

# TYC Materials Modelling

## 1: Introduction & The Uniform Electron Gas

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### 1 Introduction

#### 1.1 Wave-functions for systems of more than one electron

The wave-function for a system of two electrons must depend on the positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  of the two electrons and their spin variables  $\sigma_1$  and  $\sigma_2$ . If we write  $\mathbf{x}_1 = (\mathbf{r}_1, \sigma_1)$  and  $\mathbf{x}_2 = (\mathbf{r}_2, \sigma_2)$ , then the wave-function is some function  $\psi(\mathbf{x}_1, \mathbf{x}_2)$ . If the two electrons do not interact with each other, and electron 1 is in a state described by wave-function  $\psi_a(\mathbf{x}_1)$ , while electron 2 is in a state  $\psi_b(\mathbf{x}_2)$ , then the overall wave-function of the two-electron system is:

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2). \quad (1)$$

This would be correct if the two electrons were distinguishable from each other, but in fact electrons are indistinguishable, and this imposes a symmetry on the wave-function (exchange symmetry), which we review next.

### 1.2 Pauli exclusion principle

This states that you cannot have more than one electron in a given space-spin state  $\psi(\mathbf{x})$ . The exclusion principle is a consequence of the more general requirement that for all fermion particles (the electron is a fermion) the overall wave-function must be anti-symmetric in the coordinates of the particles. This means that if you swap the coordinates of a chosen pair of particles the overall wave-function must change sign. So for a 2-electron system a simple product  $\psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2)$  is not acceptable, because  $\psi_a(\mathbf{x}_2)\psi_b(\mathbf{x}_1) \neq -\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2)$ .

Acceptable wave-functions have the anti-symmetrised form, e.g:

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = c(\psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) - \psi_b(\mathbf{x}_1)\psi_a(\mathbf{x}_2)) . \quad (2)$$

This changes sign if we swap  $\mathbf{x}_1$  and  $\mathbf{x}_2$ . Note that we cannot have  $\psi_a = \psi_b$ , because in this case  $\psi$  would be zero. This is the reason for the Pauli exclusion principle. (Note that the constant  $c$  is included to ensure normalisation of the wavefunction.)

For many-electron systems, the general acceptable wave-functions can be made by forming the linear superposition of all permutations of the electron variables, with the appropriate sign:

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = C \sum_P (-1)^P \hat{P} \psi_a(\mathbf{x}_1)\psi_b(\mathbf{x}_2) \dots \psi_n(\mathbf{x}_N) , \quad (3)$$

where  $\hat{P}$  is an operator that permutes the variables  $\mathbf{x}_1 \dots \mathbf{x}_N$  and we sum over all permutations. The sign  $(-1)^P$  is positive if  $P$  consists of an even number of interchanges, and is negative if the number of interchanges is odd. The constant  $C$  is there for the purpose of normalisation.

### 1.3 Operators for kinetic and potential energy

In quantum mechanics, all observable quantities are represented by operators. The observables we will be concerned with in the first few lectures are kinetic and potential energy. The operator  $\hat{T}$  for kinetic energy of a single electron is:

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2 . \quad (4)$$

If we have  $N$  electrons, then their total kinetic energy is represented by:

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 , \quad (5)$$

where  $\nabla_i^2$  operates only on the position of electron  $i$ .

Electrons in atoms, molecules and solids are acted on by the electrostatic field of the nuclei. Let the potential energy of an electron at position  $\mathbf{r}$  due to this field be  $v(\mathbf{r})$ . Then for a system of  $N$  electrons whose positions are  $\mathbf{r}_i$ , the total potential energy  $\hat{V}$  due to interaction with the nuclei is:

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i) . \quad (6)$$

Electrons interact with each other by Coulomb's law, so that the potential energy of two electrons at positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  due to their mutual electrostatic interaction is  $e^2/4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|$ . So the total electrostatic energy of a system of  $N$  electrons due to their interaction with each other is the operator  $\hat{U}$  given by:

$$\hat{U} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} \quad (7)$$

(notice the factor of  $\frac{1}{2}$  to avoid double-counting).

The operator representing the total energy is the Hamiltonian  $\hat{H}$ , which is the sum of  $\hat{T}$ ,  $\hat{V}$  and  $\hat{U}$ :

$$\hat{H} = \hat{T} + \hat{V} + \hat{U}. \quad (8)$$

For a system of  $N$  electrons, the time-independent Schrödinger equation is:

$$\hat{H}\Psi_n(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E_n\Psi_n(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (9)$$

where  $\Psi_n$  is the  $N$ -electron eigenfunction, dependant on the positions and spins of the electrons, and  $E_n$  is the corresponding energy eigenvalue. For a system of more than a single electron, we cannot expect to find the energy eigenvalues and eigenfunctions exactly, so we want to find useful approximations. This is the challenge discussed in these lectures.

#### 1.4 Expectation values

In quantum mechanics, if a system is in a state described by wavefunction  $\psi$  and you make a measurement of some observable  $A$ , then the outcome of the measurement is generally uncertain. The outcomes can be any of the eigenvalues  $a_n$  of the operator  $\hat{A}$  representing the observable. If we denote by  $p_n$  the probability that the outcome is  $a_n$ , then the average measured value when we repeat the measurement many times is:

$$\langle A \rangle = \sum_n p_n a_n. \quad (10)$$

This average value is called the expectation value of the observable  $A$  in state  $\psi$ . To make it clear that this depends on  $\psi$ , it is often convenient to write the expectation value like this:

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle, \quad (11)$$

which is an example of the Dirac bra-ket notation.

As a simple example, suppose you have a single electron in three dimensions and its wavefunction is  $\psi(\mathbf{r})$ . Then the expectation value of its kinetic energy  $T$  is:

$$\langle T \rangle = \langle \psi | \hat{T} | \psi \rangle = \int d\mathbf{r} \psi^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi(\mathbf{r}), \quad (12)$$

where  $\psi^*$  is the complex conjugate of  $\psi$ , we have used the kinetic energy operator given in eqn (4), and the integral goes over the whole of 3-dimensional space.

**NB:** When you write the expectation value of an observable in terms of the wavefunction as in eqn (12), the wavefunction must be correctly normalised to unity, which means that:

$$\int d\mathbf{r} |\psi(\mathbf{r})|^2 = \int d\mathbf{r} \psi^*(\mathbf{r})\psi(\mathbf{r}) = 1 . \quad (13)$$

### 1.5 Orthogonality

We sometimes need to use the fact that different eigenfunctions are *orthogonal* to each other. The meaning of this for a system of one electron is that for any two eigenfunctions  $\psi_m(\mathbf{x})$  and  $\psi_n(\mathbf{x})$  belonging to different energy eigenvalues  $E_m$  and  $E_n$ :

$$\int d\mathbf{x} \psi_m^*(\mathbf{x})\psi_n(\mathbf{x}) \equiv \sum_{\sigma} \int d\mathbf{r} \psi_m^*(\mathbf{r},\sigma)\psi_n(\mathbf{r},\sigma) = 0 . \quad (14)$$

(Notation:  $\int d\mathbf{x}$  means integration over spatial position  $\mathbf{r}$  and summation over the two spin states  $\uparrow$  and  $\downarrow$ .) Recall that there can be degenerate states, i.e. distinct eigenstates having exactly the same energy eigenvalues, usually because of some symmetry. In such cases, it is always possible to choose the eigenfunctions of degenerate states to be orthogonal.

For many-electron systems, orthogonality means the same thing, but now the generalisation of eqn (14) involves integration over *all* electron positions and summation over all spins.

### 1.6 The variational principle

In practice, we are often interested only in the ground-state energy of a system. (The reason is that electron excitation energies are usually much greater than typical thermal energies  $k_B T$ , so that the probability of finding the system in an excited electronic state at ambient temperature is negligibly small.)

We cannot generally compute the ground-state energy exactly, and the variational principle comes to our rescue. This states that the expectation value of the Hamiltonian  $\hat{H}$  in an arbitrarily chosen state  $\psi$  is guaranteed to be above the ground-state energy  $E_0$ :

$$\langle \psi | \hat{H} | \psi \rangle \geq E_0 . \quad (15)$$

The proof of this principle can be found in standard text-books (or see Wikipedia article “Variational method (quantum mechanics)”).

The principle is applied by choosing a “trial wave-function”  $\psi_T$  depending on one or more parameters and then minimising the expectation value  $\langle \psi_T | \hat{H} | \psi_T \rangle$  with respect to the parameters. Then the minimum expectation value gives the best approximation to the true ground-state energy within the given family of trial wavefunctions.

## 2 The Hartree-Fock approximation

### 2.1 Introduction

One of the main challenges in computational chemistry and the computational science of materials is to calculate the ground-state energy of an assembly of atoms with the nuclei in specified positions. The Hartree-Fock approximation was the first practically useful method for doing this.

The basic idea is simple. The  $N$  electrons are treated as independent particles occupying single-electron spin-orbitals  $\psi_a(\mathbf{x})$ ,  $\psi_b(\mathbf{r})$ , ...  $\psi_n(\mathbf{r})$ , so that the many-electron trial wavefunction is:

$$\Psi_T(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = C \sum_P (-1)^P \hat{P} \psi_a(\mathbf{x}_1) \psi_b(\mathbf{x}_2) \dots \psi_n(\mathbf{x}_N). \quad (16)$$

(See Sec. 1.1.) The expectation value of the total energy is:

$$E = \langle \Psi_T | \hat{H} | \Psi_T \rangle. \quad (17)$$

Then, using the variational principle, we vary the single-electron orbitals to minimise the energy. The lowest possible energy in this independent-electron approximation is the Hartree-Fock approximation to the ground-state energy. It is an approximation because it ignores electron correlation.

### 2.2 Single-electron operators

The details of the HF approximation are covered later in the lectures, so only a brief sketch is given here. The Hamiltonian  $\hat{H}$  is the sum of  $\hat{T}$ ,  $\hat{V}$  and  $\hat{U}$ ; the first two of these only involve a single electron position, while the final one involves two electron positions. Consider first the expectation value of kinetic energy:

$$\langle T \rangle = \langle \Psi_T | -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 | \Psi_T \rangle. \quad (18)$$

The trial wavefunction  $\Psi_T$  is the sum of  $N!$  terms (see eqn (16)), so at first sight this looks a bit complicated. But it is enormously simplified by the fact that all the single-electron orbitals,  $\psi_a(\mathbf{x})$  etc, can be assumed orthogonal to each other. The consequence is that when you integrate over all the space-spin coordinates  $\mathbf{x}_i$ , for each of the  $N!$  terms on the left, only a single one of the  $N!$  terms on the right gives a non-zero result. With only a little maths, you can show that:

$$\langle T \rangle = \sum_{i=1}^N \langle \psi_i | -\frac{\hbar^2}{2m} \nabla^2 | \psi_i \rangle, \quad (19)$$

so that the expectation value of total kinetic energy is just the sum of the individual kinetic energies of the  $N$  electrons in the  $N$  single-electron orbitals  $\psi_i(\mathbf{x})$ .

Next, consider the expectation value of  $V$ , the total interaction energy of the electrons with the field  $v(\mathbf{r})$  due to the nuclei:

$$\langle V \rangle = \langle \Psi_T | \sum_{i=1}^N v(\mathbf{r}_i) | \Psi_T \rangle. \quad (20)$$

The maths works just the same as for the kinetic energy, and you find that:

$$\langle V \rangle = \sum_{i=1}^N \langle \psi_i | v(\mathbf{r}) | \psi_i \rangle, \quad (21)$$

so that it is just the sum of the average values of the interactions of the  $N$  electrons in the  $N$  single-electron orbitals  $\psi_i$  with the nuclei.

### 2.3 The two-electron operator

The final energy to consider is the expectation value of the interaction between the electrons, which involves two *different* electrons:

$$\langle U \rangle = \left\langle \Psi_T \left| \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right| \Psi_T \right\rangle. \quad (22)$$

This is a bit more complicated, but it can be shown that there are just two kinds of terms. The first is the energy of electrostatic interaction between an electron in one orbital  $\psi_s$  with another electron in orbital  $\psi_t$ . If you sum over all pairs of different orbitals, this gives:

$$\frac{1}{2} \sum_{s \neq t} \int d\mathbf{x}_1 d\mathbf{x}_2 |\psi_s(\mathbf{x}_1)|^2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} |\psi_t(\mathbf{x}_2)|^2. \quad (23)$$

The second kind of term comes from the exchange of a pair of electrons. This kind of term exists only for spin-orbitals having the same spins and it is negative because of the antisymmetry. It looks like this:

$$-\frac{1}{2} \sum_{s \neq t} \int d\mathbf{x}_1 d\mathbf{x}_2 \psi_s^*(\mathbf{x}_1) \psi_t(\mathbf{x}_1) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \psi_s(\mathbf{x}_2) \psi_t^*(\mathbf{x}_2). \quad (24)$$

If we wish, we can include the terms  $s = t$  in the above summations, because the  $s = t$  terms in eqn (23) cancel exactly against the  $s = t$  terms in eqn (24). It is convenient and conventional to include these  $s = t$  terms, and the two parts of the energy  $\langle U \rangle$  are then called the Hartree energy  $E_H$ :

$$E_H = \frac{1}{2} \sum_{s,t} \int d\mathbf{x}_1 d\mathbf{x}_2 |\psi_s(\mathbf{x}_1)|^2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} |\psi_t(\mathbf{x}_2)|^2, \quad (25)$$

and the exchange energy:

$$E_X = -\frac{1}{2} \sum_{s,t} \int d\mathbf{x}_1 d\mathbf{x}_2 \psi_s^*(\mathbf{x}_1) \psi_t(\mathbf{x}_1) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \psi_s(\mathbf{x}_2) \psi_t^*(\mathbf{x}_2). \quad (26)$$

Exchange energy is very important in atoms, molecules and solids, and it will be discussed more in later lectures.

The Hartree-Fock approximation has been widely used in the past, but it is usually too inaccurate to be very useful. Density functional theory uses some of the same ideas as Hartree-Fock theory, but is generally much more accurate, and is also much less computationally demanding.

### 3 The Uniform Electron Gas

#### 3.1 The concept of the uniform electron gas

A large part of this lecture course is concerned with density functional theory (DFT), and this theory relies quite heavily on the concept of the uniform electron gas. The origin of this concept is the idea of treating electrons in a solid as though they are completely free particles confined in a box representing the volume of the material. This idea is actually well suited to describing the conduction electrons in simple “free-electron-like” metals such as sodium and aluminium, in which the conduction electrons do, indeed, behave like almost free particles. More surprisingly, it turns out that the uniform electron gas can also help us to understand the properties of semiconductors like silicon, and even insulators, such as oxides and silicates.

The uniform electron gas consists of a very large number of electrons contained in a box. The electrons are acted on by no potential in the interior of the box, so that they move completely freely. The average density of the gas is the same everywhere inside the box, except perhaps in a small region near the walls of the box, this region being negligible in macroscopic systems. Initially, we will ignore the interactions between the electrons. To simplify things still further, we will start by describing non-interacting electrons in one dimension. Then, we will generalise the theory to non-interacting electrons in three dimensions. At the end of this section, we will indicate how to include the electrostatic repulsion between the electrons in the Hartree-Fock approximation. The interacting electron gas in three dimensions is often called “jellium”, and in the next lecture we will show how jellium forms the basis for a primitive form of density functional theory called Thomas-Fermi theory, which prepares the way for the full DFT presented in later Topics.

#### 3.2 The uniform electron gas in one dimension

Consider a system of  $N$  non-interacting electrons in one dimension, confined in a box of length  $L$ , with the origin at the centre of the box. In the introductory theory of a particle in a box, the walls of the box are impenetrable, so that the wave-functions  $\psi(x)$  must go to zero at the ends of the box:  $\psi(-\frac{1}{2}L) = \psi(\frac{1}{2}L) = 0$ . With these boundary conditions, the energy eigenfunctions are  $\cos(n\pi x/L)$ , with  $n = \text{odd integer}$ , and  $\sin(n\pi x/L)$  with  $n = \text{even integer}$ . However, instead of using these “rigid” boundary conditions, it is more convenient for present purposes to use so-called “periodic” boundary conditions, according to which the wave-function has to repeat exactly with a spatial period  $L$ . With these boundary conditions, we can take the eigenfunctions to be:

$$\psi_n(x) = L^{-1/2} \exp(2\pi i n x / L), \quad (27)$$

where  $n$  is a positive, zero or negative integer. If we have a large number of electrons in a large box, it can be shown that its properties do not depend on the detailed boundary conditions, so the periodic boundary conditions are perfectly acceptable.

Recalling that the wave-function of a free particle having momentum  $p$  in one dimension is  $\exp(ikx)$ , where the wave-vector  $k = p/\hbar$  (de Broglie relation), one sees that the  $\psi_n(x)$  are free-particle states whose wave-vector is  $k_n = 2\pi n/L$ , their wavelength is  $\lambda = 2\pi/k = L/n$ , so that an integer number of wavelengths fit exactly into the box. If  $k$  is positive, the electron is moving to the right, and if  $k$  is negative, it is moving to the left. The allowed wavevectors  $k_n = 2\pi n/L$  thus form an equally spaced sequence with successive wave-vectors separated by  $2\pi/L$ . The “space” of wave-vectors is called  $k$ -space, or reciprocal space. For a one-dimensional system,  $k$ -space is one-dimensional.

If  $L$  and  $N$  are large, it is now easy to calculate all the properties of the ground-state of the system. We apply exactly the Aufbau principle used for atoms: we fill up the allowed single-electron states with two electrons each (spin-up and spin-down), in order of increasing energy. Since increasing energy means increasing  $|k|$ , this means that the occupied states have wave-vectors in the range:

$$-k_F \leq k \leq k_F, \quad (28)$$

where  $|k_F|$  is the magnitude of the wave-vector of the occupied state of highest energy. The energy of an electron having wave-vector  $k$  is  $\epsilon_k = \hbar^2 k^2 / 2m$ . The energy  $\epsilon_F$  of this highest occupied state is thus given by:

$$\epsilon_F = \hbar^2 k_F^2 / 2m. \quad (29)$$

The energy  $\epsilon_F$  is called the Fermi energy, and  $k_F$  is called the Fermi wave-vector.

There is a relationship between  $\epsilon_F$  and the density of electrons  $\rho = N/L$  (number of electrons per unit length in the box). Since the spacing between allowed wave-vectors is  $2\pi/L$ , and the wave-vectors extend from  $-k_F$  to  $k_F$ , the number of occupied states is  $2k_F/(2\pi/L) = k_FL/\pi$ . Each of these states contains two electrons, so that:

$$N = 2k_FL/\pi. \quad (30)$$

Hence  $k_F = \pi\rho/2$ , so that the Fermi wave-vector is proportional to the density. The Fermi energy is:

$$\epsilon_F = \frac{\hbar^2 \pi^2 \rho^2}{8m}. \quad (31)$$

It is also interesting to calculate the *total* energy  $E_{\text{tot}}$  of the system. We get this by adding up the energies of all the electrons in the occupied states:

$$E_{\text{tot}} = 2 \sum_{k=-k_F}^{k_F} \epsilon_k. \quad (32)$$



Since the system is very large, the spacing  $2\pi/L$  between allowed wave-vectors is very small, and we can replace the sum by an integral, by noting that:

$$\frac{2\pi}{L} \sum_{k=-k_F}^{k_F} \epsilon_k \simeq \int_{-k_F}^{k_F} \epsilon_k dk . \quad (33)$$

We therefore have:

$$E_{\text{tot}} = \frac{L}{\pi} \int_{-k_F}^{k_F} \frac{\hbar^2 k^2}{2m} dk = \frac{L}{\pi} \cdot \frac{\hbar^2}{3m} \cdot k_F^3 . \quad (34)$$

The average energy per electron is thus:

$$\epsilon_{\text{kin}} = E_{\text{tot}}/N = \frac{\hbar^2}{3\pi m} \cdot \frac{k_F^3}{\rho} = \frac{\hbar^2 k_F^2}{6m} , \quad (35)$$

which is 1/3 of the Fermi energy.

### 3.3 The uniform electron gas in three dimensions

The above theory can be extended to the non-interacting electron gas in three dimensions, which is the case of real interest.

In this case, we have  $N$  electrons contained in a box that we assume to be cubic, the edges of the cube being of length  $L$ , so that the volume is  $\Omega = L^3$ , and the electron density is  $\rho = N/L^3$ . The momentum  $\mathbf{p}$  is now a vector, and the wave-function of an electron moving with momentum  $\mathbf{p}$  is:

$$\psi(\mathbf{r}) = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} , \quad (36)$$

where the momentum and wavevector are related by  $\mathbf{p} = \hbar\mathbf{k}$ .

As before, we impose periodic boundary conditions, so that  $\psi(\mathbf{r})$  repeats exactly if we make any displacement  $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}$ , where the three Cartesian components of  $\mathbf{R}$  are:

$$\mathbf{R} = L(l_1, l_2, l_3) , \quad (37)$$

with  $l_\alpha$  being positive, zero or negative integers. We satisfy this condition by requiring that the  $\mathbf{k}$  have the form:

$$\mathbf{k}_{n_1, n_2, n_3} = \frac{2\pi}{L} (n_1, n_2, n_3) , \quad (38)$$

where  $n_\alpha$  are three positive, zero or negative integers, because then:

$$\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}) \exp(2\pi i(l_1 n_1 + l_2 n_2 + l_3 n_3)) = \psi(\mathbf{r}) . \quad (39)$$

In one dimension, the allowed wavevectors  $k_n$  formed a uniformly spaced grid. In the present three-dimensional case, the wavevectors  $k_{n_1, n_2, n_3}$  form a uniformly spaced cubic grid in three-dimensional "reciprocal space", and the spacing of the grid in all three Cartesian directions is  $2\pi/L$ .

As before, to get the ground state, we fill these states (two electrons in each) in order of increasing energy. The energy  $\epsilon_{\mathbf{k}}$  of a state having wavevector  $\mathbf{k}$  is:

$$\epsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m . \quad (40)$$

This means that all states are filled, for which the magnitude  $|\mathbf{k}|$  of the wavevector is less than some value  $k_F$ :  $k < k_F$ . As before,  $k_F$  is called the Fermi wavevector. The energy of the highest occupied state is  $\epsilon_F = \hbar^2 k_F^2 / 2m$ , which is the Fermi energy.

How many occupied states are there? All the occupied states are contained in a sphere in reciprocal space (the Fermi sphere). The volume of this sphere is  $4\pi k_F^3 / 3$ . But since the spacing between the allowed wavevectors is  $2\pi/L$  in each Cartesian direction, the volume per wavevector is  $(2\pi/L)^3$ . Hence, the number of states is  $(4\pi k_F^3 / 3) / (2\pi/L)^3$ . With two electrons in each state, the number of electrons is then:

$$N = k_F^3 L^3 / 3\pi^2 . \quad (41)$$

The relation between density  $\rho = N/L^3$  and Fermi wavevector is thus:

$$k_F = (3\pi^2 \rho)^{1/3} , \quad (42)$$

and the Fermi energy is:

$$\epsilon_F = \hbar^2 (3\pi^2 \rho)^{2/3} / 2m . \quad (43)$$

We now want to find the total energy of the system:

$$E_{\text{tot}} = 2 \sum_{\mathbf{k} \in \text{occ}} \epsilon_{\mathbf{k}} , \quad (44)$$

where the notation  $\mathbf{k} \in \text{occ}$  means that we sum over all wavevectors belonging to occupied states, in other words all wavevectors for which  $k < k_F$ . We replace the sum by an integral, making use of the fact that the reciprocal-space volume per state is  $(2\pi/L)^3$ :

$$\begin{aligned} E_{\text{tot}} &= 2 \left( \frac{L}{2\pi} \right)^3 \int_{k < k_F} \left( \hbar^2 k^2 / 2m \right) d\mathbf{k} \\ &= \frac{\Omega}{4\pi^3} \cdot \frac{\hbar^2}{2m} \cdot 4\pi \int_0^{k_F} k^4 dk = \frac{\Omega \hbar^2 k_F^5}{10\pi^2 m} . \end{aligned} \quad (45)$$

The energy per electron is then:

$$\epsilon_{\text{kin}} = E_{\text{tot}} / N = \frac{\hbar^2}{10\pi^2 m} \cdot \frac{k_F^5}{\rho} . \quad (46)$$

Since  $\rho = k_F^3 / 3\pi^2$ , this is the same as:

$$\epsilon_{\text{kin}} = \frac{\hbar^2}{10\pi^2 m} \cdot 3\pi^2 \cdot k_F^2 = 3\hbar^2 k_F^2 / 10m , \quad (47)$$

which is 3/5 of the Fermi energy. This factor will be noted again when we discuss Thomas-Fermi theory.

The kinetic energy can also be written in another useful way, using the fact that  $k_F = (3\pi^2 \rho)^{1/3}$ :

$$\epsilon_{\text{kin}} = \frac{3\hbar^2}{10m} (3\pi^2 \rho)^{2/3} . \quad (48)$$

### 3.4 The interacting electron gas (jellium) in the Hartree-Fock approximation

In a real material, overall electrical neutrality is ensured by the fact that the total (negative) charge on the electrons is equal and opposite to the total positive charge on the nuclei. However, in the uniform electron gas in which each electron carries a charge  $-e$ , there are no nuclei. But it is essential to ensure electrical neutrality, because otherwise the total Coulomb energy per electron will diverge in the limit of an infinite system, so the energy per electron will not be well defined. To ensure electrical neutrality, it is necessary to assume the presence of a rigid uniform positive “background” charge density, which exactly compensates the total charge of the electrons. The charge density of this rigid background is  $e\rho$ , where  $\rho = N/\Omega$  is the number of electrons per unit volume.

It is impossible to calculate exactly the ground-state energy of interacting jellium. Nevertheless, by a combination of analytic calculations and computer simulations, it is possible nowadays to compute the energy per electron in jellium *almost* exactly. We sketch briefly here how the interaction energy per electron can be calculated in the Hartree-Fock approximation.

As before, we denote the number of electrons by  $N$ , the total volume by  $\Omega$ . We assume that there are equal numbers  $\nu$  of up-spin and down-spin electrons ( $\nu = \frac{1}{2}N$ ). There are therefore  $\nu$  occupied spatial orbitals, which we denote by  $i = 1, 2, \dots, \nu$ , each of these orbitals being occupied by an up-spin electron and a down-spin electron. We denote the space-spin orbitals corresponding to spatial orbital  $i$  and spin-up or spin-down by  $\phi_{i\uparrow}(\mathbf{x})$  and  $\phi_{i\downarrow}(\mathbf{x})$ , where  $\mathbf{x} \equiv (\mathbf{r}, \sigma)$  is the collection of space and spin coordinates. Then the fully anti-symmetric  $N$ -electron wave-function is:

$$\Psi_N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{N!} \sum_P (-1)^P \hat{P} \{ \phi_{1\uparrow}(\mathbf{x}_1) \dots \phi_{\nu\uparrow}(\mathbf{x}_\nu) \phi_{1\downarrow}(\mathbf{x}_{\nu+1}) \dots \phi_{\nu\downarrow}(\mathbf{x}_N) \} . \quad (49)$$

Now the operator representing the electron-electron Coulomb interaction is:

$$\hat{U} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} . \quad (50)$$

In the Hartree-Fock approximation, the ground state is obtained by minimising the expectation value of the Hamiltonian:

$$E_{\text{tot}} = \langle \Psi_N | \hat{H} | \Psi_N \rangle = \langle \Psi_N | \hat{T} + \hat{U} | \Psi_N \rangle \quad (51)$$

with respect to the single-electron orbitals  $\phi_{i\sigma}(\mathbf{x})$ . (Here,  $\hat{T}$  is the total kinetic energy.) For the uniform interacting electron gas, it can be shown that this minimum is obtained when the single-electron orbitals are plane waves  $\exp(i\mathbf{k} \cdot \mathbf{r})$ , exactly as in the non-interacting case. This means that the many-electron Hartree-Fock ground-state wave-function  $\Psi_N(\mathbf{x}_1, \dots, \mathbf{x}_N)$  is precisely the same as the ground-state wave-function of the non-interacting electron gas. Therefore,

the interaction energy is the expectation value  $\langle \Psi_N | \hat{U} | \Psi_N \rangle$  of the interaction energy computed in the non-interacting ground state.

We now skip over some mathematical details, and go straight to the result that the interaction energy is given by:

$$\begin{aligned} \langle \Psi_N | \hat{U} | \Psi_N \rangle &= \frac{e^2}{2} \sum_{i,j=1}^v \sum_{\sigma,\tau} \int \frac{|\phi_{i\sigma}(\mathbf{x})|^2 |\phi_{j\tau}(\mathbf{x}')|^2}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} d\mathbf{x}d\mathbf{x}' \\ &- \frac{e^2}{2} \sum_{i,j=1}^v \sum_{\sigma} \int \frac{\phi_{i\sigma}^*(\mathbf{x})\phi_{j\sigma}(\mathbf{x})\phi_{i\sigma}(\mathbf{x}')\phi_{j\sigma}^*(\mathbf{x}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} d\mathbf{x}d\mathbf{x}' \end{aligned} \quad (52)$$

(Here,  $d\mathbf{x}$  means that we integrate over the volume of the system and sum over spin, and similarly for  $d\mathbf{x}'$ .) As expected, the first term is the Hartree (Coulomb) interaction energy between all the electrons, while the second term is the exchange interaction energy between electrons having the same spin.

Now the Hartree energy cancels exactly against the sum of the Coulomb interaction energy of the positive background with itself plus the interaction energy of the electrons with the background. This can easily be seen by noting that the Hartree term of eqn. (52) is simply the Coulomb interaction with itself of a uniform negative charge distribution of charge density  $-|e|N/\Omega$ . The consequence is that the total interaction energy of the whole system consists only of exchange energy  $E_x$ , which is:

$$\langle \Psi_N | \hat{U} | \Psi_N \rangle = E_x = - \sum_{i=1}^v \sum_{j=1}^v \int \phi_i(\mathbf{r})^* \phi_j(\mathbf{r}) \frac{e^2}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} \phi_i(\mathbf{r}') \phi_j(\mathbf{r}')^* d\mathbf{r} d\mathbf{r}' . \quad (53)$$

But we have noted that the spatial orbitals are plane waves  $\Omega^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r})$  (we have inserted here the normalisation constant  $\Omega^{-1/2}$ ), so that the total exchange energy is:

$$E_x = - \sum_{\mathbf{k} \in \text{occ}} \sum_{\mathbf{k}' \in \text{occ}} \frac{1}{\Omega^2} \int e^{i(\mathbf{k}'-\mathbf{k}) \cdot (\mathbf{r}-\mathbf{r}')} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' , \quad (54)$$

where the notation  $\mathbf{k} \in \text{occ}$  means that the summation goes over occupied orbitals.

The spatial integrals can be performed immediately, using the fact that:

$$\int e^{i\mathbf{k} \cdot \mathbf{r}} \frac{1}{r} d\mathbf{r} = \frac{4\pi}{k^2} , \quad (55)$$

so that we arrive at:

$$E_x = - \frac{e^2}{\epsilon_0 \Omega} \sum_{\mathbf{k} \in \text{occ}} \sum_{\mathbf{k}' \in \text{occ}} \frac{1}{|\mathbf{k}-\mathbf{k}'|^2} . \quad (56)$$

At this point, we can replace the sums over wave-vectors by integrals, using exactly the same procedure as for the non-interacting electron gas: the  $k$ -space volume per wavevector is  $(2\pi)^3/\Omega$ . We then get the exchange energy per electron  $\epsilon_x$  as:

$$\epsilon_x = E_x/N = - \frac{e^2 \Omega}{\epsilon_0 (2\pi)^6 N} \int_{\epsilon_{\mathbf{k}} < \epsilon_F} d\mathbf{k} \int_{\epsilon_{\mathbf{k}'} < \epsilon_F} d\mathbf{k}' \frac{1}{|\mathbf{k}-\mathbf{k}'|^2} . \quad (57)$$

The double integral is somewhat tricky to perform, but can be evaluated analytically, with the result:

$$\int_{\epsilon_{\mathbf{k}} < \epsilon_F} d\mathbf{k} \int_{\epsilon_{\mathbf{k}'} < \epsilon_F} d\mathbf{k}' \frac{1}{|\mathbf{k} - \mathbf{k}'|^2} = 4\pi^2 k_F^4. \quad (58)$$

The final result is:

$$\epsilon_x = -\frac{e^2}{\epsilon_0(2\pi)^6 \rho} \cdot 4\pi^2 k_F^4. \quad (59)$$

To simplify this, note that  $k_F = (3\pi^2 \rho)^{1/3}$ , so that:

$$\begin{aligned} \epsilon_x &= -\frac{e^2}{\epsilon_0(2\pi)^6} \cdot 12\pi^4 \cdot (3\pi^2 \rho)^{1/3} = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{48}{64} \cdot \left(\frac{3\rho}{\pi}\right)^{1/3} \\ &= -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{3}{4} \left(\frac{3\rho}{\pi}\right)^{1/3}. \end{aligned} \quad (60)$$

### 3.5 The energy per electron in jellium

We now summarise the energetics of the uniform interacting electron gas in the Hartree-Fock approximation. The energy per electron is the sum of (a) kinetic energy  $\epsilon_{\text{kin}}$ , which is exactly the same as in the non-interacting electron gas; and (b) exchange energy  $\epsilon_x$ . The formulas are:

$$\begin{aligned} \epsilon_{\text{kin}} &= \frac{3\hbar^2}{10m} \cdot (3\pi^2 \rho)^{2/3} \\ \epsilon_x &= -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{3}{4} \left(\frac{3\rho}{\pi}\right)^{1/3}. \end{aligned} \quad (61)$$

It is important to note that as the electron density  $\rho$  increases, the kinetic energy increases faster than the exchange energy. This means, contrary to what you might naively expect, that interactions become less important at high density.