{l'}|} , \quad \text{with} \quad \kappa \equiv \frac{1}{4\pi\varepsilon_0} .$$

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 \(V(r)\).

If we try to solve the eigenvalue equation for \(\mathcal{H}\) in coordinate representation the e-e interaction term prevents separation of variables. Therefore, the problem cannot be reduced to that of a single electron in the presence of an external potential, 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 general, 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. They are interesting because the energies of such excitations must reproduce the noninteracting electron spectrum if the e-e interaction is reduced to zero, providing a point of contact with the independent-electron approximation.
Ground-state energy

Formally, the eigenvalue problem of the complete Hamiltonian is

\[ H \Psi = E \Psi, \]

where \( \Psi \) 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 \( \Psi_0 \), the corresponding energy would be exactly given by

\[ E_0 = \langle \Psi_0 | H | \Psi_0 \rangle. \]

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

\[ E_0 \leq E_\Phi \equiv \langle \Phi | H | \Phi \rangle, \]

where \( \Phi \) 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 \( E_\Phi \). 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 \( \Phi \) “resembles” \( \Psi_0 \) 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,

\[ \Phi_H(r_1, r_2, r_3, \ldots) = \psi_{\nu_1}(r_1)\psi_{\nu_2}(r_2)\psi_{\nu_3}(r_3) \ldots, \]

which is known as Hartree approximation. The numerical subscripts on \( r \) vectors run over all the electrons in the system, while each \( \nu_i \) subscript represents the set of quantum numbers that characterize a single-particle wavefunction. An ad hoc constraint is that all \( \nu_i \)'s in the product must be distinct because of the Pauli Exclusion Principle, but the total wavefunction \( \Phi_H \) is not antisymmetric under pair exchanges.

Using \( \Phi_H \) as trial function, and working with the corresponding vectors in abstract Hilbert space, we have

\[ E_{\Phi_H} = \sum_\mu \langle \psi_\mu | H_0 | \psi_\mu \rangle + \frac{1}{2} \sum_{\mu \nu} \langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle, \]

where, in coordinate representation,

\[ \langle \psi_\mu | H_0 | \psi_\mu \rangle = \int d^3r \: \psi^*_\mu(r) H_0(r) \psi_\mu(r) \]

\[ \langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle = \int d^3r \int d^3r' \: \psi^*_\mu(r) \psi^*_\nu(r') U(r - r') \psi_\nu(r') \psi_\mu(r) = \int d^3r \int d^3r' \: | \psi_\mu(r) |^2 | \psi_\nu(r') |^2 U(r - r'). \]
Minimization of $E_{\Phi H}$ must be done with the constraint of preserving the normalization of functions $\psi_\mu$. This means that

$$\delta \left[ E_{\Phi H} - \sum_\mu \epsilon_\mu (\langle \psi_\mu | \psi_\mu \rangle - 1) \right] = 0,$$

where the $\epsilon_\mu$ are Lagrange multipliers (with physical dimension of energy). Using Eq. (8) for $E_{\Phi H}$, and varying $\psi_\mu^*$ (i.e., $\langle \psi_\mu \rangle$), we have

$$\langle \delta \psi_\mu | H_0 | \psi_\mu \rangle + \sum_\nu (\delta \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle - \epsilon_\mu \langle \delta \psi_\mu | \psi_\mu \rangle) = 0,$$

or

$$\langle \delta \psi_\mu | \left[ H_0 + \sum_\nu (\langle \psi_\nu | U | \psi_\nu \rangle - \epsilon_\mu) \right] | \psi_\mu \rangle = 0.$$

As $\langle \delta \psi_\mu \rangle$ is arbitrary, it follows that

$$\left[ H_0 + \sum_\nu (\langle \psi_\nu | U | \psi_\nu \rangle) \right] | \psi_\mu \rangle = \epsilon_\mu | \psi_\mu \rangle.$$

This is the Hartree equation. In coordinate representation it becomes

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

The last term in 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.,

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

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

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

where

$$V^{\text{eff}}(r) = V(r) + \kappa e^2 \int d^3 r' \frac{\rho(r')}{|r-r'|}.$$
The ground-state energy obtained by this method is

\[ E_0^H = \sum_\mu \varepsilon_\mu - \frac{1}{2} \sum_{\mu\nu} \langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle . \]  

(18)

This shows that the total energy is not simply the sum of “energies” \( \varepsilon_\mu \), which therefore cannot be interpreted as individual energies. Another point to emphasize is that the set of functions \( \{ \psi_\mu \} \) so obtained 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 takes explicitly into account the wavefunction antisymmetry with respect to exchange of two electrons.

Choosing a single-particle basis \( \{ \psi_\mu \} \), as in the Hartree approximation, the trial function \( \Phi_{HF} \) is written as a Slater determinant of individual functions. This determinant has dimension \( N \times N \) for a system with \( N \) electrons.

Using the same procedure as before, we obtain

\[ E_{\Phi_{HF}} = \sum_\mu \langle \psi_\mu | H_0 | \psi_\mu \rangle + \frac{1}{2} \sum_{\mu\nu} [\langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle - \langle \psi_\mu | \langle \psi_\nu | U | \psi_\mu \rangle | \psi_\nu \rangle] . \]  

(19)

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

\[ \langle \psi_\mu | \langle \psi_\nu | U | \psi_\mu \rangle | \psi_\nu \rangle = \int d^3r \int d^3r' \psi_\mu^*(r) \psi_\nu^*(r') U(r - r') \psi_\mu(r') \psi_\nu(r) . \]  

(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 \( \mu \) and \( \nu \) are the same.

Repeating the previous variational development, we obtain the equation

\[ \left( \frac{-\hbar^2}{2m} \nabla^2 + V(r) + \kappa e^2 \sum_\nu \int d^3r' \frac{\psi_\nu(r')^2}{|r - r'|} \right) \psi_\mu(r) \]

\[ - \kappa e^2 \sum_\nu \int d^3r' \frac{\psi_\nu^*(r') \psi_\mu(r)}{|r - r'|} \psi_\mu(r') = \varepsilon_\mu \psi_\mu(r) . \]  

(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, i.e.,

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi_\mu(r) + \int d^3r' \tilde{V}_{eff}(r, r') \psi_\mu(r') = \varepsilon_\mu \psi_\mu(r) . \]  

(22)
One can recover an equation with a local potential through the following procedure. In the exchange term of Eq. (21), both numerator and denominator are multiplied by $|\psi_\mu(r)|^2 = \psi_\mu^*(r)\psi_\mu(r)$. One then defines

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

(23)
in analogy to the electron density.

With this, we have

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

(24)

where

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

(25)
The effective potential so obtained is now local. However, it is not unique but depends on the particular state occupied by the electron. To avoid this, an additional approximation, known as the *Slater approximation*, makes the substitution

$$\rho_{HF}^{\mu}(r, r') \rightarrow \bar{\rho}^{HF}(r, r') \equiv \frac{\sum_\mu |\psi_\mu(r)|^2 \rho_{HF}^{\mu}(r, r')}{\sum_\mu |\psi_\mu(r)|^2}.$$  

(26)

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

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

(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 the *exchange hole*.

Once more, we find that the set of individual functions $\{\psi_\mu\}$ (and corresponding parameters $\varepsilon_\mu$) is 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

$$E_{HF}^0 = \sum_\mu \varepsilon_\mu - \frac{1}{2} \sum_\mu \sum_\nu \left[\langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle - \langle \psi_\mu | \langle \psi_\nu | U | \psi_\nu \rangle | \psi_\mu \rangle \right].$$  

(28)

Here again it is clear that the quantities $\varepsilon_\mu$ cannot be identified with individual-electron energies.
Density Functional Theory

The evaluation of ground-state energy by solving a one-electron Schrödinger equation, which appears 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)].

**Theorem 1** - The ground-state energy of a many-electron system subjected to an external potential \( V(r) \) is a functional of the electron density \( \rho(r) \) which can be written in the form
\[
E[\rho] = \int d^3r \, V(r) \rho(r) + F[\rho],
\]
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 \( \rho(r) \), we suppose that it can be written as
\[
\rho(r) = \langle \Psi | \hat{\rho}(r) | \Psi \rangle,
\]
that is, the expectation value of a **density operator** in the state of an \( N \)-electron system described by the wave function \( \Psi \). We will see later how to define such an operator. It is assumed that this wave function belongs to a set \( S(\rho) \) of a certain number of wavefunctions, all yielding the same density \( \rho(r) \). For any operator \( A \), one can define a density-functional \( A[\rho] \) so that
\[
A[\rho] = \min_{|\Psi \rangle \in S(\rho)} \langle \Psi | A | \Psi \rangle.
\]
Therefore, we can define
\[
F[\rho] = \min_{|\Psi \rangle \in S(\rho)} \langle \Psi | T + U | \Psi \rangle,
\]
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 \( V(r) \). Since \( V(r) \) is a purely multiplicative function of \( r \), the first term in the right-hand side of Eq. (29) can be identified with \( V[\rho] \), where \( V \) is the Hamiltonian part accounting for the sum of single-particle potential energies.

**Demonstration of Theorem 2** - Let \( |\Psi_0 \rangle \) be the ground-state wavefunction and \( \rho_0(r) \) the corresponding density. Consider now a density \( \rho_1(r) \) and let \( |\Psi_1 \rangle \) be the wavefunction belonging to the set \( S(\rho_1) \) that defines the functional \( F[\rho_1] \), i.e.,
\[
F[\rho_1] = \langle \Psi_1 | T + U | \Psi_1 \rangle.
\]
The inequality
\[ \langle \Psi_1 | T + U + V | \Psi_1 \rangle \geq \langle \Psi_0 | T + U + V | \Psi_0 \rangle \] (34)
is obviously true because \(| \Psi_0 \rangle\) is the ground state. Therefore,
\[ E[\rho_1] \geq E_0 = E[\rho_0] . \] (35)

As we mentioned before, although \( F[\rho] \) is a unique functional of the density \( \rho(r) \), 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
\[ F[\rho] = \frac{\kappa e^2}{2} \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r-r'|} + T_0[\rho] + E_{xc}[\rho] , \] (36)
where part of the e-e interaction term and part of the kinetic energy term have been separated. These parts are the Hartree term and the functional \( T_0[\rho] \), defined as the kinetic energy of a noninteracting electron system with the same density of the interacting one. What remains after these subtractions is represented by the functional \( E_{xc}[\rho] \), 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.

Minimization of the functional \( E[\rho] \) yields the variational equation
\[ \int d^3r \ \delta \rho(r) \left\{ V(r) + \kappa e^2 \int d^3r' \frac{\rho(r')}{|r-r'|} + \frac{\delta T_0[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \right\} = 0 , \] (37)
while conservation of electron number introduces the subsidiary condition
\[ \int d^3r \ \delta \rho(r) = 0 . \] (38)

The problem is formally equivalent to a noninteracting electron system subjected to the effective potential
\[ V_{\text{eff}}(r) = V(r) + \kappa e^2 \int d^3r' \frac{\rho(r')}{|r-r'|} + v_{xc}(r) , \] (39)
where we defined the exchange-correlation potential
\[ v_{xc}(r) \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} . \] (40)

One can thus determine \( \rho(r) \) by solving a Schrödinger equation,
\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \psi_\mu(r) = \varepsilon_\mu \psi_\mu(r) \] (41)
and evaluating the electron density as

$$\rho(r) = \sum_\mu |\psi_\mu(r)|^2 .$$  \hspace{1cm} (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 $\varepsilon_\mu$ cannot be identified with individual-electron energies, as is evident from the form of the ground-state energy,

$$E_0 = \sum_\mu \varepsilon_\mu - \frac{\kappa e^2}{4\pi} \int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r - r'|} + E_{xc}[\rho] - \int d^3r v_{xc}(r)\rho(r) .$$  \hspace{1cm} (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 $E_{xc}[\rho]$ leads to approximations. The simplest (and most commonly employed) one is LDA (Local-Density Approximation), which uses the functional $E[\rho]$ corresponding to a homogeneous system of interacting electrons (jellium model) whose (uniform) density coincides locally with $\rho(r)$. 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 more than once that Kohn-Sham eigenvalues 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., 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 in many cases a good one.

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