

Electronic states in confined systems and low dimensions

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Abstract

In this topic we will analyze the properties of electrons in confined systems and low dimensions mainly making use of the free electron approximation. We will first review the general properties of the electronic system; second, the independent electron approximation in 1D, 2D, and 3D; third, the role of confinement in different directions; and, finally, the role of interactions and the effective mass approximation in semiconductors.

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1 Electrons in solids

All the properties of solids are derived from the Coulomb interactions that couple the set of ions and electrons that form a solid or, in general, any material. If we forget about spin degrees of freedom, the Hamiltonian that couples all the electrons and ions is the following:

$$H = \sum_i \frac{-\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{ij} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{iI} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_I \frac{-\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{IJ} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (1)$$

Here lowercase indexes denote electrons and uppercase indexes ions, m is the electron mass, M_I the mass of ion I with charge eZ_I , e is the electron charge, \mathbf{r}_i is the position vector of the electron i , and \mathbf{R}_I is the position vector of the ion I . We are assuming that $4\pi\epsilon_0 = 1$. Diagonalizing this many-body problem is too complex.

If we assume that ions are static and we neglect the kinetic energy of the ions, we can focus first on the electronic part of the problem. This is equivalent to assuming that ions are static particles that stay fixed at their $\mathbf{R} = \{\mathbf{R}_I\}$ positions. In this case, the Hamiltonian to be solved can be written as

$$H = T_e + V_{ee} + V_{ext}, \quad (2)$$

where

$$T_e = \sum_i \frac{-\hbar^2}{2m} \nabla_i^2 \quad (3)$$

is the kinetic energy of the electrons,

$$V_{ee} = \frac{1}{2} \sum_{ij} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (4)$$

is the Coulomb interaction between the electrons, and

$$V_{ext} = - \sum_{iI} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (5)$$

is the external potential that acts upon the electrons, which in this case is the Coulomb interaction between the electrons and the ions. We could also consider any other external potential that affects the electronic system, for instance, the potential imposed by an electromagnetic probe (Raman, Infrared, etc.) or the one imposed by an impurity. Note that in Eq. (2) we have neglected the $\frac{1}{2} \sum_{IJ} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$ Coulomb interaction between the ions. We can safely do that because this term simply adds a constant energy to the electronic system. This term cannot be disregarded, however, if we want to study the dynamics of the ions, i.e., lattice vibrations (phonons).

In order to calculate the properties of the electronic system we need to solve the Schrödinger equation of the electronic Hamiltonian in Eq. (2):

$$H(\mathbf{r})\psi_A(\mathbf{r}) = E_A\psi_A(\mathbf{r}). \quad (6)$$

Here $\mathbf{r} = \{\mathbf{r}_i\}$ is a collective variable that describes the positions of all electrons. This problem is unsolvable because the V_{ee} potential is inseparable.

1.1 Separable potentials and independent electrons

The V_{ee} potential is inseparable because it cannot be written as a sum of potentials in which each addend only affects one electron. The denominator in Eq. (4) makes it impossible as it involves the positions of two electrons. If we neglect the V_{ee} term in the potential and the external potential is separable, i.e it can be written as

$$V_{ext}(\mathbf{r}) = \sum_i V(\mathbf{r}_i), \quad (7)$$

the problem becomes tractable. An example of a separable external potential is indeed the electron-ion potential of Eq. (84), since it can be written as in Eq. (7) with

$$V(\mathbf{r}_i) = \sum_I \frac{-Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}. \quad (8)$$

In this situations in which V_{ee} is neglected and $V_{ext}(\mathbf{r})$ is separable, we are dealing with independent electrons.

In the independent electron case the Hamiltonian can be written as a sum of independent Hamiltonians that act upon only one electron:

$$H(\mathbf{r}) = \sum_i H(\mathbf{r}_i) = \sum_i \left[\frac{-\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r}_i) \right]. \quad (9)$$

Let's assume now that we can write the total wave-function of the whole electron system $\psi_A(\mathbf{r})$ as a product of single-electron wave functions:

$$\psi_{A \equiv \alpha_1, \dots, \alpha_{N_e}}(\mathbf{r}) = \psi_{\alpha_1}(\mathbf{r}_1) \cdots \psi_{\alpha_{N_e}}(\mathbf{r}_{N_e}), \quad (10)$$

where N_e is the total number of electrons in the system. In this case, if we are able to solve the single-electron Hamiltonian,

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_{\alpha}(\mathbf{r}) = E_{\alpha} \psi_{\alpha}(\mathbf{r}), \quad (11)$$

it is straightforward to show that $\psi_{A \equiv \alpha_1, \dots, \alpha_{N_e}}(\mathbf{r})$ is an eigenfunction of the system and

$$E_{A \equiv \alpha_1, \dots, \alpha_{N_e}} = E_{\alpha_1} + \cdots + E_{\alpha_{N_e}} \quad (12)$$

is the eigenenergy of the system. In this sense the independent electrons problem is easy to tackle as long as the single-electron Schrödinger equation in Eq. (11) is solvable.

The fact that electrons are indistinguishable fermionic particles implies that the total wave-function of the system must be antisymmetric to the exchange of any two electrons:

$$\psi_{\alpha_1, \dots, \alpha_{N_e}}(\dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots) = -\psi_{\alpha_1, \dots, \alpha_{N_e}}(\dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots). \quad (13)$$

Therefore, the product of single-particle wave-functions in Eq. (11) cannot be the true wave-function of the electronic system as it is symmetric to the exchange of electrons. An antisymmetric wave-function can be built out of single-particle electronic wave-functions instead with the so-called Slater determinant:

$$\psi_{\alpha_1, \dots, \alpha_{N_e}}(\mathbf{r}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \psi_{\alpha_1}(\mathbf{r}_1) & \dots & \psi_{\alpha_1}(\mathbf{r}_{N_e}) \\ \vdots & \ddots & \vdots \\ \psi_{\alpha_{N_e}}(\mathbf{r}_1) & \dots & \psi_{\alpha_{N_e}}(\mathbf{r}_{N_e}) \end{vmatrix} \quad (14)$$

A Slater determinant is thus the true wave-function of an independent electron many-body system.

An important conclusion from the antisymmetric character of the electronic wave-function is that all single-particle wave-functions must have a different quantum number: $\alpha_i \neq \alpha_j$ for any i and j . In other words, all electrons must have a different quantum number. If this is not the case the wave-function would not be antisymmetric for the exchange of all electron pairs. Therefore, the ground state energy of the system is formed when electrons fill the lowest energy states until we run out of electrons:

$$E_{GS} = E_0 + E_1 + E_2 + \dots + E_F. \quad (15)$$

The highest occupied electronic energy is called the Fermi energy E_F . Here we are assuming that E_0, E_1, \dots are, respectively, the lowest energy of the solution of Eq. (11), the second lowest energy, etc.

It is important to note that electrons are spin 1/2 fermions and, thus, can be on spin up ($|\uparrow\rangle$) or spin down ($|\downarrow\rangle$) states. As we will not consider spin-orbit coupling nor the presence of magnetic fields, both spin up and down states will be degenerate. Therefore, the Slater determinant above can be perfectly used as long as it is assumed that each state is doubly degenerate. If that was not the case each state should be divided in two different states, i.e., $\psi_{\alpha_i}(\mathbf{r}_i)$ into $\psi_{\alpha_i}(\mathbf{r}_i)|\uparrow\rangle$ and $\psi_{\alpha_i}(\mathbf{r}_i)|\downarrow\rangle$.

2 Free electrons

The free electron system is a particular version of the independent electron system in which there is no external potential. Thus, in the free electron case the Hamiltonian is simply $H = T_e$. Obviously the Hamiltonian is separable and everything described in Sec. 1.1 holds. The Schrödinger equation that needs to be solved is thus the following:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_{\alpha}(\mathbf{r}) = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_{\alpha}(\mathbf{r}) = E_{\alpha} \psi_{\alpha}(\mathbf{r}). \quad (16)$$

In the following we will solve this simple differential equation for the 1D, 2D, and 3D cases.

2.1 Free electrons in 1D

In 1D, assuming that the one-dimensional electron gas expands in the x direction, Eq. (16) simply becomes:

$$\frac{-\hbar^2}{2m} \frac{d^2\psi_\alpha(x)}{dx^2} = E_\alpha\psi_\alpha(x). \quad (17)$$

This equation is trivially solved with plane waves:

$$\psi_\alpha(x) \rightarrow \psi_k(x) = e^{ikx}. \quad (18)$$

Plugging in the plane-wave solution into the Schrödinger equation we obtain the dispersion relation of the 1D free electron gas:

$$E_k = \frac{\hbar^2 k^2}{2m}. \quad (19)$$

We see, therefore, that the wave number k is the good quantum number for the free electron gas and it determines the wave function.

The dispersion relation, the relation between the wave number and the energy of the state, shows a parabolic dependence as shown in Fig. 2.1. The ground state of the 1D free electron gas would therefore be formed by occupying all the electronic states up to the Fermi energy E_F . The largest occupied wave number, the quantum number associated to the states with energy E_F , is called the Fermi wave number k_F . In the 1D case, the ground state of the free electron gas is thus formed by occupying all the states from $-k_F$ to k_F .

It is customary to assume that the free electron gas is formed by wire of macroscopic length L , which is much larger than the Fermi wavelength $\lambda_F = 2\pi/k_F$. The plane wave solutions are normalized to this length as

$$\psi_k(x) = \langle x|k \rangle = \frac{1}{\sqrt{L}} e^{ikx}, \quad (20)$$

where we are introducing Dirac's notation. Then, the eigenfunctions are orthonormal,

$$\langle k|k' \rangle = \int_0^L dx \langle k|x \rangle \langle x|k' \rangle = \int_0^L dx \psi_k(x)^* \psi_{k'}(x) = \frac{1}{L} \int_0^L dx e^{i(k-k')x} = \delta_{kk'}, \quad (21)$$

as it must be the case for any eigenfunctions of a Hamiltonian.

It is illustrative to say that the probability density defined by the plane-wave solution of the free electron gas is homogeneous:

$$|\psi_k(x)|^2 = 1/L. \quad (22)$$

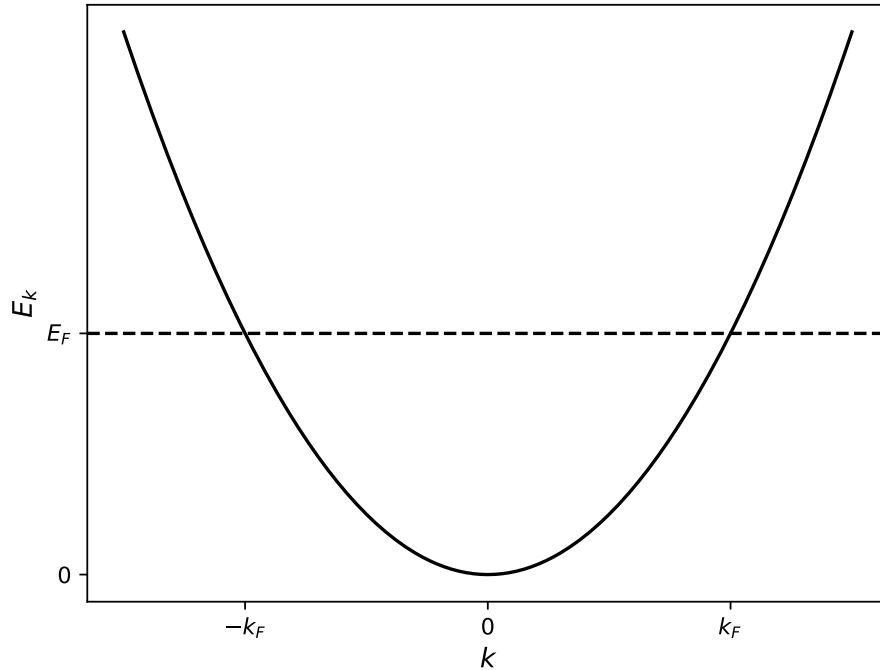


Figure 1: Dispersion relation of the 1D free electron gas.

This means that the probability to find a free electron is the same at any point of space.

The plane wave solutions of the free electron gas, interestingly, are eigenvalues of the momentum operator $p = -i\hbar \frac{d}{dx}$:

$$p\psi_k(x) = -i\hbar ik \frac{1}{\sqrt{L}} e^{ikx} = \hbar k \psi_k(x). \quad (23)$$

Thus, the momentum of a plane wave with wave number k is $p_k = \hbar k$. This allows to define the Fermi momentum as $p_F = \hbar k_F$ as well as the Fermi velocity with this classical analogy:

$$v_F = \frac{\hbar k_F}{m}. \quad (24)$$

Even if this electron gas is finite in size, we do not want to consider surface effects at the moment, but just focus on its bulk properties. In order to suppress the surface, periodic boundary conditions are assumed:

$$\psi_k(x) = \psi_k(x + L). \quad (25)$$

This implies that not all wave numbers are allowed: $kL = 2\pi n$, where n is an

integer. Therefore the allowed wave numbers are

$$k = \frac{2\pi n}{L}. \quad (26)$$

Considering that L is of a macroscopic size the states can be assumed to form a continuous. We see that there is one state (doubly degenerate due to spin) per $2\pi/L$ wave number length.

The number of allowed states due to periodic boundary conditions determines the relation between the electronic density of the system (N_e/L in this 1D case) and the Fermi wave number. The total number of electrons can be calculated simply counting the number of allowed states in the range going from $-k_F$ to k_F :

$$N_e = 2 \times 2k_F \times \frac{1}{2\pi/L}. \quad (27)$$

The first 2 comes from the spin degeneracy. Thus, the electronic density of the 1D free electron gas is

$$n = \frac{N}{L} = \frac{2}{\pi}k_F. \quad (28)$$

The Fermi energy is therefore also exclusively dependent on the density:

$$E_F = \frac{\hbar^2\pi^2n^2}{8m}. \quad (29)$$

So far we have assumed that the electronic system is at 0 K. In this limit all states are occupied up to the Fermi level and unoccupied above. However, at finite temperature this is not exactly true as states are occupied following the Fermi-Dirac distribution function

$$f_F(\varepsilon) = \frac{1}{e^{\frac{\varepsilon-\mu}{k_B T}} + 1}, \quad (30)$$

where k_B is Boltzmann's constant and μ the chemical potential, whose limit at 0 K is E_F . The Fermi-Dirac distribution function is shown in Fig. 2.1.

2.2 Free electrons in 2D

In the 2D case, a similar procedure (Exercise 1) as the one followed for the 1D case in Sec. 2.1 yields the wave functions of the free electron gas of a macroscopic area A :

$$\psi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{A}} e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (31)$$

Here, we assume that the 2D electron gas expands in the x and y directions, thus, $\mathbf{r} = (x, y)$ and $\mathbf{k} = (k_x, k_y)$. Again the wave number \mathbf{k} is a good quantum number. The eigenenergy for each state is

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}, \quad (32)$$

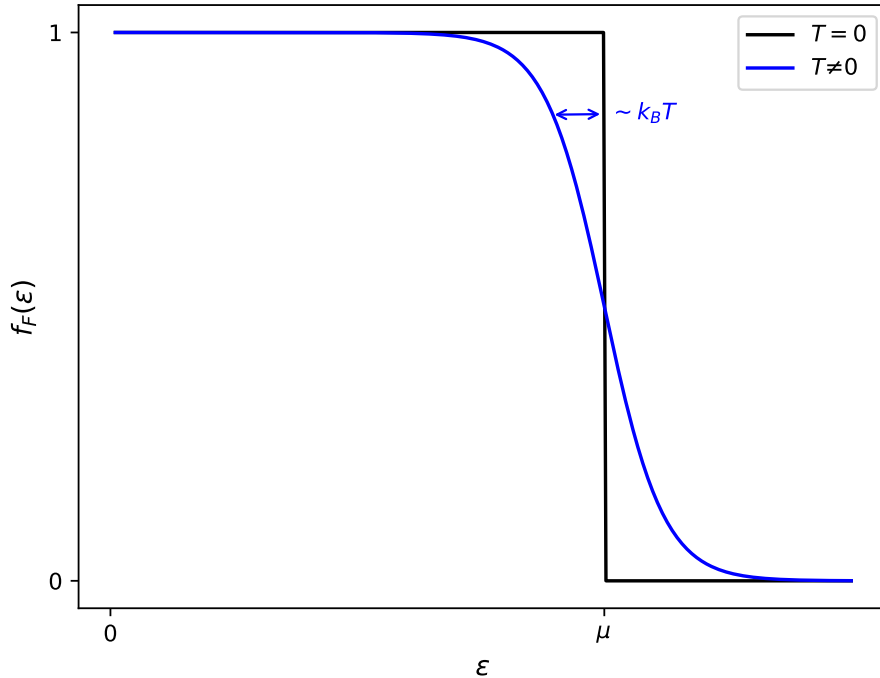


Figure 2: Fermi-Dirac distribution function at different temperatures.

where $k^2 = k_x^2 + k_y^2$. The dispersion describes, thus, a paraboloid.

It is useful to define at this stage the Fermi line, which is the geometric line that is defined by the states at the Fermi level:

$$k_F^2 = k_x^2 + k_y^2. \quad (33)$$

We can see trivially that in the 2D free electron gas the Fermi line is a circle.

Periodic boundary conditions in this case impose that

$$\psi_{\mathbf{k}}(x, y) = \psi_{\mathbf{k}}(x + L_x, y) \quad (34)$$

$$\psi_{\mathbf{k}}(x, y) = \psi_{\mathbf{k}}(x, y + L_y), \quad (35)$$

where L_x and L_y are the macroscopic dimensions of the 2D electron gas, which is assumed to be a square with area $A = L_x L_y$. Consequently, the allowed wave vectors need to fulfill the following conditions:

$$k_x = \frac{2\pi n_x}{L_x} \quad (36)$$

$$k_y = \frac{2\pi n_y}{L_y}, \quad (37)$$

with n_x and n_y integers. This means that for the area occupied by each \mathbf{k} state (doubly degenerate due to spin) in the (k_x, k_y) space is $(2\pi)^2/A$. Considering this feature it is trivial to show that for 2D electron gas with electronic density $n = N_e/A$, the Fermi wave number depends on n as

$$k_F = \sqrt{2\pi n} \quad (38)$$

and the Fermi energy as

$$E_F = \frac{\hbar^2 \pi n}{m}. \quad (39)$$

2.3 Free electrons in 3D

In the 3D case the results are obtained following a similar procedure again (Exercise 2). The 3D electron gas is contained in a box of size L_x , L_y , and L_z whose volume is $V = L_x L_y L_z$. Its orthonormal wavefunctions, normalized in this volume, are:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (40)$$

The eigenenergy for each state is

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}, \quad (41)$$

where $k^2 = k_x^2 + k_y^2 + k_z^2$. The dispersion describes again paraboloid but in higher dimensions that cannot be visualized.

In 3D instead of the Fermi line, the Fermi surface is defined. The Fermi surface is formed by all the \mathbf{k} points that are at the Fermi level. In the case of the 3D free electron gas it is given by

$$k_F^2 = k_x^2 + k_y^2 + k_z^2, \quad (42)$$

which is exactly the equation of a sphere. Thus, the Fermi surface of a 3D free electron gas is a sphere.

Periodic boundary conditions in this case impose that

$$\psi_{\mathbf{k}}(x, y, z) = \psi_{\mathbf{k}}(x + L_x, y, z) \quad (43)$$

$$\psi_{\mathbf{k}}(x, y, z) = \psi_{\mathbf{k}}(x, y + L_y, z) \quad (44)$$

$$\psi_{\mathbf{k}}(x, y, z) = \psi_{\mathbf{k}}(x, y, z + L_z), \quad (45)$$

$$(46)$$

The allowed wave vectors need to fulfill the following conditions:

$$k_x = \frac{2\pi n_x}{L_x} \quad (47)$$

$$k_y = \frac{2\pi n_y}{L_y} \quad (48)$$

$$k_z = \frac{2\pi n_z}{L_z} \quad (49)$$

with n_x , n_y , and n_z integers. This means that for the volume occupied by each \mathbf{k} state (doubly degenerate due to spin) in the (k_x, k_y, k_z) space is $(2\pi)^3/V$. Considering this feature it is trivial to show that for the 3D electron gas with electronic density $n = N_e/V$, the Fermi wave number depends on n as

$$k_F = (3\pi^2 n)^{1/3} \quad (50)$$

and the Fermi energy as

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}. \quad (51)$$

3 Density of states of the free electron gas

In Sec. 2 we have studied the free electron gas and we have seen that indeed there are some differences depending on the dimension. An important magnitude that is useful to calculate properties of compounds is the density of state (DOS), which, as we will see, has clear differences for the free electron gas depending on the dimensionality. The DOS $g(\varepsilon)$ measures the number of available states for a given energy ε . The DOS is normally defined as the number of states per volume, per area, per length, respectively, for the 3D case, 2D case, and 1D cases.

3.1 3D

Following this definition, the DOS should be calculated in the 3D case as

$$g(\varepsilon) = \frac{1}{V} \sum_{\mathbf{k}} 2\delta(\varepsilon - E_{\mathbf{k}}), \quad (52)$$

where the factor 2 comes from the spin degeneracy and $E_{\mathbf{k}}$ is the dispersion relation. The calculation can be performed rather straightforwardly substituting the sum with an integral:

$$\sum_{\mathbf{k}} \rightarrow \frac{1}{(2\pi)^3/V} \int d\mathbf{k}. \quad (53)$$

This is possible since the states are very close together in \mathbf{k} space and each state occupies a volume in this space of $(2\pi)^3/V$. Thus,

$$g(\varepsilon) = \frac{1}{8\pi^3} \int d\mathbf{k} 2\delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) = \frac{1}{\pi^2} \int_0^\infty dk k^2 \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right). \quad (54)$$

Making use of the property of the Dirac delta that states that

$$\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}, \quad (55)$$

where x_i are the poles of $f(x)$,

$$\delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) = \sqrt{\frac{m}{2\hbar^2\varepsilon}} \left[\delta\left(k - \sqrt{\frac{2m\varepsilon}{\hbar^2}}\right) + \delta\left(k + \sqrt{\frac{2m\varepsilon}{\hbar^2}}\right) \right]. \quad (56)$$

With this the DOS becomes of the 3D electron gas becomes

$$g(\varepsilon) = \frac{m}{\pi^2 \hbar^3} \sqrt{2m\varepsilon}. \quad (57)$$

The DOS is useful to calculate several properties that depend on the energy. For example, if we want to calculate the energy density of the 3D electron gas we should simply sum all energies of the electrons and include the spin degeneracy for all occupied states according to the Fermi-Dirac distribution function:

$$u = \frac{1}{V} \sum_{\mathbf{k}} 2E_{\mathbf{k}} f_F(E_{\mathbf{k}}). \quad (58)$$

This can be calculated rather easily with the DOS since

$$u = \int_0^\infty d\varepsilon \frac{1}{V} \sum_{\mathbf{k}} 2\varepsilon f_F(\varepsilon) \delta(\varepsilon - E_{\mathbf{k}}) = \int_0^\infty d\varepsilon \varepsilon g(\varepsilon) f_F(\varepsilon). \quad (59)$$

For the 3D case at 0 K, limit in which the Fermi-Dirac distribution function is a step function, substituting Eq. (57) into the equation above, it is easy to obtain that the energy density is

$$u = \frac{m\sqrt{2m}}{\pi^2 \hbar^3} \frac{2}{5} E_F^{5/2}. \quad (60)$$

3.2 2D

In the 2D limit the DOS is calculated as the number of possible states per area:

$$g(\varepsilon) = \frac{1}{A} \sum_{\mathbf{k}} 2\delta(\varepsilon - E_{\mathbf{k}}). \quad (61)$$

The calculation should be performed substituting the sum with an integral, which in the 2D case should be performed as

$$\sum_{\mathbf{k}} \rightarrow \frac{1}{(2\pi)^2/A} \int d\mathbf{k}, \quad (62)$$

as the area occupied per state is $(2\pi)^2/A$. It is rather straightforward to show that

$$g(\varepsilon) = \frac{m}{\pi \hbar^2} \quad (63)$$

in the 2D limit.

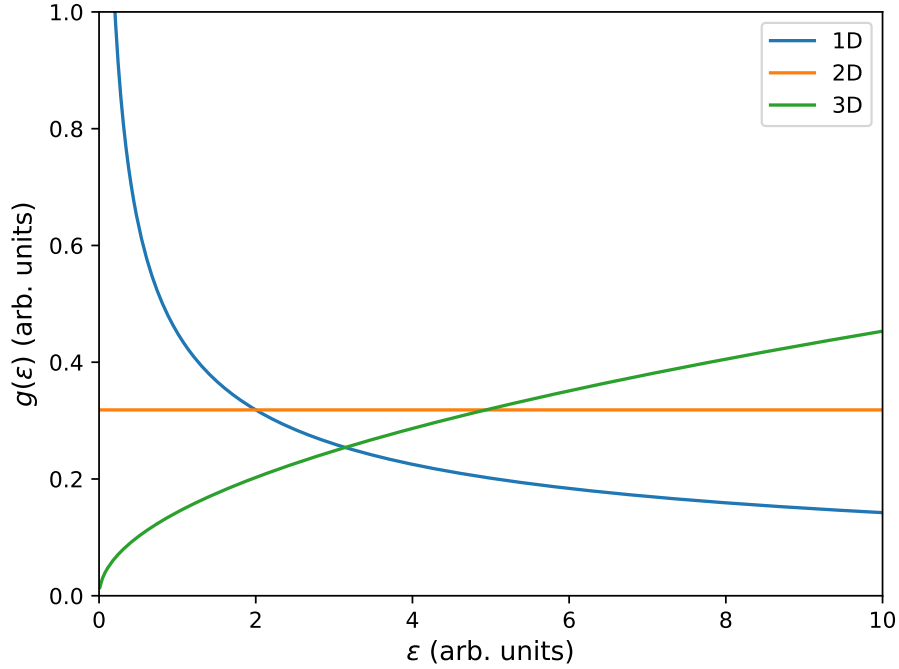


Figure 3: DOS of the free electron gas in different dimensions.

3.3 1D

In the 1D limit the DOS should be calculated as the number of possible states per length:

$$g(\varepsilon) = \frac{1}{L} \sum_k 2\delta(\varepsilon - E_k). \quad (64)$$

The calculation should be performed substituting the sum with an integral, which in the 1D case should be performed as

$$\sum_k \rightarrow \frac{1}{(2\pi)/L} \int dk, \quad (65)$$

as the length occupied per state is $(2\pi)/L$. It is rather straightforward to show that

$$g(\varepsilon) = \frac{1}{\pi\hbar} \sqrt{\frac{2m}{\varepsilon}} \quad (66)$$

in the 1D limit.

Comparing Eqs. (57), (63), and (66) we can see that the dependence on energy of the DOS is extremely different depending on the dimension. In the 3D case the number of allowed states increases with the energy, in the 2D limit

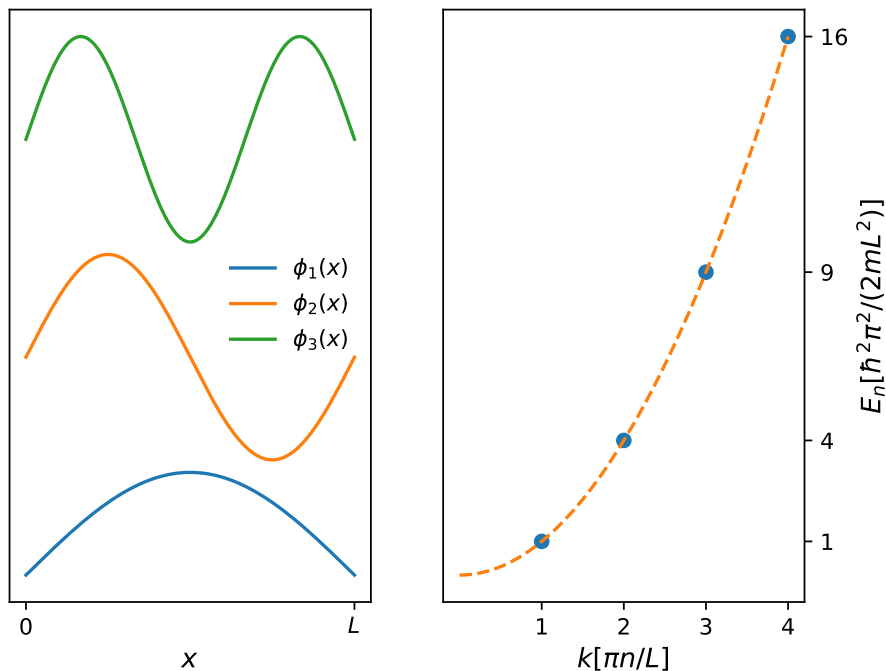


Figure 4: $\phi_n(x)$ wave functions for the electrons in a 1D box of length L (left panel). Discretized dispersion relation compared to the quadratic dispersion of the free electron gas (right).

it is constant, and in the 1D limit it decreases with energy. The three different curves are compared in Fig. 3.3.

4 Confinement

We have thus far studied the free electron gas in different dimensions. However, even if the free electron gas can be realized in low dimensions, for instance in interfaces, it is more common to find systems that are confined in one or several of the Cartesian directions. We will study now the effect of confinement on the electronic states, but first we will overview the simple example of 1D electrons confined in a 1D box.

4.1 Electrons in a 1D box

Let's assume we have a 1D system confined in the space that goes from $x = 0$ to $x = L$. This is obtained by setting the potential to be 0 in this region, and infinity outside. The equation that we need to solve is again Eq. (17), but

now the boundary conditions are different: the wave functions need to vanish at the edges of the box: $\phi_\alpha(0) = \phi_\alpha(L) = 0$. As the Schrödinger equation is a second-order equation, the most general solution can be written as

$$\phi_\alpha(x) = Ae^{ikx} + Be^{-ikx} \quad (67)$$

considering that k is positive. It is easy to show that in order to satisfy these conditions the wave number must be quantized as

$$k_n = \frac{\pi n}{L}, \quad (68)$$

where n is in this case a natural number (1,2,3,...). This result immediately yields to the wavefunctions

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n}{L}x\right) \quad (69)$$

and the corresponding eigenvalues

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2. \quad (70)$$

The dispersion relation and the eigenfunctions are shown in Fig. 4.1. As we can see confinement discretizes the energies and momentum available, contrary to the free electron case, where both the energies and the available wave numbers are continuous. The discretization is larger for smaller L . In fact, in the $L \rightarrow \infty$ limit, the energy jumps vanish and the wave functions become a plane wave.

4.2 2D electron gas confined in one direction

Let's assume now a set of electrons in 3D space, confined in the third direction. Let's assume that the electrons live in a box of dimension $L_x \times L_y \times L_z$, but while L_x and L_y are large, i.e. of macroscopic size, L_z is smaller than the Fermi wavelength. This means that while in the xy plane electrons are not confined, they are strongly confined in the z direction. This is what we call a quantum well. The simplest approximation we can do to analyze this system is to assume that electrons are free, i.e. they satisfy Eq. (16), but with periodic boundary conditions in the xy plane, while in the z direction the wave function must vanish at $z = 0$ and $z = L_z$. Considering that the latter are the boundary conditions of the electrons in a box, the solution of the Schrödinger equation will be a product of the 2D free electron gas and the solution of the electrons in a box:

$$\phi_{k_x, k_y, n}(\mathbf{r}) = \frac{1}{\sqrt{A}} e^{i(k_x x + k_y y)} \sqrt{\frac{2}{L_z}} \sin\left(\frac{\pi n}{L_z} z\right) \quad (71)$$

where n is a natural number. The eigenvalues, or the dispersion relation, will be the following in consequence:

$$E_{k_x, k_y, n} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2) + \frac{\hbar^2 \pi^2}{2mL_z^2} n^2. \quad (72)$$

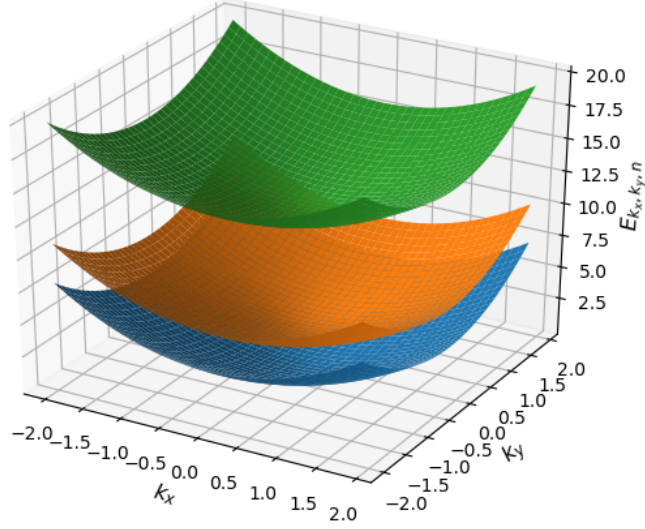


Figure 5: $E_{k_x, k_y, n}$ energy dispersion of free electrons confined in the z direction. The dispersion is formed by paraboloids.

We can see that the dispersion relation is formed by a paraboloid for each value of the quantum number n associated with the confined direction.

With this dispersion relation, the DOS (per volume) of the 2D electron gas confined in the z direction will be

$$g(\varepsilon) = \frac{1}{V} \sum_{\mathbf{k}n} 2\delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m} - E_n\right), \quad (73)$$

where we have assumed that in this case $\mathbf{k} = (k_x, k_y)$ and $E_n = \frac{\hbar^2 \pi^2}{2mL_z^2} n^2$. This can be calculated as follows:

$$\begin{aligned} g(\varepsilon) &= \frac{1}{L_z} \frac{1}{(2\pi)^2} \sum_n \int d\mathbf{k} 2\delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m} - E_n\right) \\ &= \frac{1}{L_z} \sum_n \int_0^\infty dk \frac{k}{\pi} \frac{\delta\left(k - \sqrt{\frac{2m}{\hbar^2}(\varepsilon - E_n)}\right)}{\frac{\hbar^2}{m} \sqrt{\frac{2m}{\hbar^2}(\varepsilon - E_n)}}, \end{aligned} \quad (74)$$

which simplifies to

$$g(\varepsilon) = \frac{1}{L_z} \frac{m}{\pi \hbar^2} \sum_n \theta(\varepsilon - E_n). \quad (75)$$

As we can see the DOS is formed by different steps that increase the DOS each time an energy E_n is reached.

4.3 1D electron gas confined in two directions

Now we assume that the confinement is both in y and z direction, i.e., $L_y, L_z < \lambda_F$. We are talking about a quantum wire. Again the simplest approximation is to assume that we have free electrons, with periodic boundary conditions along x , but the box-like boundary conditions along y and z . In analogy, the eigenfunctions will be

$$\phi_{k,n,m}(\mathbf{r}) = \frac{1}{L_x} e^{ikx} \frac{2}{\sqrt{L_y L_z}} \sin\left(\frac{\pi n}{L_y} y\right) \sin\left(\frac{\pi m}{L_z} z\right), \quad (76)$$

where both n and m are natural numbers. The eigenenergies, or the dispersion relation, is thus

$$E_{k,n,m} = \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2 \pi^2}{2m} \left(\frac{n^2}{L_y^2} + \frac{m^2}{L_z^2} \right). \quad (77)$$

The dispersion relation shows parabolas for each value of n and m .

Let's calculate the DOS of the 1D electron gas confined in y and z :

$$g(\varepsilon) = \frac{1}{V} \sum_{k,n,m} 2\delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m} - E_{n,m}\right), \quad (78)$$

where $E_{n,m} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n^2}{L_y^2} + \frac{m^2}{L_z^2} \right)$. This is equal to

$$g(\varepsilon) = \frac{1}{L_y L_z} \sum_{n,m} \int_{-\infty}^{\infty} \frac{dk}{\pi} \frac{1}{\hbar \sqrt{\frac{2}{m}(\varepsilon - E_{n,m})}} \times \left[\delta\left(k - \sqrt{\frac{2m}{\hbar^2}(\varepsilon - E_{n,m})}\right) + \delta\left(k + \sqrt{\frac{2m}{\hbar^2}(\varepsilon - E_{n,m})}\right) \right], \quad (79)$$

which leads to the final result:

$$g(\varepsilon) = \frac{1}{L_y L_z} \frac{\sqrt{2m}}{\pi \hbar} \sum_{n,m} \frac{1}{\sqrt{\varepsilon - E_{n,m}}} \theta(\varepsilon - E_{n,m}). \quad (80)$$

As we can see, the DOS in this case will have singularities at $\varepsilon - E_{n,m}$, and will decrease as $\varepsilon^{-1/2}$ out of it.

4.4 Electrons in 0D: confinement in three directions

Let's assume now that the confinement is in the three Cartesian directions so that $L_x, L_y, L_z < \lambda_F$. This is what we call a quantum dot. In this case the simplest approximation in which we can describe the electrons in this system is imposing the 3D box boundary conditions on the 3 Cartesian directions to a free electron gas. In analogy with the 1D box, the eigenfunctions of this system are

$$\phi_{n,m,l}(\mathbf{r}) = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin\left(\frac{\pi n}{L_x} x\right) \sin\left(\frac{\pi m}{L_y} y\right) \sin\left(\frac{\pi l}{L_z} z\right), \quad (81)$$

and the eigenenergies

$$E_{n,m,l} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_z^2} \right). \quad (82)$$

$n, m,$ and l are natural numbers. As we can see the eigenenergies form a discrete spectrum that recalls atomic states, clearly different to extended systems like those described above. The DOS is therefore simply

$$g(\varepsilon) = \frac{1}{V} \sum_{n,m,l} 2\delta(\varepsilon - E_{n,m,l}), \quad (83)$$

a collection of Dirac delta functions at the eigenenergies.

In Fig. 4.4 we compare the DOS calculated for the different levels of confinement studied.

5 Crystal structure and effective mass approximation in semiconductors

All the properties we have described so far are based on the free electron system. We have just basically solved the Schrödinger equation Eq. (16) with different boundary conditions, periodic in the extended case and box-like in the confined case. However, electrons interact in solids with the periodic lattice potential

$$V_{ext}(\mathbf{r}) = - \sum_{iI} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}. \quad (84)$$

Indeed, the potential is periodic with the lattice periodicity

$$V_{ext}(\mathbf{r} + \mathbf{R}) = V_{ext}(\mathbf{r}), \quad (85)$$

where \mathbf{R} is a lattice vector:

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3. \quad (86)$$

Here $n_1, n_2,$ and n_3 are integers, while $\mathbf{a}_1, \mathbf{a}_2,$ and \mathbf{a}_3 are the unit cell vectors. Obviously, this potential will affect the electrons and deviate the solution from the free electron description we have thus far studied.

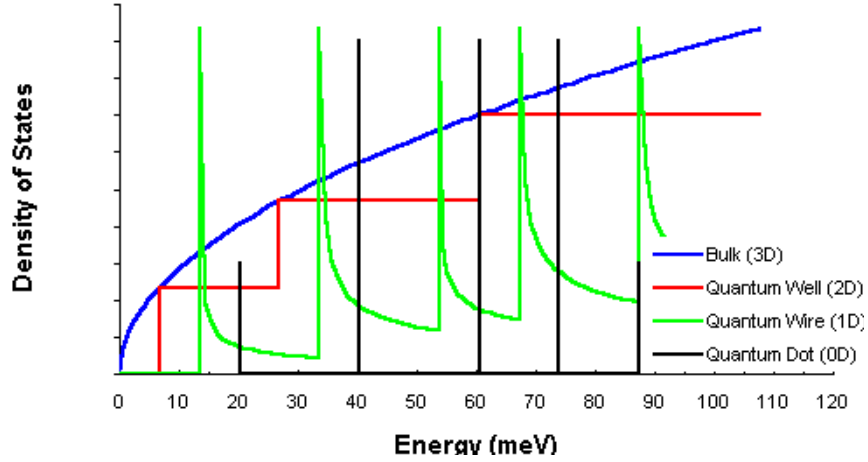


Figure 6: Comparison of the DOS of the 3D free electron gas with the one with confinement to 2D (quantum well), to 1D (quantum wire), and to 0D (quantum dot).

Before starting with the effects of the lattice potential on electrons, let's recall what the reciprocal lattice is. The basis vectors of reciprocal lattice are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad (87)$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \quad (88)$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \quad (89)$$

Any reciprocal lattice vector \mathbf{G} can be written as

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \quad (90)$$

with m_1 , m_2 , and m_3 integers. By construction,

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}. \quad (91)$$

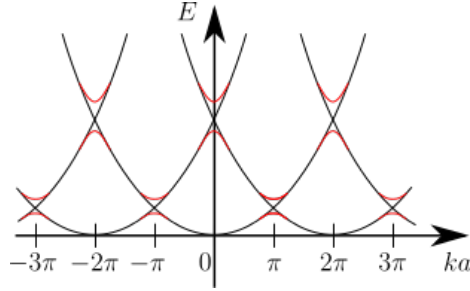


Figure 7: Dispersion relation of the 1D free electron gas (black) and the opening of the gaps due to the interaction with the lattice (red). The lattice has a periodicity of a and the Brillouin zone goes from $k = -\pi/a$ to $k = \pi/a$.

5.1 Bloch's theorem

Bloch's theorem states that for an external lattice-periodic potential that fulfills Eq. (85), the solution of the

$$H\psi_\alpha(\mathbf{r}) = \left(\frac{-\hbar^2}{2m}\nabla^2 + V_{ext}(\mathbf{r}) \right) \psi_\alpha(\mathbf{r}) = E_\alpha\psi_\alpha(\mathbf{r}) \quad (92)$$

Schrödinger equation must be equal to

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}), \quad (93)$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is lattice periodic, i.e. $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$. These are called Bloch states and have a plane wave component plus a lattice-periodic part. Note that the quantum number α has been split in two different quantum numbers, the wave number \mathbf{k} and n . The dependence of the $E_{n\mathbf{k}}$ on the wave number creates the so called band structure of solids, which as a consequence is usually only plotted for states in the Brillouin zone.

Due to the shape of the Bloch states we see that the quantum number \mathbf{k} can be restricted to the Brillouin zone, as the eigenvalues and eigenfunctions of $\mathbf{k}' = \mathbf{k} + \mathbf{G}$ are the same:

$$E_{n\mathbf{k}} = E_{n\mathbf{k}+\mathbf{G}}. \quad (94)$$

Thus, it is enough to calculate the eigenenergies for the first Brillouin zone only. For a 1D lattice with periodicity a we show the band structure of the free electron gas in Fig. 5.1. As we can see the parabolic band appears folded into the Brillouin zone (from $k = -\pi/a$ to $k = \pi/a$) creating more than one state for each \mathbf{k} , which yields to a band structure like dispersion $E_{n\mathbf{k}}$.

5.2 The effect of the lattice on the band structure

Let's assume we want to analyze the effect on the lattice potential on the band structure. Let's assume that the lattice potential is weak and can be treated

perturbatively. In this limit the first order correction to the the plane wave quadratic dispersion will be

$$\langle \mathbf{k} | V_{ext} | \mathbf{k} \rangle = \frac{1}{V} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} V_{ext}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{V} \int d\mathbf{r} V_{ext}(\mathbf{r}). \quad (95)$$

As we can see the correction is independent of \mathbf{k} , thus, this simply implies a rigid correction to the energies. This is a completely negligible effect.

However, in order to reach that conclusion we have assumed that there are no degenerate states. In case, plane-wave states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ are degenerate we should diagonalize the $\langle \mathbf{k}' | V_{ext} | \mathbf{k} \rangle$ matrix to see what the correction on the states is.

$$\begin{aligned} \langle \mathbf{k}' | V_{ext} | \mathbf{k} \rangle &= \frac{1}{V} \int d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} V_{ext}(\mathbf{r}) \\ &= \frac{1}{V} \sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} \int_{unit\ cell} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} V_{ext}(\mathbf{r}) \\ &= \frac{N}{V} \delta_{\mathbf{k}-\mathbf{k}',\mathbf{G}} \int_{unit\ cell} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} V_{ext}(\mathbf{r}) \\ &= V_{ext}(\mathbf{G}) \delta_{\mathbf{k}-\mathbf{k}',\mathbf{G}}, \end{aligned} \quad (96)$$

where $V_{ext}(\mathbf{G})$ is the Fourier transform for the reciprocal lattice \mathbf{G} . So if the difference between the wave numbers of two degenerate states equals a reciprocal lattice vector, the degeneracy will be split and the opened energy gap will be of the order of $V_{ext}(\mathbf{G})$. In the free electron system this happens at zone border. At these points, as shown in Fig. 5.1, gaps will be opened.

5.3 Effective mass in semiconductors

Due to the interaction with the lattice (or potentially other type of interactions as well) gaps are opened in the band structure. It could happen that electrons occupy all states up to the gap. In this case we have an insulator, as there are no free electrons to move. If the gap is small (~ 1 eV) we have a semiconductor. In a semiconductor a small number of electrons might be excited to the unoccupied conduction band from the occupied valence band due to thermal effects or other reasons. When electrons are excited to the conduction band they leave in top of the valence bands empty states that effectively have positive charge. These are called holes. See Fig. 5.3 for a simple sketch of the situation.

The simplest approximation to understand both electrons and holes is to assume they are free electrons and they have a parabolic dispersion. However, electrons or holes do not have the mass of electrons m because the width of the parabola depends on the interaction that opens the gap. This is usually treated assuming that electrons or holes have an effective mass m^* , whose dispersion is then

$$E_{\mathbf{k}} = E_0 + \frac{\hbar^2 k^2}{2m_e^*} \quad (97)$$

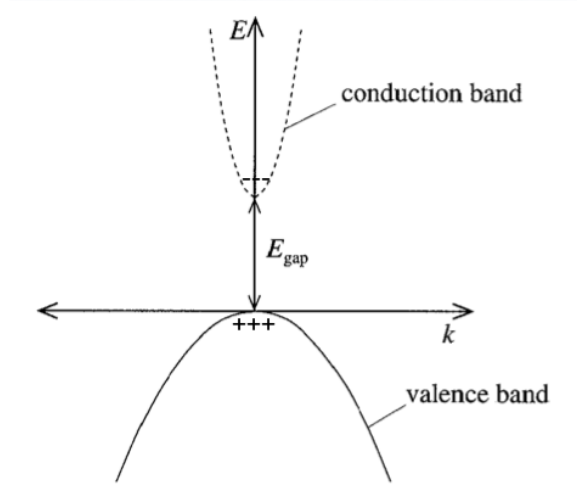


Figure 8: Conduction and valence bands of a semiconductor of gap E_g . Some electrons are excited in the conduction, which leave holes in the valence band.

for electrons and

$$E_{\mathbf{k}} = E_0 - \frac{\hbar^2 k^2}{2m_h^*} \quad (98)$$

for holes (note the dispersion is concave).

Once the effective mass is defined, the DOS for semiconductors with given effective mass can also be calculated with the equations we have obtained for the confined free electron gas before. These equations will be valid in the vicinity of the gap. For the electrons in 3D:

$$g(\varepsilon) = \frac{m_e^*}{\pi^2 \hbar^3} \sqrt{2m_e^* (\varepsilon - E_c)}, \quad (99)$$

where E_c is the minimum energy of the conduction band. For holes in 3D:

$$g(\varepsilon) = \frac{m_h^*}{\pi^2 \hbar^3} \sqrt{2m_h^* (E_v - \varepsilon)}, \quad (100)$$

where E_v is the top energy of the valence band. In the case we have a 2D free electron gas confined in one direction we will have for electrons

$$g(\varepsilon) = \frac{1}{L_z} \frac{m_e^*}{\pi \hbar^2} \sum_n \theta(\varepsilon - E_c - E_n) \quad (101)$$

and

$$g(\varepsilon) = \frac{1}{L_z} \frac{m_h^*}{\pi \hbar^2} \sum_n \theta(-\varepsilon + E_v + E_n) \quad (102)$$

for holes. For the 1D free electron gas confined in two directions we have for electrons

$$g(\varepsilon) = \frac{1}{L_y L_z} \frac{\sqrt{2m_e^*}}{\pi \hbar} \sum_{n,m} \frac{1}{\sqrt{\varepsilon - E_c - E_{n,m}}} \theta(\varepsilon - E_c - E_{n,m}) \quad (103)$$

and for holes

$$g(\varepsilon) = \frac{1}{L_y L_z} \frac{\sqrt{2m_h^*}}{\pi \hbar} \sum_{n,m} \frac{1}{\sqrt{-\varepsilon + E_v + E_{n,m}}} \theta(-\varepsilon + E_v + E_{n,m}). \quad (104)$$

In the equations above m_e^* and m_h^* are the effective masses for electrons and holes, respectively.

6 Exercises

1. Show that the wave functions of the 2D free electron gas of macroscopic area A (with $A = L_x L_y$, L_x and L_y being the dimensions of the square that contain the 2D electron gas) are given by Eq. (31) and the dispersion relation is $\hbar^2 k^2 / (2m)$. Show also the relations between the Fermi energy and wave number and the electronic densities given in Eqs. (38) and (39).
2. Show that the wave functions of the 3D free electron gas of macroscopic volume V (with $V = L_x L_y L_z$, and L_x , L_y , L_z being the dimensions of the box that contains the 3D electron gas) are given by Eq. (40) and the dispersion relation is $\hbar^2 k^2 / (2m)$. Show also the relations between the Fermi energy and wave number and the electronic densities given in Eqs. (50) and (51).
3. Calculate the energy density (total energy per length) of the 1D electron gas.
4. Calculate the total number of electrons per unit area of a 2D free electron gas confined in one direction (quantum well).
5. Calculate the total number of electrons per unit length of a 1D free electron gas confined in two directions (quantum wire).