



Quantum Mechanics 2

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Current version: February 23, 2021

3 Chapter 5: Identical Particles in Quantum Mechanics

Learning Goals

- To formulate and solve the Schrodinger equation in the case of **two-particle systems**.
- To determine the implications that in quantum mechanics we deal with systems of **genuinely indistinguishable particles**.
- To formulate the **Pauli exclusion principle** and to derive its consequences for the structure of multi-electron atoms.
- To explain fundamental properties about the general **structure of solids** by means of basic quantum-mechanical properties.
- To formulate the concept of **band structure** in solids and use it to classify materials in terms of their electrical conductivity properties.

In this section of the lecture notes we present the main concepts discussed in **Chapter 5** (“**Identical Particles**”) of the course textbook. The goal of these lecture notes is to provide a self-consistent study resource for the students, which is then complemented by the live lectures (and their recordings), the tutorial sessions, as well as their own study of the textbook. The relevant textbook sections are indicated below, material from other sections not listed there will not be required for the examination.

Textbook sections

- **5.1:** Two-Particle Systems.
- **5.2:** Atoms.
- **5.3:** Solids.

Up to now, in your study of quantum mechanics you have only considered **one-particle systems** (including the hydrogen atom, which can be expressed essentially as a one-particle problem). As you know from classical mechanics, in general the description of many-body systems ramps up quickly in difficulty: the two-body problem in classical mechanics can be solved exactly but already the three-body problem does not admit a closed solution. However, at the classical level, systems of **non-interacting particles** are trivial, in that their solution is the combination of independent solutions of the one-particle problem.

However, the situation is completely different in the case of quantum mechanics, and the state vectors for systems composed by more than one particle will in general be different from a trivial combination of one-particle states. The reason for this marked difference is that in quantum mechanics we often deal with systems of **indistinguishable particles**: an electron is identical to any other electron anywhere in the Universe.

This appears at first sight to be a rather minor point, but careful consideration of the implications that dealing with identical particles has in quantum mechanics has deep consequences, from explaining what makes a solid well, “solid”, to the allowed options in which spins can be combined in many-particle states (which has impact in for instance in quantum technologies). And these implications are already there even for **non-interacting particles**: as we will see we can obtain many interesting results even neglecting the interactions between the particles in our system.

3.1 Two-particle systems

As mentioned above, up to now we have considered quantum systems composed by a **single particle**. For example, we have solved the Schroedinger equation in three dimensions for the hydrogen atom and found the wave functions of the electronic orbitals $\psi_{nlm}(r, \theta, \phi)$. Note that although in this case the system was composed by a proton and an electron, the proton did not play any role other than generating the electric potential thus was not part of the wave function of the system (technically, it did not play any **dynamical role** in the system).

We will consider now a quantum state composed by **two dynamical particles**. Its wave function will now depend on the position of the two particles, $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ and its time evolution will be determined by the solution of the time-dependent Schroedinger equation

$$i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \left(-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t) \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, t), \quad (3.1)$$

where in general the two particles will have different masses m_1 and m_2 , and the potential energy now depends on the position vectors of the two particles as well as on the time, $V(\mathbf{r}_1, \mathbf{r}_2, t)$. The generalised statistical interpretation tells us that the square of the wave function, $|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2$, will be normalised to one when integrating over all possible values of \mathbf{r}_1 and \mathbf{r}_2 .

Here we will consider *time-independent potentials*, such that the time evolution of the eigenfunctions of the Hamiltonian is given as usual by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2) \exp\left(-\frac{iEt}{\hbar}\right), \quad (3.2)$$

where the spatial component of the wave function satisfies the time-independent Schroedinger equation

$$\left(\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2) \right) \psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2), \quad (3.3)$$

in terms of the kinetic terms for the two particles and of the potential energy. Solving a two-body Schroedinger equation is in general much more difficult than its one-body counterparts, but in some cases we actually can reduce the solution of Eq. (3.3) to the solutions of separate one-body problems.

The simplest scenario for Eq. (3.3) is that of **non-interacting particles**, where each particle moves in some external potential but they do not interact among them. Note that here the meaning of “non-interacting” is *not* that we have two free particles, but that the two particles in the system interact only with an external potential but not among them. In this case, the potential energy simplifies to

$$V(\mathbf{r}_1, \mathbf{r}_2) = V_1(\mathbf{r}_1) + V_2(\mathbf{r}_2), \quad (3.4)$$

and it is easy to see that Eq. (3.3) admits a solution where the total wave function **factorises** into two one-particle wave functions

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2), \quad (3.5)$$

where ψ_a and ψ_b indicate two different one-particle wavefunctions, each of which satisfies their a separate one-particle Schroedinger equation:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m_1}\nabla_1^2 + V_1(\mathbf{r}_1)\right)\psi_a(\mathbf{r}_1) &= E_a\psi_a(\mathbf{r}_1), \\ \left(-\frac{\hbar^2}{2m_2}\nabla_2^2 + V_2(\mathbf{r}_2)\right)\psi_b(\mathbf{r}_2) &= E_b\psi_b(\mathbf{r}_2), \end{aligned} \quad (3.6)$$

with the total energy of the system being given by $E = E_a + E_b$. Note that the situation where we have **two free particles** is a particular case of this, and the equations that we need to solve are:

$$\begin{aligned} -\frac{\hbar^2}{2m_1}\nabla_1^2\psi_a(\mathbf{r}_1) &= E_1\psi_a(\mathbf{r}_1), \\ -\frac{\hbar^2}{2m_2}\nabla_2^2\psi_b(\mathbf{r}_2) &= E_2\psi_b(\mathbf{r}_2). \end{aligned} \quad (3.7)$$

Note, however, that if we know the solutions of the one-particle equations, Eq. (3.6), then the case of two particles interacting in some external potential falls on the same complexity class as that of a system composed by two free particles, and it is *not* more difficult to solve.

Entanglement in two-particle systems

For non-interacting particles, the two-body wave function factorises into two one-body wave functions of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2),$$

which are eigenvalues of the total Hamiltonian \hat{H} with energy $E = E_a + E_b$. However, this does not imply that all valid quantum states of this two particle system can be described by such factorisable state vectors. For example, if ψ_c and ψ_d are two other one-particle solutions, surely I can have

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sqrt{\frac{1}{3}}\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \sqrt{\frac{2}{3}}\psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2) \quad (3.8)$$

which **cannot be expressed as a product of one-particle wavefunctions**. These states are called **entangled states** and are of huge importance in quantum mechanics.

Another situation that admits a relatively compact analytic treatment is that of **central potentials**, such as the Coulomb potential that we discussed in the case of the hydrogen atom. In this case, the interaction between the two particles depends only on their **relative distance** but not on their relative orientation

$$V(\mathbf{r}_1, \mathbf{r}_2) = V(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (3.9)$$

Then the two-body Schroedinger equation

$$\left(\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|) \right) \psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2), \quad (3.10)$$

can be factorised into **two separate one-body equations**, one for the motion around the center of mass of the system and the other for the free motion of the center of mass.

Thus we have found that there are two situations where solving a two-particle Schroedinger equation is relatively feasible:

- When the two particles **do not interact with each other**, but only with some external potential.
- When the two particles **interact with each other via a central potential**, but then do not interact with any external potential.

In both cases, we can reduce the two-body system to two one-particle problems that can be solved separately. However, in general the two particles will experience **both** interactions with some external force and mutual interactions between them. An important example in this context is the helium atom, a system composed by an atomic nucleus with two protons $Z = 2$ and then two electrons orbiting around it. The potential experienced by the electrons receives contributions both from the electrical attraction with the positively charged nucleus and from the negative repulsion between the two electrons:

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi\epsilon_0} \left(-\frac{2e^2}{|\mathbf{r}_1|} - \frac{2e^2}{|\mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \quad (3.11)$$

The Schroedinger equation for the Helium atom cannot be solved analytically in closed form. We will need to introduce some approximations such as perturbation theory and the variational principle, which we will introduce later in the course.

Now, as we discuss next, even for the cases where we can solve exactly the Schroedinger equation for the two body problem (say for non-interacting particles), there remain some important issues to be addressed in the case that the two particles that compose the system are **indistinguishable**. To illustrate this point, when we wrote the factorised solution for the total wave function of a system composed by two non-interacting particles we had

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2), \quad (3.12)$$

we implicitly assumed that we could **distinguish the two particles**, since we assume that the first particle occupies the one-particle state ψ_a and the second ψ_b . But this is not possible if I can tell apart the two particles! We will see next how to quantum mechanics solves this conundrum.

Indistinguishable particles: fermions and bosons Let us assume that we have now two noninteracting particles, the first one occupying the one-particle state $\psi_a(\mathbf{r})$ and the second one in another one-particle state $\psi_b(\mathbf{r})$.¹⁰ As demonstrated above, the total wave function of the two-particle system will be the product of

¹⁰While here I work with position-representation wavefunctions, the concept is fully general and can also be formulated in terms of the Dirac notation.

the two one-particle states:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2). \quad (3.13)$$

Now, by writing the total wave function in this manner I am assuming that somehow we can **tell apart** the “first particle” from “the second particle” (that is, that we can stick labels on them). But in quantum mechanics **particles are indistinguishable**, not because of some technical limitation of our measurement apparatus, but because **every electron is identical to every other electron**, and every hydrogen atom is identical (and will always be) identical to any other hydrogen atom. In other words, in quantum mechanics it is not possible to say “this electron” or “that electron”, but only “a electron”.

To take into account that quantum mechanics deals with particles that are indistinguishable, we need to modify the two-body wavefunction for **identical particles** in a way that it does not implicitly assume that we can tell particles apart. This can be done in two ways. First, we can write

$$\psi_+(\mathbf{r}_1, \mathbf{r}_2) = A [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]. \quad (3.14)$$

where the only thing that we assume is that there is “a particle” in orbital ψ_a and another of the same particles in orbital ψ_b , and where A is an overall normalisation constant. Another possible option that achieves the same goal is

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = A [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]. \quad (3.15)$$

with the minus sign between the two terms¹¹

Actually, given a specific type of particle, only one of these two relations will be valid. If we assume normalised one-particle states, then we can have only one of the following two situations:

- We denote as **bosons** as those elementary particles for which their two-body wave function is

$$\frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)].$$

Bosons have the defining property that their total wave function is **symmetric** under the exchange of the two particles: $\psi_+(\mathbf{r}_1, \mathbf{r}_2) = \psi_+(\mathbf{r}_2, \mathbf{r}_1)$. All particles with **integer spin** are bosons (for example the photon, with $s = 1$ or the Higgs boson, with $s = 0$).

- We denote as **fermions** those elementary particles for which their two-body wave function is

$$\frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)].$$

Fermions have the defining property that their total wave function is **antisymmetric** under the exchange of the two particles: $\psi_-(\mathbf{r}_1, \mathbf{r}_2) = -\psi_-(\mathbf{r}_2, \mathbf{r}_1)$. All particles with **half-integer spin** are fermions (for example the electron and the proton, both with $s = 1/2$).

Here we take this property as an axiom of **quantum mechanics**. The formal connection between the spin of a particle and the symmetry properties of the total wave function under the exchange of two particles can be demonstrated in quantum field theory and is known as the **spin-statistics theorem**. Here the situation is similar as for the Heisenberg uncertainty principle, which despite its name was not a fundamental principle but rather a consequence of the more fundamental axioms of quantum mechanics.

¹¹Actually, there are cases where one can have also a *complex phase* between the two terms, leading to exotic quasi-particles such as anyons, but we will not discuss this case further in this course.

The Pauli exclusion principle

A direct consequence of the of the **spin-statistics axiom** of quantum mechanics is that **two fermions cannot occupy the same quantum state**. To see this, consider two non-interacting fermions that occupy the same one-particle quantum state ψ_a . The combined two particle wave function would then be:

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] = 0. \quad (3.16)$$

hence only when the two one-particle states are different from each other the two-particle wave function of a fermion system will be non-zero. This central result of quantum theory is known as the **Pauli exclusion principle** and as we will see later in this chapter has crucial implications for the structure of matter.

The infinite square well with two particles. In order to illustrate how differences between fermions and bosons can have very significant consequences for the properties of quantum systems, let us consider the following system. Assume that we have **two noninteracting particles** with the same mass confined in the infinite square well potential in one dimension. For simplicity, let's work in units where the width of the well is $L = 1$ and that the particle mass is $m = 1$. The potential energy for this system is then

$$\begin{aligned} V(x) &= 0 & 0 < x < 1, \\ V(x) &= \infty & x \leq 0, x \geq 1. \end{aligned}$$

The one-particle states and energies of this potential are are quantised in terms of a single principle quantum number n and are given by

$$\psi_n(x) = \sqrt{2} \sin(n\pi x), \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2}, \quad n = 1, 2, 3, \dots \quad (3.17)$$

Let us consider three different scenarios for this system, and as we will see whether or not particles are distinguishable or indistinguishable, and in the latter case whether they are fermions or bosons, has important consequences for the resulting energy spectrum of this system.

- The two particles are **distinguishable**, that is, they are **not identical**.

If we call n_1 the energy level occupied by the first particle and n_2 that by the second particle, the total wave function is just the regular product of one-particle wave functions

$$\psi_{n_1 n_2}(x) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \quad E_{n_1 n_2} = E_{n_1} + E_{n_2} = \frac{(n_1^2 + n_2^2)\pi^2 \hbar^2}{2} \equiv (n_1^2 + n_2^2)K. \quad (3.18)$$

For example, the ground state is $\psi_{11}(x)$ with energy $E_{11} = 2K$ and the first excited state is double-degenerate, with two possible two-particle states having associated the same total energy

$$\begin{aligned} \psi_{21}(x_1, x_2) &= 2 \sin(2\pi x_1) \sin(\pi x_2), & E_{21} &= 5K, \\ \psi_{12}(x_1, x_2) &= 2 \sin(\pi x_1) \sin(2\pi x_2), & E_{12} &= 5K. \end{aligned} \quad (3.19)$$

By varying n_1 and n_2 , we can then construct all the possible two-particle wave functions allowed for this system.

Note that each two-particle state is **uniquely specified** by the choice of the two one-particle quantum numbers n_1 and n_2 . In this respect, the two-particle states are trivial combinations of one-particle states, much in the same way as what would happen in classical physics for non-interacting particles.

- The two particles are **indistinguishable**, that is, they are **identical**, and specifically they are **bosons**¹²

In this case, the ground state will be unchanged, since clearly the two-particle wave function

$$\psi_{11}(x_1, x_2) = 2 \sin(\pi x_1) \sin(\pi x_2), \quad (3.20)$$

is **symmetric** under the exchange of the two particles:

$$\psi_{11}(x_2, x_1) = 2 \sin(\pi x_2) \sin(\pi x_1) = \psi_{11}(x_1, x_2), \quad (3.21)$$

as should be the case for the wave function of a system composed by bosons.

However, you also notice that the (degenerate) first excited states in Eq. (3.19) are *not symmetric* under the exchange of the two particles. For example, if I take ψ_{21} and I exchange the particles

$$\psi_{21}(x_2, x_1) = 2 \sin(2\pi x_2) \sin(\pi x_1) = \psi_{12}(x_1, x_2) \neq \psi_{21}(x_1, x_2), \quad (3.22)$$

and hence $\psi_{21}(x_2, x_1)$ and $\psi_{12}(x_2, x_1)$ constructed as in Eq. (3.19) are not acceptable for a system composed by two identical bosons.

Instead, we must symmetrise the two-particle wave function corresponding to the first excited state of the system by using the appropriate prescription for bosons. In this way we find that the wave function of the first excited state is given by

$$\psi(x_1, x_2) = \sqrt{2} [\sin(2\pi x_1) \sin(\pi x_2) + \sin(\pi x_1) \sin(2\pi x_2)], \quad E = 5K, \quad (3.23)$$

which is obviously invariant under the exchange of the two particles, $\psi(x_2, x_1) = \psi(x_1, x_2)$.

This result illustrates a first important consequence of the quantum statistics: the first excited state, which is degenerate in the case of distinguishable particles, becomes **non-degenerate** in the case of indistinguishable bosons. That is, quantum statistics breaks the degeneracy which is present in the case of distinguishable particles.

- The two particles are **indistinguishable**, that is, they are **identical**, and specifically they are **fermions**.

In this case the two-particle state which corresponding to the ground state of the previous two cases is not allowed due to the **Pauli exclusion principle**: two fermions cannot occupy the same one-particle quantum state. In this case the wave function of the ground state (the state with the lowest energy) is

$$\psi(x_1, x_2) = \sqrt{2} [\sin(2\pi x_1) \sin(\pi x_2) - \sin(\pi x_1) \sin(2\pi x_2)], \quad E = 5K, \quad (3.24)$$

which as requested for fermion systems is **antisymmetric** under the exchange of any two particles, given that $\psi(x_1, x_2) = -\psi(x_2, x_1)$.

Here we note another very powerful consequence of quantum statistics: as compared to the case with distinguishable particles, or to the case with indistinguishable bosons, in the case of fermions the

¹²Note that the following discussion requires the two particles to be identical bosons, not *only* bosons. For example, a system composed by two *distinct* spin-1 particles can still be treated as in the previous case, since here we do not deal with genuinely indistinguishable particles.

energy of the ground state is increased. In other words, keeping everything the same (mass, potential etc) the **zero-point energy** of this quantum system is increases by a factor 2.5 just from replacing bosons by fermions, which is quite a remarkable result.

Hence, to summarize we have illustrated with this relatively simple example some important consequences of accounting for the fact that quantum mechanics deals with indistinguishable particles: as compared to system composed by distinguishable particles, we can

- Change the energy and eigenfunctions spectrum of the system by **removing degeneracies**.
- Change the energy and eigenfunctions spectrum of the system by **increasing the zero-point energy of the ground state**.

In the rest of this chapter, we will study other implications that systems of indistinguishable particles have in quantum mechanics.

Exchange forces. The previous example demonstrates that the quantum statistics that apply in systems composed by identical particles can lead to significance consequences in the properties of quantum states. Let us investigate a bit more what is the underlying reason for this behaviour.

Consider now a one-dimensional system composed by two particles, and consider two one-particle quantum states $\psi_a(x)$ and $\psi_b(x)$ (orthonormal between them). Following the previous discussion, the two-particle wave function will be given in the various relevant cases by:

- **Distinguishable particles:** $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$.
- **Indistinguishable particles (bosons):** $\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2))$.
- **Indistinguishable particles (fermions):** $\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}} (\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2))$.

Let us now evaluate the expectation value of the **square of the separation between the two particles**:

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle, \quad (3.25)$$

in the three cases under consideration, and compare their results. The reason to choose this quantity is that, as we will demonstrate, quantum statistics leads to an effect on the average distance between the two particles which is akin to either a repulsive or attractive force, known as **exchange forces**. However, this term is a bit of a misnomer since the particles are **non-interacting**: it will *look like* there is a force acting upon them, but it is just a geometrical consequence of how wave functions of identical particles must be constructed in quantum mechanics.

- **Distinguishable particles:** in this case the relevant expectation values are

$$\langle x_1^2 \rangle = \int dx_1 \int dx_2 x_1 |\psi(x_1, x_2)|^2 = \int dx_1 x_1 |\psi_a(x_1)|^2 \int dx_2 |\psi_b(x_2)|^2 = \langle x^2 \rangle_a, \quad (3.26)$$

where we have used that the one-particle wave functions are appropriately normalised. The result is then the expectation value of the position squared in the one-particle state $\psi_a(x)$. Using a similar strategy, we can easily evaluate the other matrix elements to find:

$$\langle x_2^2 \rangle = \langle x^2 \rangle_b, \quad \langle x_1 x_2 \rangle = \langle x \rangle_a \langle x \rangle_b, \quad (3.27)$$

and hence the sought-for expectation value for the square of the distance between the two particles in the system is given by

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b . \quad (3.28)$$

Note how this result is consistent with the particles being distinguishable: $\langle (x_1 - x_2)^2 \rangle$ is determined by combining matrix elements that only involve *one-particle states*: the two particles **don't talk to each other at all** (as should be the case, since these are non-interacting particles).

Let's compare this result with the other two cases, corresponding now to indistinguishable particles.

- **Indistinguishable particles:** now the same calculation yields

$$\begin{aligned} \langle x_1^2 \rangle &= \int dx_1 \int dx_2 x_1^2 |\psi_{\pm}(x_1, x_2)|^2 = \frac{1}{2} \int dx_1 \int dx_2 x_1^2 |(\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2))|^2 \\ &= \frac{1}{2} \int dx_1 \int dx_2 x_1^2 \left(|\psi_a(x_1)\psi_b(x_2)|^2 + |\psi_b(x_1)\psi_a(x_2)|^2 \right. \\ &\quad \left. \pm \psi_a^*(x_1)\psi_b^*(x_2)\psi_b(x_1)\psi_a(x_2) \pm \psi_b^*(x_1)\psi_a^*(x_2)\psi_a(x_1)\psi_b(x_2) \right) \\ &= \frac{1}{2} \int dx_1 x_1^2 |\psi_a(x_1)|^2 \int dx_2 |\psi_b(x_2)|^2 + \frac{1}{2} \int dx_1 x_1^2 |\psi_b(x_1)|^2 \int dx_2 |\psi_a(x_2)|^2 \\ &\quad \pm \frac{1}{2} \int dx_1 x_1^2 \psi_a^*(x_1)\psi_b(x_1) \int dx_2 \psi_b^*(x_2)\psi_a(x_2) \\ &\quad \pm \frac{1}{2} \int dx_1 x_1^2 \psi_b^*(x_1)\psi_a(x_1) \int dx_2 \psi_a^*(x_2)\psi_b(x_2) = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b) , \end{aligned} \quad (3.29)$$

where we have used that the one-particle states are normalised and *orthogonal* among them. Clearly, we will get the same result for $\langle x_2^2 \rangle$, since the two particles are indistinguishable. Now for the third term in the calculation, it is when things become interesting:

$$\begin{aligned} \langle x_1 x_2 \rangle &= \int dx_1 \int dx_2 x_1 x_2 |\psi_{\pm}(x_1, x_2)|^2 \\ &= \frac{1}{2} \int dx_1 \int dx_2 x_1 x_2 |(\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2))|^2 \\ &= \frac{1}{2} \int dx_1 \int dx_2 x_1 x_2 \left(|\psi_a(x_1)\psi_b(x_2)|^2 + |\psi_b(x_1)\psi_a(x_2)|^2 \right. \\ &\quad \left. \pm \psi_a^*(x_1)\psi_b^*(x_2)\psi_b(x_1)\psi_a(x_2) \pm \psi_b^*(x_1)\psi_a^*(x_2)\psi_a(x_1)\psi_b(x_2) \right) \end{aligned}$$

which by evaluating each of the individual integrals gives

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{1}{2} \int dx_1 x_1 |\psi_a(x_1)|^2 \int dx_2 x_2 |\psi_b(x_2)|^2 \\ &\quad + \frac{1}{2} \int dx_1 x_1 |\psi_b(x_1)|^2 \int dx_2 x_2 |\psi_a(x_2)|^2 \\ &\quad \pm \frac{1}{2} \int dx_1 x_1 \psi_a^*(x_1)\psi_b(x_1) \int dx_2 x_2 \psi_b^*(x_2)\psi_a(x_2) \\ &\quad \pm \frac{1}{2} \int dx_1 x_1 \psi_b^*(x_1)\psi_a(x_1) \int dx_2 x_2 \psi_a^*(x_2)\psi_b(x_2) \\ &= \frac{1}{2} (2 \langle x \rangle_a \langle x \rangle_b \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) = \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2 , \end{aligned} \quad (3.30)$$

in terms of the **overlap integral** between the two one-particle states defined as

$$\langle x \rangle_{ab} \equiv \int dx x \psi_a^*(x) \psi_b(x). \quad (3.31)$$

Note that this overlap integral arises only when we have indistinguishable particles: it is a consequence of the cross-terms that we get when we square the (anti-)symmetric two-particle wave function $\psi_{\pm}(x_1, x_2)$ (so it is a direct consequence of the quantum statistics requirements).

Putting together the three terms, we obtain the counterpart of Eq. (3.28) for indistinguishable particles:

$$\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2, \quad (3.32)$$

which is different from the case of the system composed by two distinguishable particles, and furthermore the result varies if we consider a system of bosons and a system of fermions.

Combining these results together, we therefore obtain that the distinguishability or not of the particles that compose a two-particle quantum system has a direct physical consequence in the expectation value of the square of their average spatial distance:

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp |\langle x \rangle_{ab}|^2, \quad (3.33)$$

which is different for bosons than for fermions:

- For *identical bosons*, on average the two particles will tend to be **closer together** as compared to the case of two distinguishable particles.
- For *identical fermions*, on average the two particles will tend to be **farther apart** as compared to the case of two distinguishable particles.

The exchange force for identical particles

The result of Eq. (3.33) indicates that a system of two identical bosons behaves as if there was an **attractive force** between them, while a system of two identical fermions behaves on the contrary as if there was a **repulsive force** between them. This putative force is often called **exchange force**, which is not really accurate since there is no physical interactions between the two particles (the system is non-interacting!), it is a consequence of the symmetry requirements on the two-particle state vectors of indistinguishable particles without classical counterpart.

We note that there is an interesting limit of the above result which corresponds to those configurations where the overlap integral vanishes (or becomes infinitesimally small):

$$\langle x \rangle_{ab} \equiv \int dx x \psi_a^*(x) \psi_b(x) \rightarrow 0. \quad (3.34)$$

For instance, this would be the case in situations where the one-particle states $\psi_a(x)$ and $\psi_b(x)$ are only non-zero in different regions of x , like when two electrons are really far from each other. This implies that systems of two identical particles for which the overlap integral Eq. (3.31) can be treated **as if they were distinguishable**: it makes full sense to tell two electrons apart if they are separated by kilometers (but not if the separation is of a few nanometers!).

The electron spin reloaded. In Sect. 2.5 we discussed how to combine the spin of two particles and to determine the possible options for the total spin S and its z -component S_z of the system. There we saw that we can combine the spin of two spin-1/2 fermions (such as electrons) into four states, three of them characterised by a total spin $s = 1$,

$$\begin{aligned} |1\ 1\rangle &= |\uparrow\uparrow\rangle \quad (s = 1, m = 1), \\ |1\ 0\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad (s = 1, m = 0), \\ |1\ -1\rangle &= |\downarrow\downarrow\rangle \quad (s = 1, m = -1). \end{aligned} \quad (3.35)$$

which are known as the **triplet states**, and another with vanishing total spin $s = 0$, the **singlet state**:

$$|0\ 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

As we discussed, the triplet states are *symmetric* under the exchange of two particles, while the singlet one is instead **antisymmetric**: if you exchange the two electrons you get

$$\frac{1}{\sqrt{2}} (|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) = -\frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = -|0\ 0\rangle. \quad (3.36)$$

What is the connection between the spin combinations of a two-particle system and the general requirement that the wave function of a system of two fermions must be antisymmetric upon their exchange? Well, for a two electron system, the **total wave function** is the product of the spatial and the spin parts of the wave function. For example, we could have

$$\psi(\mathbf{r}_1, \mathbf{r}_2) |s\ m\rangle, \quad (3.37)$$

with the spin part $|s\ m\rangle$ being either one of the three triplet states or the singlet state defined above.¹³ In such a case, the antisymmetry requirement of the total wave function of the two-electron system then implies:

- If the two electrons occupy the *same position state*, one has that $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1)$, so then the spin state must be the antisymmetric *singlet state* to ensure that the total wave function is antisymmetric upon the exchange of the two particles.
- If the two electrons have associated a *symmetric singlet state*, then the spatial part of the wave function will be non-zero only if it is antisymmetric $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$ to ensure that the total wave function is antisymmetric upon the exchange of the two particles.

The Pauli exclusion principle for electrons

We have thus demonstrated that **two electrons can occupy the same position state** (say, the same electronic orbital ψ_{nlm} in the hydrogen atom) only if their spin state is the **singlet state**, that is, only if the z -component of their spins points in opposite directions. This is why in a given non-degenerate quantum state we can only accommodate two fermions: provided their spins are in opposite direction, this is the only configuration that ensures an antisymmetric total wave function.

¹³At least, if we want our state to have well defined s and m values: as you know, any linear superposition of valid spin states represents also a *bona fide* state of the system.

The generalised symmetrisation principle. In the previous discussion we have restricted ourselves to systems of two non-interacting particles. However, the **generalised symmetrisation principle** of quantum mechanics has associated a much stronger requirement: a system of identical particles must be either **symmetric** (for bosons) or **antisymmetric** (for fermions) upon the exchange of any of the particles that compose it.

Let us denote the state vector of a general two-particle system as $|(1, 2)\rangle$. Then we define the **exchange operator** \hat{P} as follows

$$\hat{P}|(1, 2)\rangle = |(2, 1)\rangle. \quad (3.38)$$

The square of this operator is the identity operator $\mathbb{1}$, given that

$$\hat{P}^2|(1, 2)\rangle = \hat{P}\left(\hat{P}|(1, 2)\rangle\right) = \hat{P}|(2, 1)\rangle = |(1, 2)\rangle, \quad (3.39)$$

from where it follows that the eigenvalues of \hat{P} are ± 1 . If two particles are identical, clearly the Hamiltonian will be invariant under the exchange $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ and therefore \hat{P} and \hat{H} commute and represent compatible observables:

$$\left[\hat{H}, \hat{P}\right] = 0. \quad (3.40)$$

Now, recall the **generalised Ehrenfest theorem** that determined the time evolution of an observable in terms of its commutation relations with the Hamiltonian operator:

$$\frac{d}{dt}\langle\mathcal{O}\rangle = \frac{i}{\hbar}\langle\left[\hat{H}, \hat{\mathcal{O}}\right]\rangle + \left\langle\frac{\partial\hat{\mathcal{O}}}{\partial t}\right\rangle, \quad (3.41)$$

This relation applied to the case of the exchange operator yields

$$\frac{d}{dt}\langle P\rangle = 0 \quad (3.42)$$

implying that if a quantum system starts in one of the eigenstates of \hat{P} (that is, it is either symmetric $\langle P\rangle = 1$ or antisymmetric $\langle P\rangle = -1$ upon the exchange of the two particles), it will remain this way forever. In other words, the **symmetry properties** of a quantum state upon the exchange of two particles are **time-invariant**.

The **generalised symmetrisation axiom** of quantum mechanics tells us that these properties are the same for n -particle system composed by indistinguishable fermions or bosons. That is, only states which satisfy

$$\hat{P}_{ij}|(1, 2, \dots, i, \dots, j, \dots, n)\rangle = |(1, 2, \dots, j, \dots, i, \dots, n)\rangle = \pm|(1, 2, \dots, i, \dots, j, \dots, n)\rangle, \quad (3.43)$$

are **allowed** in quantum mechanics, where \hat{P}_{ij} is the exchange operator applied to particles i and j of the system, and the positive sign holds for bosons and the negative one for fermions.

As mentioned above, actually this generalised symmetrisation requirement is not an axiom but a consequence of the principles of relativistic quantum mechanics (the **spin-statistics theorem**), though this difference will not have any practical implication for the discussions that we will have in the rest of the course.

3.2 Considerations for multi-electron atoms

Equipped with a better understanding of the quantum mechanical consequences and requirements of systems composed by identical (indistinguishable) particles, we can extend our discussion of the hydrogen atoms to **atoms composed by more than one electron**. The starting point is the Hamiltonian operator \hat{H} for a neutral atom with Z protons, $A - Z$ neutrons, and Z electrons, which is given by

$$\hat{H} = \sum_{j=1}^Z \left[\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right) \right] + \frac{1}{2} \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}, \quad (3.44)$$

which is composed by the kinetic energy term for each electron, the attractive potential between each electron and the positive charge $+Ze$ of the atomic nucleus, and the **electric pair-wise repulsion** between electrons. Note that the factor $1/2$ in the repulsive term is introduced to avoid double counting. Except for the hydrogen case ($Z = 1$), this Hamiltonian is not solvable unless we introduce some approximations such as perturbation theory, which we will do later in the course.

The simplest possible multi-electron atom is helium ($Z = 2$), for which the above Hamiltonian reduces to the following operator:

$$\hat{H} = \sum_{j=1}^2 \left[\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right) \right] + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (3.45)$$

The most drastic approximation which allows us to solve the corresponding Schrodinger equation is to completely **neglect the electron repulsion**. In this case, the system reduces to two non-interacting particles (since the electrons now experience only the attractive potential from the atomic nucleus) and as we know from the previous discussion the total two-particle wave function can now be computed exactly in terms of the one-particle wave functions.

With this approximation, the Hamiltonian of the helium atom simplifies to

$$\hat{H} = \sum_{j=1}^2 \left[\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j} \right) \right], \quad (3.46)$$

which has the same form of the Hamiltonian for a system of non-interacting particles. Therefore, we know that in this crude approximation the Helium wave function can be **factorised** into the product of the one-particle wavefunctions of a **hydrogen-like atom**, such that

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2), \quad (3.47)$$

where note that in general the quantum numbers of the two one-particle wave functions will be different.

Entangled states

However, this is certainly not the only option for the possible electronic wave functions of the Helium atom: we can have also linear combinations of the one-body eigenstates of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{3}{5}\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2) + \frac{4}{5}\psi_{\tilde{n}\tilde{l}\tilde{m}}(\mathbf{r}_1)\psi_{\tilde{n}'\tilde{l}'\tilde{m}'}(\mathbf{r}_2). \quad (3.48)$$

Note that these will be **entangled states** in that they cannot be written as a combination of specific one-particle states.

In these entangled states, the two particles are intrinsically, well, entangled: if I measure the energy (or the angular momentum) of particle 1, I will know for sure what will be the energy (or the angular momentum) of particle 2 **without measuring it**, even if the two particles are separated by a very large spatial distance.

Since the energies of hydrogen-like atoms with Z protons scale as $Z^2 E_n^H$ in terms of the energy levels of the hydrogen atom, recall Eq. (2.72), we know that in this approximation the total energy of the Helium atom system will be specified by the two principal quantum numbers n and n' and given by

$$E_{n,n'} = 4(E_n + E_{n'}) , \quad (3.49)$$

in terms of the energies E_n of the electronic orbitals of the hydrogen atom. The ground state in this approximation for the Helium atom will now be given by

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} . \quad (3.50)$$

To derive this expression, we have used that the ground state wave function of the hydrogen atom is

$$\psi_{100}(\mathbf{r}) = R_{10}(r)Y_{00}(\theta, \phi) = \frac{2}{a^{3/2}} e^{-r/a} \sqrt{\frac{1}{4\pi}} = \frac{1}{\pi a^{3/2}} e^{-r/a} , \quad (3.51)$$

and then used that from the definition of the Bohr radius, Eq. (2.58), I need to replace a by a/Z if instead of a single proton I have Z protons in the atomic nucleus, as is the case for hydrogen-like atoms.

Since the spatial part of this Helium ground state wave function, Eq. (3.50), is symmetric, $\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_2, \mathbf{r}_1)$, then the fact that electrons are fermions implies that the spin part of the wave function must be **antisymmetric**, and thus can only be the **singlet configuration**, with the z component of their spins pointing in opposite directions. Hence we conclude that the total wave function of the helium atom will be given by

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2)|0\ 0\rangle = \frac{1}{\sqrt{2}}\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (3.52)$$

in terms of the tensor product of the spatial and spin states of the wavefunctions, in the approximation where we neglect the electrostatic repulsion between the two electrons.

Neglecting the repulsive interactions between the two electrons is of course not a good approximation in any sense (note that the strength of the mutual electron repulsion is only half of the effect of the positive attraction from the nucleus). Below we provide some strategies in which to improve our predictions for the energies and the wave functions of the Helium atom.

Shielding and the effective charge. In the very crude approximation where we completely neglect the repulsive interaction between the two electrons, the ground state of Helium has an energy of

$$E_0 = 4 \times 2 \times (-13.6 \text{ eV}) = -109 \text{ eV} , \quad (3.53)$$

to be compared with the experimentally determined value of $E_0 = -78.975 \text{ eV}$, which is off by almost 30%. Of course, this is not unexpected: the electron repulsive interactions is by no means a subleading effect, and hence it is expected that our crude approximation is not very close to the actual result.

The basic assumption that underlies the orbital approximation that we have used is that the motion of the two electrons in the system is *uncorrelated* between them: it is not affected by its mutual repulsive interaction. However, we know that this is not the case: the mutual repulsion between the two electrons will modify their motion around the nucleus to some extent. While we cannot compute fully this effect, we can

account for it in an approximate manner:

The effective electric charge

In multi-electron atoms, one electron feels the **average presence** of the other electron. For example, for some configurations the two electrons will have little overlap, while for other configurations they will be on average closer. So effectively, the total positive electric charge felt by the electron will be smaller than the value Z from the protons in the nucleus, since the presence of the other electron will be reducing it. One then defines the **effective charge of the atomic nucleus** as the one that one electron experiences due to the *smearing* induced by the presence of the other electron.

In the case of the helium atom, we will have that this smearing will lead to an effective charge $Z_{\text{eff}} < Z = 2$ smaller than the number of protons in the nucleus. This effect is also known as **shielding**: the positive charge of the nucleus felt by a given electron is partially shielded by the other electrons that are also orbiting around it. In this case, this effective electric charge of the nucleus turns out to be $Z_{\text{eff}} = 1.62$. Note that in principle the value of Z_{eff} can be different depending on the specific orbital, but for the He atom with only two electrons it is the same for all electronic orbitals.

Hence we find that once we account for the effects of shielding via the effective electric charge, the spatial wave function of the ground state of the Helium atom will be

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{Z_{\text{eff}}^3}{\pi a^3} e^{-Z_{\text{eff}}(r_1+r_2)/a}, \quad (3.54)$$

with $1 \leq Z_{\text{eff}} \leq 2$ quantifying the strength of the shielding effect. Therefore, we have shown how, within the **orbital approximation**, one can construct the wave functions for the electronic orbitals of the helium atom in terms of the wave functions that we derived in the previous chapter for the hydrogen-like atoms.

Furthermore, we know already that s -type orbitals have a higher likelihood to be found close to the nucleus at $r = 0$ and therefore the effective charge that they experience will be larger than that of the p -type orbitals, which on average are further away from the protons in the nucleus. This effect can be observed from the table below, which compares the value of the effective electric charge Z_{eff} of Helium with that associated to the different orbitals of Carbon (with $Z = 6$):

Element	Z	Orbital	Z_{eff}
He	2	1s	1.6875
C	6	1s	5.6727
		2s	3.2166
		2p	3.1358

For similar reasons, the value of the shielding constant for d -type orbitals will also be different than for the s - and d -type orbitals: an electron in a d -type orbital is on average more likely to be found farther from the nucleus than that of an p -type orbital, and thus one expects a more intense shielding. We can also see that for a given type of orbital, say a s -type orbital, the shielding constant will be larger for more excited states with larger n , which on average are found farther from the atomic nucleus.

Therefore, if we denote by $\sigma_{n,l}$ the shielding constant associated to an orbital with quantum numbers (n, l) , we will have the following rules of thumb:

- For orbitals with a fixed principal quantum number n , the larger the value of l the higher the value of

the shielding constant, for example we have that

$$\sigma_{3,s} \leq \sigma_{3,p} \leq \sigma_{3,l}. \quad (3.55)$$

- For orbitals with a fixed angular quantum number l , the larger the value of the principal quantum number n the higher the value of the shielding constant, for example we have that

$$\sigma_{1,s} \leq \sigma_{2,s} \leq \sigma_{3,s}. \quad (3.56)$$

Note also that this is not a fundamental rule and that there are exceptions to the above general principle.

Therefore, we see that in a multi-electron atom the amount of shielding experienced by the electrons will **depend on the orbital that they occupy**. For this reason, in order to evaluate for example the wavelength of photons involved in the transitions between the orbitals of a multi-electron atom, we need to use the following expression for the electron energy:

$$E_{n,\ell} = - \left[\frac{m_e}{2\hbar^2} \left(\frac{Z_{\text{eff}}^{(n,\ell)} e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{\left(Z_{\text{eff}}^{(n,\ell)} \right)^2 E_1^H}{n^2} = - \frac{(13.6 \text{ eV}) \times \left(Z_{\text{eff}}^{(n,\ell)} \right)^2}{n^2}, \quad (3.57)$$

Note that now the energy levels depend **both** on the quantum numbers n and ℓ , rather than only an n as is the case of the hydrogen-like atoms. The reason of this difference is that now the electric charge $Z_{\text{eff}}^{(n,\ell)}$ will vary with the orbital, and different values of ℓ will have associated different effective charges.

To summarise, the effective charge approximation allows us to improve our estimates of the energies and wave functions for multi-electron atoms, as compared to the scenario where we completely neglect the electrostatic repulsion between their electrons.

3.3 Implications for solid-state structure

The quantum mechanical theory of identical particles in general, and the associated Pauli exclusion principle in particular, have huge implications for our understanding of the structure of **solid-state matter**, such as crystalline solids. Here we will introduce two quantum-mechanical models for the solid state and highlight the role of quantum mechanical statistics in determining its properties.

3.3.1 The free-electron gas

We can understand a crystalline solid as a three-dimensional system of atoms (or molecules) which occupy some geometric, periodic lattice structure. The electrons in these atoms can be classified into **core electrons**, that do not participate in chemical bonding, and **valence electrons**, which correspond to those electrons occupying the outermost orbitals and that are responsible to establish chemical bonds. These valence electrons are known to be **delocalized**: they are not bound to their original atoms, but can rather move freely across the whole solid, jumping their way across the different atoms in the crystalline lattice. Furthermore, these valence electrons are known to form a **electronic band**, which is a region of the phase space where the electrons can occupy any of a continuum of energy values (as opposed to the discrete energy spectrum that characterise the electronic orbitals of individual atoms).

Here, first of all we will study the consequences of the fact that the electrons are delocalised in the solid by means of the **free electron gas model**, and afterwards we will quantify the implications of the periodicity

of the atoms in a crystal to explain the appearance of the electronic energy bands using a periodic potential composed by Dirac delta functions.

To very first approximation, we can therefore consider a solid as an **infinite square potential well** in three dimensions: an electron is free to move everywhere within the solid but cannot jump outside it. In other words, the potential that the electron will experience in this system is given by

$$\begin{aligned} V(x, y, z) &= 0 & 0 < x < l_x, 0 < y < l_y, 0 < z < l_z \\ V(x, y, z) &= \infty & \text{otherwise} \end{aligned} \quad (3.58)$$

where l_x, l_y, l_z are the dimensions of the solid (the potential well) across the x , y , and z directions. For this potential, the Schroedinger equation is nothing but the free-particle Schroedinger equation in three dimensions. Its solutions will be subject to the usual **boundary condition** that the wave function must vanish at the surface of the solid, in the same way as in the infinite quantum well in one dimension:

$$\psi(x=0, y, z) = \psi(x=l_x, y, z) = \psi(x, y=0, z) = \psi(x, y=l_y, z) = \psi(x, y, z=0) = \psi(x, y, z=l_z) = 0.$$

Since we have a free-particle time of equation, It is then to convince yourselves that its wave function factorises into a product of the one-particle solutions of the infinite quantum well,

$$\psi(x, y, z) = X(x)Y(y)Z(z), \quad (3.59)$$

where we have defined the individual components of the wave function as:

$$\begin{aligned} X(x) &= A_x \cos(k_x x) + B_x \sin(k_x x), & k_x &= \sqrt{\frac{2mE_x}{\hbar^2}}, \\ Y(y) &= A_y \cos(k_y y) + B_y \sin(k_y y), & k_y &= \sqrt{\frac{2mE_y}{\hbar^2}}, \\ Z(z) &= A_z \cos(k_z z) + B_z \sin(k_z z), & k_z &= \sqrt{\frac{2mE_z}{\hbar^2}}, \end{aligned}$$

which satisfy the boundary conditions if $A_x = A_y = A_z = 0$ and $k_x l_x = n_x \pi$, $k_y l_y = n_y \pi$ and $k_z l_z = n_z \pi$ where as usual n_i are positive integers and B_i are integration constants fixed by the normalisation of the wave function.

Therefore we have demonstrated that the wave function for an electron confined into a three-dimensional box (our model for a solid) is given by

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right), \quad (3.60)$$

while the corresponding electron energies will be

$$E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m}, \quad (3.61)$$

in terms of the magnitude of the **wave vector** $\mathbf{k} = (k_x, k_y, k_z)$. Every possible value of the wave vector

corresponds to a different choice of quantum numbers:

$$(k_x, k_y, k_z) = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z} \right), \quad n_x, n_y, n_z = 1, 2, 3, \dots, \quad (3.62)$$

and therefore to a different electronic wavefunction. Note that the wave vector has units of 1/length, and it is often referred as to spanning the **conjugate space** of position space.

In order to understand the properties of this free-electron gas system, it is useful to think in terms of the three-dimensional vector space spanned by the **wave vector** $\mathbf{k} = (k_x, k_y, k_z)$. If you imagine a grid at integer values of k_i , then every node in the grid represents a possible **one-particle state** of the system. Since each grid point is separated by π/l_x , π/l_y , and π/l_z in the x , y , and z directions respectively, the volume of each block in the grid is

$$V_{\text{k-block}} = \frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}. \quad (3.63)$$

In these discussions one must be careful, since $V_{\text{k-block}}$ refers to a **volume in the k -space** (the conjugate space), rather than V which is volume in position space.

If we had a single electron in this system, we would be done and we could end the discussion here. But of course, a solid is not composed by a single electron but by a **very large number of them**. For example, for a solid composed by N atoms, each atom will contribute with handful d of valence electrons, and hence the total number of electrons that will compose our **free electron gas** (free, except for not being able to jump outside the boundaries of the material) will be

$$N_{\text{electrons}} = Nd. \quad (3.64)$$

Since electrons are fermions, they must obey the Pauli exclusion principle, and hence for a given value of wave vector $\mathbf{k} = (k_x, k_y, k_z)$ (hence, for a given volume $V_{\text{k-block}} = \pi^3/V$) we can have at most **two electrons**. These electrons must form a **singlet state** with spins pointing in opposite directions.

Therefore, the total volume in k -space occupied by the electrons in this system will be

$$\frac{1}{2} \times V_{\text{k-block}} \times N_{\text{electrons}} = \frac{1}{2} \times \frac{\pi^3}{V} \times Nd, \quad (3.65)$$

where the 1/2 factor comes since two electrons occupy one $V_{\text{k-block}}$. Since (k_x, k_y, k_z) is an array of positive integer numbers, electrons will occupy first the states with lowest k_i and once these are occupied they will occupy higher wave vectors. The volume of the resulting octant of a sphere in k -space, once all electrons have filled the available states, will be given by

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nd}{2} \left(\frac{\pi^3}{V} \right), \quad (3.66)$$

where the radius of this k -space sphere is known as the Fermi momentum:

$$k_F = \left(\frac{3Nd\pi^2}{V} \right)^{1/3} = (3\rho\pi^2)^{1/3} \quad (3.67)$$

where we have defined the **free electron density** as $\rho \equiv Nd/V$, namely the number of free (valence) electrons in the free electron gas system per (physical) unit volume. The surface of this sphere, populated by the electrons with the highest values of the wave vector \mathbf{k} , is known as the **Fermi surface**.

The electrons with wave vector \mathbf{k} spanning the surface of the Fermi sphere will have the highest energies

in the whole material. By recalling the dispersion relation for free particles, $E = \hbar^2 k^2 / 2m$, we can determine the energy of those electrons, which is denoted as the **Fermi energy**:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3} \quad (3.68)$$

The position of the Fermi energy has a crucial impact of the properties of a solid, for example in determining its electrical conductivity properties. From this result we observe how the denser the material, the higher the value of its Fermi energy.

Position versus moment (wave number) space

You should be careful with the distinction between **position** and **moment** space, also denoted as x -space and k -space. The electrons occupy only a sphere (octant) in moment (that is, in energy space), but they remain **delocalised** in position space. Each electron, irrespectively of its wave vector \mathbf{k} , has some finite probability of being found everywhere within the solid, as indicated by the wave function Eq. (3.60). Hence the Fermi sphere is a geometrical construct in moment space, which does not have a counterpart in position space.

We can now evaluate the total energy of my system of Nd electrons in this free-electron gas model. Within the Fermi sphere in k -space, a shell with (infinitesimal) thickness dk contains a volume

$$dV = \frac{1}{8} (4\pi k^2) dk. \quad (3.69)$$

Now, the **density of electrons in k -space** is $2/V_{k\text{-block}} = 2V/\pi^3$, since each k -block within the Fermi sphere contains two electrons. Hence, we have that the number of electrons in this infinitesimal shell is

$$dN_{\text{el}} = \frac{1}{8} (4\pi k^2) dk \times \frac{2V}{\pi^3} = \frac{V}{\pi^2} k^2 dk. \quad (3.70)$$

Furthermore, a state represented by the wave vector \mathbf{k} has associated an energy of $E = \hbar^2 k^2 / 2m$, and therefore the energy of the shell will be

$$dE = dN_{\text{el}} \times \frac{\hbar^2 k^2}{2m} = \left(\frac{V}{\pi^2} k^2 dk \right) \times \left(\frac{\hbar^2 k^2}{2m} \right) = \frac{V \hbar^2 k^4}{2\pi^2 m} dk. \quad (3.71)$$

At this point, in order to evaluate the total energy of the free-electron gas system, I only need to integrate over all available wave vectors, from $k \simeq 0$ for the ground state up to the Fermi energy k_F . We obtain the following result:

$$E_{\text{tot}} = \int_0^{k_F} \frac{V \hbar^2 k^4}{2\pi^2 m} dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m}. \quad (3.72)$$

It is convenient to simplify this important result by exploiting the expression of the Fermi energy Eq. (3.68), which remember is the energy of the electrons with the highest wave numbers \mathbf{k} of the system. By doing this we find that the total energy of the free electron gas is:

$$E_{\text{tot}} = \frac{\hbar^2 (3\pi^2 Nd)^{5/3}}{10\pi^2 m} V^{-2/3}. \quad (3.73)$$

The total energy grows with the number of free electrons as $N_{\text{el}}^{5/3}$, and decreases with the volume of the solid. The latter result can be understood by the fact that in the $V \rightarrow \infty$ limit and fixed number of electrons, the

volume of the k -block vanishes and electrons occupy states with very low energies.

While we are referring of this system as a free-electron gas, this *gas* is very different from the usual gases in that the electrons themselves are **non-interacting**, and thus their energy Eq. (3.73) is **purely quantum mechanical** in origin (as opposed to a regular gas, whose energy is ultimately thermal in origin). Despite this different origin, this quantum mechanical energy exerts a very measurable pressure on the walls of a solid, in the same way as the pressure of a gas arises from the collisions of its constituent molecules with the walls of the contained.

We can determine the **quantum mechanical pressure** exerted by our free-electron gas as follows. If the solid (container of the electron gas) expands by an amount dV , you can see that its total energy decreases:

$$dE_{\text{tot}} = -\frac{2}{3} \frac{\hbar^2 (3\pi^2 N d)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{\text{tot}} \frac{dV}{V}. \quad (3.74)$$

If you recall from your thermal physics course the relation between **work, pressure and volume**,

$$dW = PdV, \quad (3.75)$$

we find that the quantum mechanical pressure exerted by the electrons on the walls of the solid is given by:

$$P = \frac{2}{3} \frac{E_{\text{tot}}}{V} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3}, \quad (3.76)$$

which is stronger the higher the electron density of the material.

The existence of such quantum mechanical pressure, sometimes referred to as **degeneracy pressure**, provides some input to the question of why a **cold solid does not collapse**, demonstrating that what (partially) ensures its “solidity” is not thermal effects (which have been ignored) nor the interactions of the electrons among them or with the atomic nuclei (which we have neglected). A cold solid does not collapse because it is composed of identical fermions, and fermions do not like to occupy the same quantum state!

Note that it is quite remarkable how we have managed to produce a reasonably good prediction for the properties of a solid using exclusively the fact that **electrons are fermions**, without saying a single word about their interactions. This demonstrates that many of the fundamental properties of solids are dictated by basic quantum mechanical considerations, rather than from the details of the specific interactions present within in the system.

3.3.2 Band structure in solids

The main limitation of the free electron gas model is that it considers a solid as a collection of non-interacting electrons restricted to the material volume, but ignores the fact that these electrons arise from the valence orbitals of atoms that are distributed in a more or less **regular manner** within the solid. Thus this model neglects the interactions of these valence electrons with the atoms that compose the solid. In order to improve the free electron model, we need to account for, at least in an approximate way, the **interactions between the atoms in the solid and the electrons**.

As in the case of the free-electron gas, it can be shown that the specific **details of the atom-electron interactions** are not relevant, and that many important properties of solids can be recovered just by taking into account the fact that the atomic nuclei are stationary and **distributed regularly** within the solid. Hence, the defining feature of the model we are going to present now is that the regular arrangement of the atoms within a crystalline solid gives rise to **periodic potential**, which repeats itself in the three spatial directions.

The discussion of quantum systems characterised by periodic potentials is greatly simplified by the powerful **Bloch's Theorem**. Consider a one-dimensional quantum system characterised by a periodic potential, namely a potential that repeats itself after a distance a :

$$V(x + a) = V(x), \quad (3.77)$$

which of course implies that $V(x + 2a) = V(x + a) = V(x)$ or in general that

$$V(x + na) = V(x) \quad \text{for } n = 1, 2, 3, \dots \quad (3.78)$$

The wave function for a particle propagating through this potential energy will satisfy the one-dimensional Schroedinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x). \quad (3.79)$$

Bloch's Theorem tells us that, given the periodic nature of the potential defined by Eq. (3.78), the solution of the one-dimensional Schroedinger equation, must satisfy:

$$\psi(x + a) = e^{iqa} \psi(x), \quad (3.80)$$

with q some constant number independent of the position x . To demonstrate this property, note that if $\psi(x)$ satisfies Eq. (3.79) then it will also satisfy

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x + a) + V(x + a)\psi(x + a) = E\psi(x + a), \quad (3.81)$$

where I have rescaled $x \rightarrow x + a$. But we are dealing with a **periodic potential** as indicated by the periodicity condition Eq. (3.78), and hence:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x + a) + V(x)\psi(x + a) = E\psi(x + a), \quad (3.82)$$

and if now we replace

$$\psi(x + a) = e^{iqa} \psi(x) \quad (3.83)$$

we reproduce the original equation Eq. (3.79), demonstrating Bloch's Theorem. The overall prefactor e^{iqa} does not depend on x and thus cancels out in the Schroedinger equation.

Periodicity of the electron probability distribution

For the time being q is a general complex number, and thus it could change the normalisation of the wave function. In short we will demonstrate that $q \in \mathbb{R}$ and thus the e^{iqa} prefactor is a **complex phase**. This is a reassuring result, given the periodicity of the potential heavily suggests that the **probability distribution** associated to the electron should also be **periodic**, and hence that

$$|\psi(x + a)|^2 = |\psi(x)|^2, \quad (3.84)$$

which is indeed the case thanks to Bloch's Theorem, Eq. (3.80), given that e^{iqa} is a complex phase. Therefore in a crystalline solid with a periodic potential the probability distribution associated to its valence electrons will be periodic as well.

While any real solid is finite, finite-size effects associated to its boundaries can be neglected for macroscopic solids as compared to the dominant bulk (volume) effects. We can ignore them formally by imposing the **periodic boundary condition**

$$\psi(x + Na) = \psi(x), \quad (3.85)$$

where $N = \mathcal{O}(10^{23})$ is a macroscopic number of periods, which corresponds to a macroscopic number of atoms. Taking into account the periodicity properties of the wave function, Eq. (3.80), we find that imposing this periodic boundary conditions leads to

$$\psi(x + Na) = e^{iqNa}\psi(x) = \psi(x) \quad \rightarrow \quad qNa = 2\pi n, \quad (3.86)$$

and thus the constant q is **real and quantised**:

$$q_n = \frac{2\pi n}{Na}, \quad n = 0, \pm 1, \pm 2, \pm 3, \dots \quad (3.87)$$

Note that $(1/Na) \simeq 10^{-13}$ for a typical interatomic separation of $a = \mathcal{O}(10^{-10})$, and hence the values of q_n will form a **quasi-continuum**. Note that if we had not imposed the periodic boundary conditions then q would indeed take continuous values, but the difference between quasi-continuum actual continuum is irrelevant in practice.

The usefulness of Bloch's Theorem

The crucial relevance of Bloch's theorem is that we have reduced the problem of solving the Schrodinger equation on the whole solid to that of **solving it in a unit cell**, for example the cell defined by $0 \leq x \leq a$. Once the wave function for this unit cell is known, then Eq. (3.80) guarantees that we can evaluate it for any other cell within the solid.

Armed with the powerful Bloch Theorem, we can now present our model for the band structure of solids. Still restricting ourselves to the one-dimensional case, let us assume that our periodic potential is a linear combination of **Dirac delta functions**:

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja). \quad (3.88)$$

That is, we have infinite spikes localised at the nodes $x = ja$ of the lattice with j being an integer number. The specific details of the potential are not crucial (one could have used finite square barrier potentials, for example), the really important property is their **periodicity**. Indeed, while this potential is far from the real physical situation (we should have Coulomb-type attractive interactions between the electrons and the positive atomic cores), it allows us to evaluate the physical consequences of a periodic potential in the resulting properties of solids.

The potential energy defined by Eq. (3.88) is clearly a periodic potential, since $V(x + a) = V(x)$, as you can check as follows

$$V(x + a) = \alpha \sum_{j=0}^{N-1} \delta(x - ja + a) = \alpha \sum_{j=0}^{N-1} \delta(x - (j - 1)a), \quad (3.89)$$

but now you can redefine $j' = j - 1$ to have

$$V(x+a) = \alpha \sum_{j=0}^{N-1} \delta(x - (j-1)a) = \alpha \sum_{j'=-1}^{N-2} \delta(x - j'a) = V(x) \quad (3.90)$$

since we are imposing **periodic boundary conditions** for the potential, Eq. (3.85) such that the lattice node at $j' = -1$ in the sum is identified with the node with $j' = N - 1$. Indeed, if we plug in $x = -a$ in Eq. (3.85) we get

$$\psi(-a + Na) = \psi(-a) \quad \rightarrow \quad j' = N - 1 \quad \text{identified with} \quad j' = -1, \quad (3.91)$$

and hence the potential is indeed periodic as required.

By virtue of Bloch's Theorem, we only need to solve the Schroedinger equation for this potential in a single "crystal" cell, which we take to be $0 \leq x \leq a$. The delta function potential Eq. (3.88) is clearly zero for $0 < x < a$, and it is only non-zero for $x = 0$ and $x = a$. Therefore, for $0 \leq x \leq a$ we recover the usual free-particle wave functions

$$\psi(x) = A \sin(kx) + B \cos(kx), \quad k = \sqrt{2mE}/\hbar, \quad 0 < x < a. \quad (3.92)$$

We can now use Bloch's Theorem,

$$\psi(x+a) = e^{iqa} \psi(x) \quad \rightarrow \quad \psi(x) = e^{-iqa} \psi(x+a), \quad (3.93)$$

to compute the wave function in the cell to the left of this one, $-a < x < 0$, and we find

$$\psi(x) = e^{-iqa} (A \sin(k(x+a)) + B \cos(k(x+a))), \quad k = \sqrt{2mE}/\hbar, \quad -a < x < 0. \quad (3.94)$$

In order to determine the integration constants A and B , we need to impose the relevant **local boundary conditions** on the wave function of this system. We will this way find the conditions to be satisfied by the physical wave functions of this periodic system.

- The wave function must be **continuous everywhere**, and hence for $x = 0$ we must impose:

$$B = e^{-iqa} (A \sin(ka)) + B \cos(ka) \quad (3.95)$$

which is a transcendental equation similar to the one that arises in the finite potential barrier and related problems (which can only be solved numerically).

- The derivative of the wave function is **discontinuous across infinite potentials**, such as the Dirac delta function of this system, with the value of the discontinuity given by

$$\left. \frac{d\psi(x)}{dx} \right|_{x=+\epsilon} - \left. \frac{d\psi(x)}{dx} \right|_{x=-\epsilon} = \frac{2m}{\hbar^2} \int_{-\epsilon}^{\epsilon} dx V(x) \psi(x). \quad (3.96)$$

where I am assuming that the potential $V(x)$ is infinite at $x_0 = 0$. Our potential at $x = 0$ is a delta function and hence the RHS reads

$$\frac{2m}{\hbar^2} \int_{-\epsilon}^{\epsilon} dx V(x) \psi(x) = \frac{2m\alpha}{\hbar^2} \int_{-\epsilon}^{\epsilon} dx \delta(x) \psi(x) = \frac{2m\alpha}{\hbar^2} \psi(0) = \frac{2m\alpha}{\hbar^2} B. \quad (3.97)$$

Now in the original cell, $x = +\epsilon$, the derivative is given by

$$\frac{d\psi(x)}{dx} = Ak \cos(kx) - Bk \sin(kx), \quad \left. \frac{d\psi(x)}{dx} \right|_{+\epsilon} = kA \quad (3.98)$$

while instead for $x = -\epsilon$ the corresponding derivative is evaluated to be:

$$\begin{aligned} \frac{d\psi(x)}{dx} &= e^{-iqa} (Ak \cos(k(x+a)) - Bk \sin(k(x+a))), \\ \left. \frac{d\psi(x)}{dx} \right|_{-\epsilon} &= e^{-iqa} (Ak \cos(ka) - Bk \sin(ka)) \end{aligned} \quad (3.99)$$

and thus the boundary condition for the derivate of the wave function reads:

$$[kA - e^{-iqa} k (A \cos(ka) - B \sin(ka))] = \frac{2m\alpha}{\hbar^2} B. \quad (3.100)$$

Eqns. (3.95) and (3.100) provide two relations that constrain the integration constants A and B and the allowed values of the energy k of the particles propagating in this periodic potential.

To solve this system of equations, we can first use Eq. (3.95) to determine A in terms of B

$$A = B \frac{(e^{iqa} - \cos(ka))}{\sin(ka)} \quad (3.101)$$

and then insert this relation into Eq. (3.100), where the dependence on B cancels out. This indicates that B is a normalisation constant fixed by the wave function normalisation requirement. Doing some algebra, we end up with the following relation between the quasi-continuous parameter q and the particle wave vector k as a function of the strength α of the potential:

$$\cos(qa) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin(ka). \quad (3.102)$$

This relation illustrates how for given values of the potential strengths α and of the **lattice parameter** a the energies of the electrons $E = \hbar^2 k^2 / 2m$ in the system are related to the values of $q = 2\pi n / Na$, and hence they will be **quantised**. Indeed, for given values of q , a . and α , only electron energies such that

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{satisfying} \quad \cos(qa) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin(ka), \quad (3.103)$$

are allowed solutions of the Schroedinger equation of this periodic potential. However, there is now a marked difference with previous systems that we have considered: the fact that q is essentially a continuous variable (since N is macroscopic) implies that instead of discrete energy levels, we will have **continuous energy bands** separated by **gaps** without any allowed states.

To determine which are the allowed values of the energy E of the electrons in this system, we can write $z = ka$ and $\beta = m\alpha a / \hbar^2$ such that Eq. (3.102) becomes

$$\cos\left(\frac{2\pi n}{N}\right) = \cos(z) + \frac{\beta}{z} \sin(z) = f_\beta(z). \quad (3.104)$$

For a given value of β , which is proportional to the strength of the interaction between the electrons and the atomic nuclei, for each value of $n = 1, 2, 3, 4, \dots$ there will be a solution for z .

However, N is a huge number, so for any value of $\cos(qa)$ between -1 and +1 it is essentially guaranteed that we will find a value of n that fulfills this condition. Hence, any value of $k = z/a$ such that $|f_\beta(z)| \leq 1$ corresponds to an **allowed energy state** for my system: we therefore find that the valence electrons moving in the periodic potential of a solid cluster into **bands** of allowed energy separated by **energy gaps** (for $|f(z)| > 1$). This is a rather significant difference as compared to *e.g.* the hydrogen atom, or to any other quantum systems: in periodic potentials, the allowed levels of the electron energies cluster into **continuum bands** separated by finite gaps where no solution is possible.

Fig. 3.1 displays the function $f_\beta(z)$, Eq. (3.104) as a function of z for $\beta = 30$ and $\beta = 4$. We indicate with dashed horizontal lines the region $|f_\beta(z)| \leq 1$ which defines the allowed electronic bands. In the bottom panels, we indicate with a solid grey rectangle the location of these allowed electronic bands in the two scenarios. Note how the width of the band increases as z is increased, and eventually becomes a continuum without any gaps breaking the energy band. Note also that smaller the value of β , the earlier the energy continuum kicks in (since in $\beta \rightarrow 0$ limit the strength of the periodic potential vanishes).

Note also that in the limit $\beta \rightarrow 0$ we can always find a solution to Eq. (3.104): this means that in this limit the energies are not quantised and can take any possible value. This is not unexpected, since for $\beta \rightarrow 0$ we recover the free particle system (subject to periodic boundary condition) and there we know that any positive value of the energy is physically allowed.

Summary

We can now recapitulate what have we learned in this chapter concerning the quantum mechanics for systems composed by **identical particles**:

- I/ Quantum mechanics deals with truly indistinguishable particles: an electron is identical in all respects to every other electron in the Universe.
- II/ Systems composed by identical particles in quantum mechanics behave in a very different way as compared to systems composed by distinguishable particles.
- III/ Depending on their spin, particles can be classified into fermions and bosons. Bosons behave as if they experienced some attractive interaction and tend to cluster together in the same quantum state. Fermions, on the contrary, behave as if they experienced some repulsive interaction and tend to get far for each other.
- IV/ The Pauli exclusion principle for fermions tells us that a given quantum state can be occupied at most by one fermion at the same time.
- V/ The free electron gas model allows us to explain some important properties of solids, and shows how there exists a quantum mechanical pressure from the fermion degeneracy that partially explains the stability of solids.
- VI/ The existence of continuous energy bands for the valence electrons in solids can be explained by the presence of a periodic potential, where the electrons move, generated by the atomic cores sitting at regularly-spaced locations within the crystalline lattice of a solid.

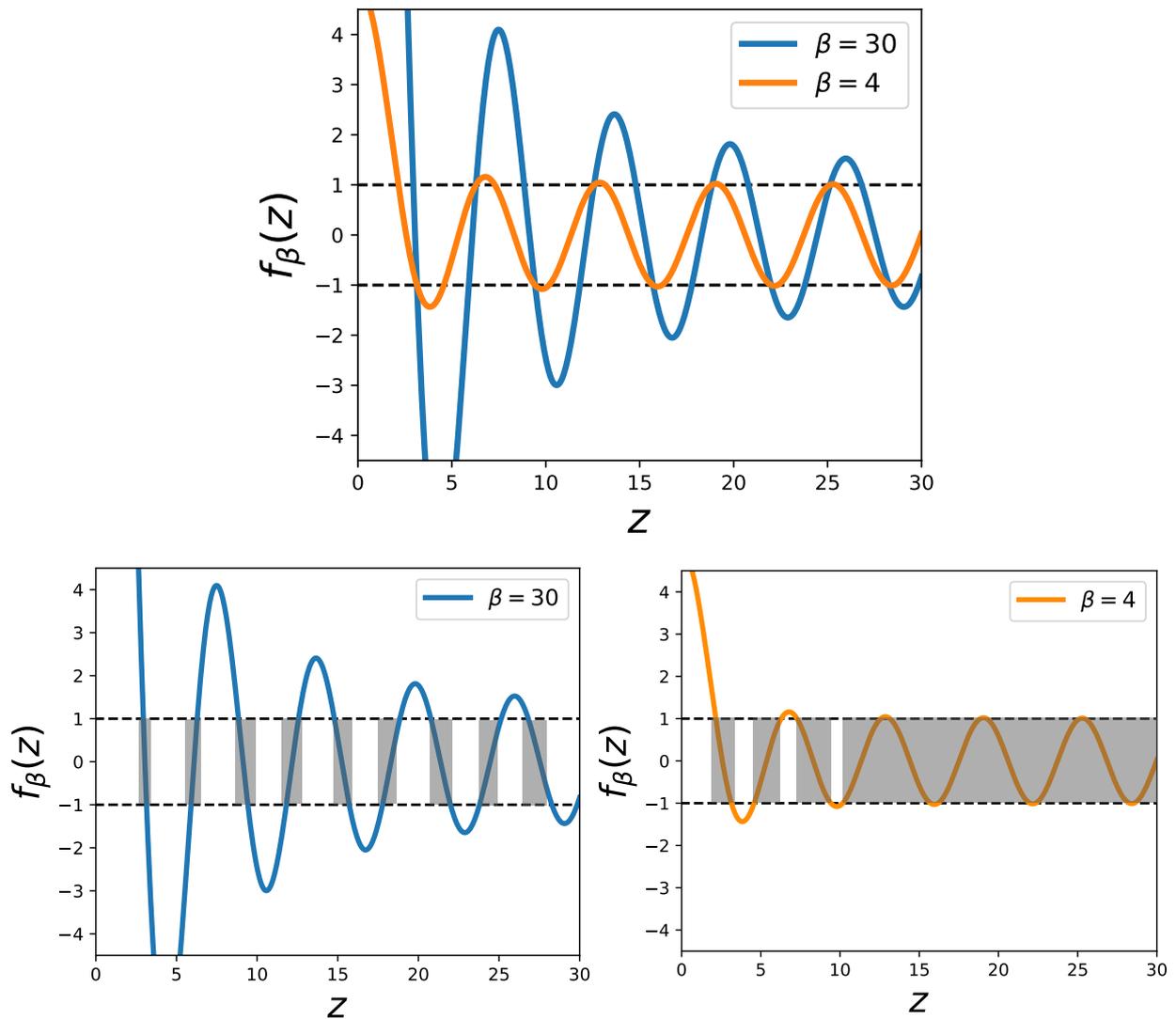


Figure 3.1: The function $f_\beta(z)$, Eq. (3.104) as a function of z for $\beta = 30$ and $\beta = 4$. We indicate with dashed horizontal lines the region $|f_\beta(z)| \leq 1$ which defines the allowed electronic bands. In the bottom panels, we indicate with a solid grey rectangle the location of these allowed electronic bands in the two scenarios. Note how the width of the band increases as z is increased, and eventually becomes a continuum without any gaps breaking the energy band. The smaller the value of β , the earlier the energy continuum kicks in.