PHY 530 Refresher Course in Physics

Ecole polytechnique - STEEM Program

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Contents

Chapter 1

Introduction to quantum mechanics

1.1 Welcome - thermodynamics

Thermodynamics is the framework of any study dedicated to energy issue. It emerged during the XIXth century as new scientific concepts were required to support the second industrial revolution. The improvement of energy converters (the steam engine being a case in point) allowed an unprecedented increase of the energy available per capita, and hence of the living conditions.

Thermodynamics is thus the compulsory first step of any program concerned with energy. We will simply summarize well-known results here, as a warm-up for this refresher.

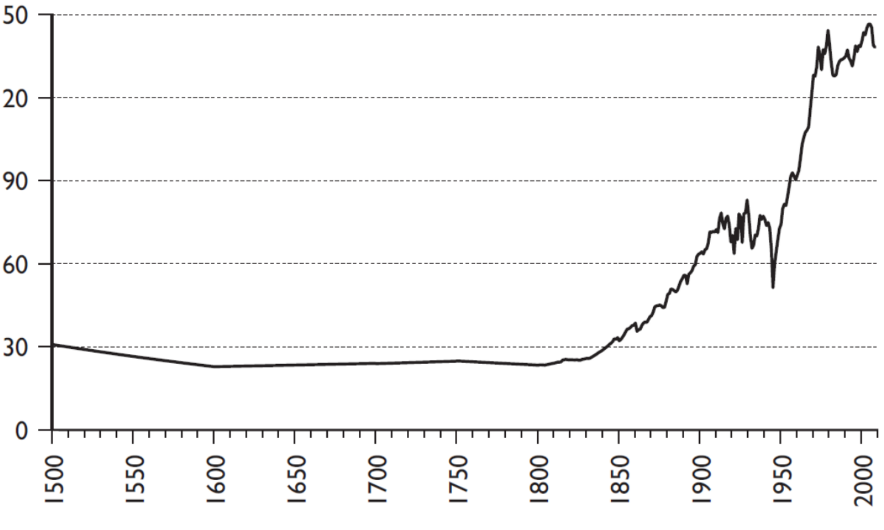


Figure 1.1: Energy per capita in GJ in Europe. Source: A. Kander *et al*, Power to the People, Princeton University Press (2013).

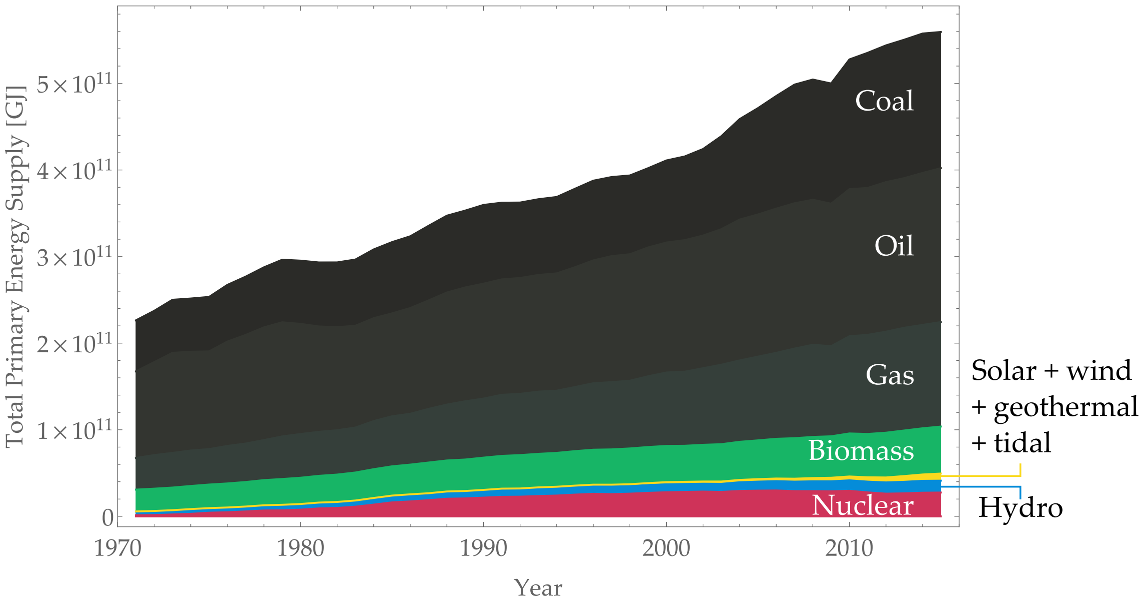


Figure 1.2: World's Total Primary Energy Supply (TPES). Source: International Energy Agency - IEA.

1.1.1 Energy and the first law

> *"Heat is nothing else than motive power (energy), or rather, a motion which has changed its form. It is a motion of the molecules of bodies. Whenever motive power is destroyed, there is, at the same time, a production of heat in quantity precisely proportional to the quantity of power destroyed. Reciprocally, wherever there is destruction of heat, there is production of power of motion. We may then state as a general law, that energy is, in nature, invariable in amount; that is, is never, properly speaking, either created or destroyed. In fact, it changes form; that is, it causes sometimes one kind of motion, sometimes another; but it is never destroyed."*
>
> Sadi Carnot, *Notes*, circa 1830

The first law of thermodynamics states two main results: 1/ energy is a conserved quantity and 2/ energy can be exchanged either through work or heat. It is usually written for a closed system as

$$\Delta E = W + Q \tag{1.1.1}$$

where ΔE is the total change in energy of the system (usually, the total energy E is expressed as the sum of the mechanical energy of the center of mass of the system E_m and of the internal energy U), W is the work provided to the system by the exterior world and Q is the heat supplied to the system.

Note that the energy variation ΔE only depends on the initial and final states. The work and heat provided to the system depend on *how* the evolution from the initial to the final state is being performed.

Power

The notion of *power* is critical in energy issues, as power measures the time evolution of energy:

$$P = \frac{dE}{dt} \tag{1.1.2}$$

During your previous studies, you probably encountered several approaches to power - all of them will be useful here !

Mechanical power

Consider a force **F** applied at the point M of a system. In a reference frame where the velocity of the application point M is $\mathbf{v}(M)$, the power applied on the system by the force is

$$P = \mathbf{F}.\mathbf{v}(M) \tag{1.1.3}$$

Equivalently, for a torque Γ applied on a system with angular velocity $\dot{\theta}$, the power is defined as

$$P = \Gamma\dot{\theta} \tag{1.1.4}$$

Forces result in a *work* being applied on the system. The infinitesimal work produced by the force **F** on the system over a period dt is defined as

$$\delta W = P\,dt = \mathbf{F}.\mathbf{dr} \tag{1.1.5}$$

where **dr** is the small displacement of the application point M during that period.

Fluid dynamics

Energy balance performed on a fluid element in a velocity field **v** gives

$$P = \frac{1}{2}\rho v^3 \tag{1.1.6}$$

Electrical power

Consider an electrical system with a voltage $U(t)$ and a current $I(t)$. The power delivered to that system is

$$P(t) = U(t)\,I(t) \tag{1.1.7}$$

For monochromatic quantities $U(t) = U_0 \cos \omega t$ and $I(t) = I_0 \cos \omega t + \varphi$, the average power is

$$\bar{P} = \frac{1}{T}\int_0^T P(t)dt = \frac{1}{2}U_0 I_0 \cos\varphi \tag{1.1.8}$$

Radiation power

Consider an electromagnetic radiation defined by an electric field **E** and a magnetic field **B**. The energy per unit of time (ie the power) passing through a surface **dS** is given by

$$P = \left(\frac{\mathbf{E}\times\mathbf{B}}{\mu_0}\right).\mathbf{dS} \tag{1.1.9}$$

Units

	eV	J	kWh	toe
eV	1	1.6×10^{-19}	-	-
J	6.3×10^{18}	1	2.7×10^{-7}	2.3×10^{-11}
kWh	-	3.6×10^{6}	1	8.6×10^{-5}
toe	-	42×10^{9}	11 630	1

There is a large mess of units used to count energy, partly because of the large variety of situations where energy is a relevant concept. Here is a selected best-of energy units.

- The standard system unit is the *Joule*, defined as

$$1\,\mathrm{J} = 1\,\mathrm{kg.m^2.s^{-2}}$$

- For most microscopic systems, the relevant unit is the *electron-volt*, defined as the potential energy of an electron under a 1V potential difference

$$1\,\mathrm{eV} = 1.6 \times 10^{-19}\,\mathrm{J}$$

- The *Calorie* (or *kcal*) is mostly used in the food industry. It is defined as the energy required to raise the temperature of 1L of water by one degree Celsius at a pressure of one atmosphere. Not to be confounded with the *calorie* (lower case):

$$1\,\mathrm{Cal} = 1000\,\mathrm{cal} \simeq 4.2\,\mathrm{kJ}$$

- The British Thermal Unit follows the same idea, but using stupid units: it is defined as the amount of heat required to raise the temperature of one pound of water by one degree Fahrenheit at a pressure of one atmosphere

$$1\,\mathrm{BTU} = 1.060\,\mathrm{kJ}$$

- The Quad is a large packet of BTU. It is notably used by the US Department of Energy to discuss energy budgets.

$$1\,\mathrm{Quad} = 10^{15}\,\mathrm{BTU}$$

- The *Watt-hour* (/!\ it's "watt times hour", not "watt per hour") is the power accumulated using a 1W source during 1h:

$$1\,\mathrm{Wh} = 3.6\,\mathrm{kJ}$$

  This unit (and its multiples kWh, MWh...) is usually used for electrical energy budget.

- The *ton of oil equivalent* is the amount of energy released by burning one tonne of crude oil:

$$1\,\mathrm{toe} \simeq 42\,\mathrm{GJ} \simeq 11.63\,\mathrm{MWh} \tag{1.1.10}$$

  It is the standard unit to discuss energy budgets for the IEA, for instance.

1.1.2 Entropy and the second law

> *"[T]he production of heat alone is not sufficient to give birth to the impelling power: it is necessary that there should also be cold; without it, the heat would be useless."*
>
> Sadi Carnot, *Reflections on the Motive Power of Heat*, 1824

The first law makes no difference between all transformations as long as they preserve energy. The second law tells which transformations are allowed, and which are impossible. The quantity at stake is the *entropy*, which accounts for the disorder in the system. The second law states three main results: 1/ any exchange of heat is equivalent to an exchange of entropy, 2/ entropy cannot be destroyed and 3/ only during reversible processes is no entropy created. It is usually written as:

$$\begin{aligned} \Delta S &= S_{\text{ex.}} + S_{\text{cr.}} \\ \text{with } \delta S_{\text{ex.}} &= \delta Q / T_{\text{ext}} \\ \text{and } \delta S_{\text{cr.}} &\geq 0 \end{aligned} \tag{1.1.11}$$

The second law has numerous consequences, one the most celebrated being the existence of an upper-bond for the efficiency at which any system can convert heat into work. This limit is called the *Carnot efficiency* and corresponds, for an energy converter connected to a heat source at temperature T_H and a heat drain at temperature T_C to:

$$\eta_C = \frac{W_{\text{provided by the system}}}{Q_{\text{delivered to the system}}} = 1 - \frac{T_C}{T_H} \tag{1.1.12}$$

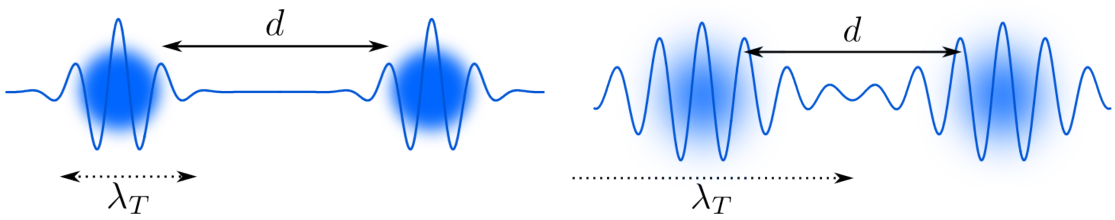
1.1.3 STEEM program

Why do we need quantum and statistical physics ?

- We want to study energy conversion. We take a system in its equilibrium state (to be defined), we apply a stimulation (illumination, heating, electrical bias...) which induces a response of the system. We need to characterize this response to determine if we can take benefit from it - that's the job of physics.

- We are talking about macroscopic systems, made of $\gg 10^{23}$ particles. We cannot determine the exact configuration of the system before the stimulation, nor compute the exact response of the system to this stimulation. We need a statistical approach, which is the foundation of thermodynamics.

- Every particle is described as a wavepacket in quantum mechanics. As a hand-waving argument, the spread of the wavepacket can be estimated by the de Broglie wavelength $\lambda_{\text{de Broglie}} = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$, which decreases with the temperature. If the de Broglie wavelength is much smaller than the average distance between two particles $d = n^{-1/3}$, then quantum mechanics can be ignored and particles can be safely described as independant marbles. Otherwise, quantum description is required.



	m	d	T_c	Quantum ?
Air (N_2)	$5\,10^{-26}$ kg	$\sim 10^{-8}$ m	1 mK	Nope
Materials (e^-)	10^{-30} kg	10^{-10} m	10^5 K	Yes
Nuclear (p^+)	10^{-27} kg	10^{-15} m	10^{12} K	Yes

Plugging in typical numbers, mechanical systems (wind...) can avoid a quantum analysis, but any problem dealing with electrons (materials, semi conductors, PV...) or with atomic nuclei (nuclear...) has to take quantum mechanics into account.

1.2 Quantum Mechanics: postulates

This part is a bit dry, but it gives the basic quantum mechanics toolbox.

1.2.1 Six rules of the quantum world

First postulate Wave function

In any field of physics, the system under scrutiny is accounted for by a mathematical description. In classical mechanics, the system is described by a position vector $\mathbf{r}$. In electromagnetism, the system is described by two vectors ($\mathbf{E}$ and $\mathbf{B}$) for each position $\mathbf{r}$.

In quantum mechanics, the system is described by a wave function, usually denoted $|\psi\rangle$. A wave function is a weird thing, and it takes some time to get used to it. Depending on the problem we consider,$|\psi\rangle$ can be an object of different nature.

Most usual examples

- *To describe the motion of a particle, we take* $|\psi\rangle$ *as a function* $\psi(\mathbf{r}) \in \mathbb{C}$.
- *To describe the spin of particle with spin 1/2, we take* $|\psi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \in \mathbb{C}^2$ *as two component vector.*

1. $|\psi\rangle$ contains *all* the information about the system (but we don't know yet how to get information from $|\psi\rangle$, cf 2nd postulate). For instance, in the first example, $|\psi(\mathbf{r})|^2$ gives the density of probability of finding the particle at position $\mathbf{r}$.
2. The best way to picture $|\psi\rangle$ is to think of a vector.
   (a) Just like a vector can be projected against another vector, a wave function can be projected against another wave function. This operation is a scalar product, and turns 2 wave functions into a complex number
      - *In our first example, the scalar product is defined as* $\langle\phi\,|\psi\rangle = \int d^3\mathbf{r}\,\phi^*(\mathbf{r})\,\psi(\mathbf{r})$.
      - *In our second example, the scalar product is defined as* $\langle\phi\,|\psi\rangle = \phi_1^*\psi_1 + \phi_2^*\psi_2$.

(b) We will see later that any operation performed on the system corresponds to changing $|\psi\rangle$ into another vector.

Note: Formally speaking, $|\psi\rangle$ is an element of a Hilbert space, which -for us- simply means that it comes with a scalar product.

$$\boxed{\text{Any quantum system can be described by an element } |\psi\rangle \text{ of a Hilbert space } \mathcal{H}.}$$

Second postulate Observable

Any measurable quantity of the system (ie energy, position, momentum, angular momentum, spin...) is associated to an "observable". An observable $\hat{O}$ is an operator, ie an object that turns a wave function into another wave function - like a function, but for vectors:

$$\hat{O}: \begin{array}{ccc} \mathcal{H} & \to & \mathcal{H} \\ |\psi\rangle & \to & \hat{O}|\psi\rangle \end{array}$$

Example:

- *For a particle in a 3D space, the position along the x axis is associated to the operator* $\hat{x}$*, which changes* $|\psi\rangle$ *into a new wave function* $\hat{x}|\psi\rangle$ *such that* $(\hat{x}|\psi\rangle)(\mathbf{r}) = x\psi(\mathbf{r})$.
- *For a particle in a 3D space, the momentum along the x axis is associated to the operator* $\hat{p_x}$*, which changes* $|\psi\rangle$ *into a new wave function* $\hat{p_x}|\psi\rangle$ *such that* $(\hat{p_x}|\psi\rangle)(\mathbf{r}) = -i\hbar\frac{\partial\psi}{\partial x}(\mathbf{r})$
- *For a* $1/2$ *spin, the spin operator along the z axis is defined by its action on a spin* $|+\rangle_z$ *aligned with the z axis and a spin* $|-\rangle_z$ *anti-aligned with the z axis:*

$$\hat{S_z}|+\rangle_z = \frac{\hbar}{2}|+\rangle_z \qquad \hat{S_z}|-\rangle_z = -\frac{\hbar}{2}|-\rangle_z$$

Note 1: We will not discuss here *how* the observable are defined (why is momentum associated to $-i\hbar\nabla$, and not to something else ?).

Note 2: This does not tell us *how* to measure anything yet.

Note 3: Most of the time, the hat ^ is omitted.

Note 4: It is often useful to think of operators as a matrix (which turns a vector into another vector).

Moreover, observables are *hermitian* operators (ie $\langle\phi|\hat{O}|\psi\rangle = (\langle\psi|\hat{O}|\phi\rangle)^*$ for all ψ and ϕ). This has a major mathematical consequence called the spectral theorem:

Spectral theorem

For any observable $\hat{O}$, there is a basis of $\mathcal{H}$ (ie an ensemble of elements $\{|\phi_i^O\rangle\}$ such that any element $|\psi\rangle$ can be written as a linear combination $|\psi\rangle = \sum c_i |\phi_i^O\rangle$) such that

1. This basis is orthonormal

$$\left\langle\phi_i^O \middle| \phi_j^O\right\rangle = \delta_{i,j}$$

2. Each element of this basis is an eigenvector of $\hat{O}$

$$\underbrace{\hat{O}\left|\phi_i^O\right\rangle}_{\text{operator applied on vector}} = \underbrace{O_i \times \left|\phi_i^O\right\rangle}_{\text{number times the vector}}$$

3. All eigenvalues $\{O_i\}$ are real (with no imaginary part).

Note 1: By considering simply the scalar product, we can express $c_i = \langle \phi_i^O \, | \psi \rangle$.

Note 2: Several eigenvector can have the same eigenvalue - in which case the value is called *degenerated*.

Note 3: If we consider two operators $\hat{O}_1$ and $\hat{O}_2$, we have to juggle with two different basis of eigenvectors - one for each operator. Sometimes, it is possible to find a basis shared by both operators - this is the case if and only if these operators commute - ie $\hat{O}_1\hat{O}_2 = \hat{O}_2\hat{O}_1$

> Any measurable quantity is associated to a hermitian operator called *observable*.

Third postulate Measurement

> Any single measurement associated to an observable $\hat{O}$ can only give an eigenvalue O_i of this observable.
>
> If the same experiment is performed several times, the average measured value is $\langle \psi | \, \hat{O} \, | \psi \rangle$.

Example:

- *The average position along the x axis of a state* $|\psi\rangle$ *is*

$$\langle \psi | \, \hat{x} \, | \psi \rangle = \int x \, |\psi(x)|^2 \, dx$$

- *The average momentum along the x axis of a state* $|\psi\rangle$ *is*

$$\langle \psi | \, \hat{p_x} \, | \psi \rangle = -i\hbar \int \psi^*(x) . \frac{\partial \psi}{\partial x}(x) \, dx$$

- *The average spin along the z axis of a state* $|\psi\rangle = c_+ \, |+\rangle_z + c_- \, |-\rangle_z$ *is*

$$\langle \psi | \, \hat{S_z} \, | \psi \rangle = \frac{\hbar}{2} \, |c_+|^2 - \frac{\hbar}{2} \, |c_-|^2$$

Fourth postulate Born Rule

> For any single measurement associated to an observable $\hat{O}$, the probability of obtaining the result O_i is $|\langle \phi_i^O \, | \psi \rangle|^2$.

Note 1: For a continuous operator (such as position and momentum), we should consider instead a probability distribution function (ie the probability of obtaining the result O_0 up to dO is $|\langle \phi(O_o) \, | \psi \rangle|^2 \, dO$.

Note 2: We suppose here that all states are normalized (ie $\langle \psi \, | \psi \rangle = 1$).

Note 3: We can easily check that this rule is compatible with the previous postulate expressing the mean value of $\hat{O}$ as $\langle \psi | \, \hat{O} \, | \psi \rangle$.

Example:

- *If we measure the spin of a state* $|\psi\rangle = \frac{\sqrt{3}}{2}|+\rangle_z + \frac{1}{2}|-\rangle_z$ *along the z axis, we have 75% chance to find* $+\frac{\hbar}{2}$ *and 25% chance to find* $-\frac{\hbar}{2}$.

Fifth postulate Collapse of the wave packet ("Effondrement du paquet d'onde" in French)

After a measurement resulting in a value O_i, the state is projected to its components with the corresponding eigenvector.

Example:

- *If we measure the spin of a state* $|\psi\rangle = \frac{\sqrt{3}}{2}|+\rangle_z + \frac{1}{2}|-\rangle_z$ *along the z axis and find* $-\frac{\hbar}{2}$, *then the system is in the state* $|\psi\rangle = |-\rangle_z$ *from now on.*

Note: We will not use that postulate so much.

Sixth postulate Time evolution

The time evolution of a system is given by Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle$$

where H is the *Hamiltonian* of the system, ie observable associated to energy.

Most critical example:

The Hamiltonian is an observable, so there is a basis $\{|\phi_i^H\rangle\}$ *such that*

$$\hat{H}\left|\phi_i^H\right\rangle = E_i\left|\phi_i^H\right\rangle$$

The time evolution of any of these states is simply given by

$$i\hbar\frac{\partial}{\partial t}\left|\phi_i^H\right\rangle = \hat{H}\left|\phi_i^H\right\rangle = E_i\left|\phi_i^H\right\rangle$$

and we find that energy eigenstates evolve simply by dephasing with a frequency given by the energy of the state

$$\left|\phi_i^H(t)\right\rangle = \exp\left(-i\frac{E_i}{\hbar}t\right)\left|\phi_i^H(0)\right\rangle$$

Note: The Hamiltonian usually resembles to the classical energy, but keep in mind it is an operator. In many cases, the Hamiltonian will include a kinetic term

$$\hat{H_{\text{kin}}} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2}\Delta$$

1.2.2 Practical applications

There are 3 typical ways to use the basic ingredients introduced above

Determine which states are accessible to the system

Starting from a physical situation, the first step is to determine which states are permitted to the system. The existence of allowed and forbidden states is not specific to quantum mechanics (vibrating string for instance).

As underlined above, energy eigenstates play a critical role in quantum mechanics. A quantum mechanics problem usually starts with the expression of a Hamiltonian, and the first step is to determine the corresponding eigenstates.

Estimate the time evolution starting from an initial state

In many cases, we want to know how the system evolves starting from known initial conditions $|\psi_0\rangle$. This is given by Schrodinger equation (postulate 6), which requires to calculate $\hat{H}|\psi\rangle$.

We don't know how to calculate $\hat{H}|\psi\rangle$ in the general case. But it is easy for eigenstates of H (example of postulate 6).

Luckily, we know that the eigenstate of H form a basis of the Hilbert space (postulate 2). So the general way of solving a quantum mechanics problem is:

1. Find the eigenstates of the Hamiltonian $\left\{|\phi_i^H\rangle\right\}$
2. Express the initial state $|\psi_0\rangle$ as a sum of these eigenstates $|\psi_0\rangle = \sum c_i |\phi_i^H\rangle$
3. Dephase each of these component
4. Get the time behavior of the eigenstate

$$\begin{array}{ccc} |\psi_0\rangle & & |\psi(t)\rangle \\ \| & & \| \\ \sum c_i |\phi_i\rangle & \rightarrow & \sum c_i \exp\left(-i\frac{E_i}{\hbar}t\right)|\phi_i\rangle \end{array}$$

Response to an external stimulation: Perturbation theory

In many cases, the problem is the following. The system is described by a Hamiltonian $\hat{H}_0$, and initially in the quantum state $|\psi_i\rangle$ (let's assume $|\psi_i\rangle$ is an eigenstate of $\hat{H}$ for simplicity). All the sudden, we apply a perturbation to the system (e.g. we add an illumination, an electrical bias or whatever). The Hamiltonian becomes $\hat{H} = \hat{H}_0 + \hat{V}$. What happens to the initial state ?

If the perturbation $\hat{V}$ was not there, the system would always remain in the state $|\psi_i\rangle$, and would simply acquire a dephasing over time. Because of $\hat{V}$, the system can evolve towards another state $\left|\psi_f\right\rangle$. Another way to say it is simply that $|\psi_i\rangle$ is an eigenstate of $\hat{H}_0$, but not of $\hat{H}$.

Of course, one possibility would be to calculate the eigenstates of H, and apply the method discussed above. But quite often, it is very hard or impossible to calculate the eigenstates of H.

Provided that the influence of the stimulation remains limited, the departure rate from $|\psi_i\rangle$ towards $\left|\psi_f\right\rangle$ is given by the Fermi Golden Rule

$$\boxed{\Gamma_{i\to f} = \frac{2\pi}{\hbar}\left|\left\langle\psi_f\right| V |\psi_i\rangle\right|^2 D(E_f)}$$

where $D(E_f)$ is the final density of state (this will make sens after lecture 4). The FGR can be derived from Schrodinger equation (not done here).

1.3 Basic applications

1.3.1 Potential well

A quantum well is a potential landscape strongly confining particles in a narrow region of space. Such potential wells are not only the most standard example of quantum mechanics - they also successful account for practical situations. From an applied perspective, potential wells are well suited to describe quantum dots, where brutal changes in the structure of the material result in a tight confinement ($\sim$ nm) of the electrons. From a more fundamental perspective, potential wells provide a good model for atomic nuclei, where nucleons (protons and neutrons) are confined in a $\sim 10^{-15}$ m radius by the strong interaction.

1. Let us consider a particle of mass m in a potential well

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ V_0 & x < 0 \,\text{or}\, x > L \end{cases} \tag{1.3.1}$$

where the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{1.3.2}$$

For simplicity, we will restrict the problem to 1D and will assume the well to be infinitely deep ($V_0 = +\infty$), such that

$$\psi(x) = 0 \,\text{if}\, x \leq 0 \,\text{or}\, x \geq L \tag{1.3.3}$$

An eigenfunction ϕ with eigenvalue E of the Hamiltonian should therefore verify the differential equation

$$\left(\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + E\right)\phi(x) = 0 \tag{1.3.4}$$

$$\Rightarrow \phi(x) = A\cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) + B\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \tag{1.3.5}$$

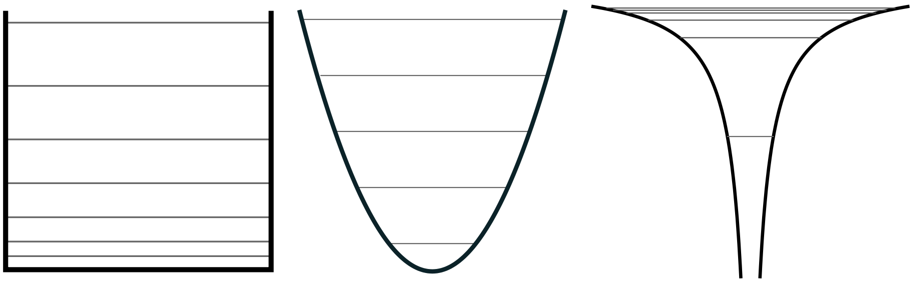
where A, $B \in \mathbb{C}$, and the boundary conditions eq.(1.3.3) leads to

$$A = 0 \qquad \& \qquad \sqrt{\frac{2mE}{\hbar^2}} = n\pi \tag{1.3.6}$$

We can therefore label the eigenfunctions according to n, and we find

$$\phi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \qquad \& \qquad E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} = n^2 E_0 \tag{1.3.7}$$

General rule: In the presence of a trapping potential, the Hamiltonian eigenstates take discrete energy values, and can be labeled by an integer number n.



$$V_{\text{well}} = 0 \text{ inside}, \infty \text{ outside} \qquad E_{\text{well}} = n^2 \frac{\pi^2\hbar^2}{2mL^2}$$

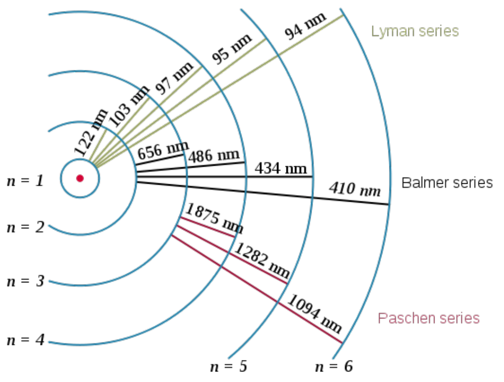
$$V_{\text{harmonic}} = \frac{1}{2}m\omega^2x^2 \qquad E_{\text{harmonic}} = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$V_{\text{atom}} = -\frac{Ze^2}{r} \text{ (in 3D)} \qquad E_{\text{atom}} = -\frac{1}{n^2}\frac{Z^2e^4m}{2\hbar^2}$$

Applications

Chemistry and nuclear power The simple model of a potential well shows that the more tightly confined a system is, the higher the typical energy scale. For an atom, where electrons ($m \sim 10^{-30}$ kg) are confined in a volume of typical size $L \sim 10^{-10}$ m, the typical energy is ~ 10 eV. For an atomic nucleus, where nucleon ($m \sim 10^{-27}$ kg) are confined in a volume of typical size $L \sim 10^{-15}$ m, the typical energy is ~ 100 MeV.

Hydrogen spectroscopy With the quantification of states in a Coulomb potential given above, we can calculate which radiation can be absorbed or emitted by a Hydrogen atom, by considering that an electromagnetic wave with pulsation ω can drive a transition between two energy levels only if its energy $\hbar\omega$ matches the energy difference between these two levels



$$\hbar\omega = \frac{Z^2e^4m}{2\hbar^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

2. To gain more intuition about quantum measurements, let's consider that the particle is in the state $|\psi\rangle = \frac{1}{\sqrt{2}}|\phi_2\rangle - \frac{1}{\sqrt{3}}|\phi_3\rangle + \frac{e^{i\pi/4}}{\sqrt{6}}|\phi_5\rangle$.

(a) We can easily verify that $\langle \psi | \psi \rangle = 1$, since

$$\left(\frac{1}{\sqrt{2}} \langle \phi_2 | - \frac{1}{\sqrt{3}} \langle \phi_3 | + \frac{e^{-i\pi/4}}{\sqrt{6}} \langle \phi_5 | \right) \left(\frac{1}{\sqrt{2}} | \phi_2 \rangle - \frac{1}{\sqrt{3}} | \phi_3 \rangle + \frac{e^{i\pi/4}}{\sqrt{6}} | \phi_5 \rangle \right) = \frac{1}{2} + \frac{1}{3} + \frac{1}{6} \tag{1.3.8}$$

where we used $\langle \phi_n | \phi_m \rangle = \delta_{m,n}$, because of the spectral theorem.

(b) This state has 0 chance to give E_0 (which is not an eigenvalue of H) or $16\,E_0$ (because there is no contribution of the corresponding eigenvector $|\phi_4\rangle$) ; there are 50% chance to measure $4\,E_0$ and 16.6% chance to measure $25\,E_0$.

(c) After any single measurement, the system is projected in the eigenspace corresponding to the measured eigenvalue. The only eigenstate which corresponds to an energy of $9\,E_0$ is $|\phi_3\rangle$. After the measurement, the system is thus in the state $|\psi'\rangle = |\phi_3\rangle$. Any further energy measurement will give the same value $9\,E_0$.

(d) The average value of the energy is given by

$$\langle \psi | H | \psi \rangle = \frac{1}{2} E_2 + \frac{1}{3} E_3 + \frac{1}{6} E_5 = \frac{55}{6} E_0 \tag{1.3.9}$$

3. If the particle is in the state $|\phi_2\rangle$, then the density of probability of presence of the particle is given by

$$|\langle x | \psi \rangle|^2 = |\phi_2(x)|^2 = \frac{2}{L} \sin^2 \left(\frac{2\pi}{L} x \right) \tag{1.3.10}$$

and the average value is therefore

$$\langle x \rangle = \langle \psi | x | \psi \rangle = \int x \, |\psi(x)|^2 \, dx = \frac{L}{2} \tag{1.3.11}$$

and does not depend on time, because $|\phi_2\rangle$ is an eigenstate of the Hamiltonian.

4. By contrast, if the system is not prepared in an eigenstate of the Hamiltonian, such as $\psi_0(x) = \sqrt{\frac{1}{L}} \sin\left(\frac{\pi x}{L}\right) + \sqrt{\frac{1}{L}} \sin\left(\frac{2\pi x}{L}\right)$, the state will evolve over time as

$$\psi(x,\,t) = \sqrt{\frac{1}{L}} \sin\left(\frac{\pi x}{L}\right) \exp\left(i \frac{E_0}{\hbar} t\right) + \sqrt{\frac{1}{L}} \sin\left(\frac{2\pi x}{L}\right) \exp\left(i 4 \frac{E_0}{\hbar} t\right) \tag{1.3.12}$$

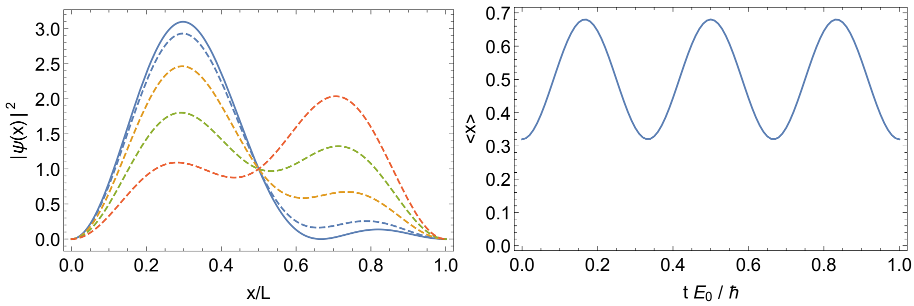
(a) The density of probability of presence is then

$$|\psi(x,t)|^2 = \frac{1}{L} \left(\sin^2\left(\frac{\pi x}{L}\right) + \sin^2\left(\frac{2\pi x}{L}\right) + 2 \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) \cos\left(3 \frac{E_0}{\hbar} t\right) \right) \tag{1.3.13}$$

(picture below for $t\,E_0/\hbar = 0$, 0.025, 0.05, 0.075 and 0.1) and the average position changes over time as

$$\langle x(t) \rangle = \int x \, |\psi(x,t)|^2 \, dx = \frac{L}{2} \left(1 - \frac{32}{9\pi^2} \cos\left(3 \frac{E_0}{\hbar} t\right) \right) \tag{1.3.14}$$

The numerical value of the horrible pre-factor has little importance here - what matters is that the particle is now bouncing back and fourth within the well.



(b) The average value of the energy is given by

$$\langle H(t)\rangle = \langle \psi(t)|\, H \,|\psi(t)\rangle = \frac{5}{2}E_0 \tag{1.3.15}$$

Note that this value does not vary over time, which proves that energy is conserved.

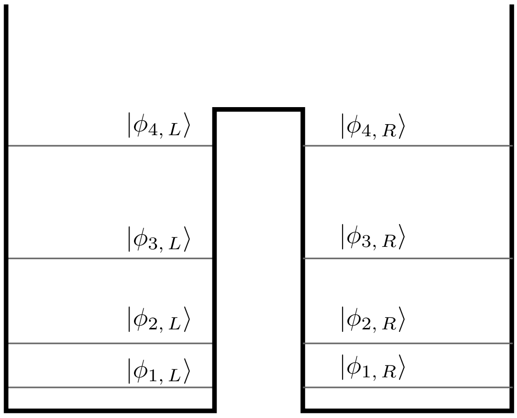
5. In a finite well, the boundaries conditions are not simply $\psi(0) = \psi(L) = 0$. Instead, we have to solve the Schrodinger equation in the three relevant regions of space ($x < 0$, $0 < x < L$, $L < x$) and consider that $\psi(x) \underset{x\to\pm\infty}{\longrightarrow} 0$ (otherwise the presence probability cannot be normalized) and that ψ and $\partial_x\psi$ should be continuous (not demonstrated here).

   Solving these equations in the walls of the well gives an exponential decay (also called *evanescent field*), with a typical damping length $\frac{\sqrt{2m}}{\hbar}\sqrt{V_0 - E}$ - ie the particle has a non zero probability to be found outside of the well ! This is the key ingredient for the tunnel effect, which we will discuss later.

1.3.2 Double well

We now consider a double well structure (see fig. below).

- We first assume that the two wells are isolated (ie the middle barrier is very high) and note H_0 the corresponding Hamiltonian - the expression of which will not be calculate. In each well, as studied above, the eigenstates of the Hamiltonian have discrete energy values and we label them $\{|\phi_{n,L}\rangle\}$ in the left well and $\{|\phi_{n,R}\rangle\}$ in the right well respectively. Each value E_n of the energy spectrum thus corresponds to two states (namely $|\phi_{n,L}\rangle$ and $|\phi_{n,R}\rangle$) - ie each energy is twice degenerated.



- We now take into account the tunnel transition through the separation wall by considering an additional coupling term V such that

$$\hat{V}\,|\phi_{n,L}\rangle = -J\,|\phi_{n,R}\rangle \tag{1.3.16}$$

$$\hat{V}\,|\phi_{n,R}\rangle = -J\,|\phi_{n,L}\rangle \tag{1.3.17}$$

1. Remember that any operator transforms a wave function into another wave function. This can be conveniently written using a matrix formalism. For instance, in the $\{|\phi_{n,L}\rangle\,,|\phi_{n,R}\rangle\}$ basis,

$$H = \begin{pmatrix} E_1 & 0 & 0 & 0 & \\ 0 & E_1 & 0 & 0 & \\ 0 & 0 & E_2 & 0 & \\ 0 & 0 & 0 & E_2 & \\ & & & & \ddots \end{pmatrix} + \begin{pmatrix} 0 & -J & 0 & 0 & \\ -J & 0 & 0 & 0 & \\ 0 & 0 & 0 & -J & \\ 0 & 0 & -J & 0 & \\ & & & & \ddots \end{pmatrix} = \begin{pmatrix} E_1 & -J & 0 & 0 & \\ -J & E_1 & 0 & 0 & \\ 0 & 0 & E_2 & -J & \\ 0 & 0 & -J & E_2 & \\ & & & & \ddots \end{pmatrix}$$

   Note that we did *not* calculate the expression of the eigenstates - but we can still use these states to express how the Hamiltonian operates.

2. The eigenstates $\{|\phi_{n,L}\rangle\,,|\phi_{n,R}\rangle\}$ of the Hamiltonian H_0 without tunneling are not anymore the eigenstates of the total Hamiltonian $H = H_0 + V$. What we are looking for are states $|\psi\rangle$ such that $H\,|\psi\rangle = E\,|\psi\rangle$. Since the Hamiltonian H is block diagonal, we can look for such eigenstates within each of these blocks:

$$\begin{cases} H\,|\phi_{n,L}\rangle = E_n\,|\phi_{n,L}\rangle - J\,|\phi_{n,R}\rangle \\ H\,|\phi_{n,R}\rangle = E_n\,|\phi_{n,R}\rangle - J\,|\phi_{n,L}\rangle \end{cases} \Rightarrow \begin{cases} H\left(\frac{|\phi_{n,L}\rangle+|\phi_{n,R}\rangle}{\sqrt{2}}\right) = (E_n - 2J)\left(\frac{|\phi_{n,L}\rangle+|\phi_{n,R}\rangle}{\sqrt{2}}\right) \\ H\left(\frac{|\phi_{n,L}\rangle-|\phi_{n,R}\rangle}{\sqrt{2}}\right) = E_n\left(\frac{|\phi_{n,L}\rangle-|\phi_{n,R}\rangle}{\sqrt{2}}\right) \end{cases}$$

   and we identify two eigenstates $|\psi_{n,S}\rangle = \frac{|\phi_{n,L}\rangle+|\phi_{n,R}\rangle}{\sqrt{2}}$ and $|\psi_{n,A}\rangle = \frac{|\phi_{n,L}\rangle-|\phi_{n,R}\rangle}{\sqrt{2}}$ with energies $(E_n - 2J)$ and E_n respectively.

General rule: any coupling between states tends to lift degeneracies. The eigenstates are then de-localized. The resulting energy splitting is larger if the coupling is stronger.

1.4 Take home message

- Keep in mind the basic postulates of QM.
- In the presence of a trapping potential, the Hamiltonian eigenstates take discrete energy values, and can be labeled by an integer number n.
- Any coupling between states tends to lift degeneracies. The eigenstates are then delocalized. The resulting energy splitting is larger if the coupling is stronger.

Chapter 2

Plane waves and density of states

2.1 Free particles

Particles in free space

Particles in free space are important for 3 reasons

- It accounts for particles not interacting with anything, or inbetween two interactions
- It happens to be a relevant description of electrons in a solid (see lecture 4)
- It is one of the few situation we can address easily

To account for free particles, we can start from the flat trap discussed yesterday and push the wall towards infinity. As usual, we will start by finding the eigenstates of the Hamiltonian describing this situation. Generalizing the previous result for a box $L_x \times L_y \times L_z$,

$$\phi_{\mathbf{n}}(x) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right) \tag{2.1.1}$$

with $n \in \mathbb{N}$ and the corresponding energy is

$$E_{\mathbf{n}} = \frac{\hbar^2}{2m}\left(\frac{\pi^2}{L_x^2} n_x^2 + \frac{\pi^2}{L_y^2} n_y^2 + \frac{\pi^2}{L_z^2} n_z^2\right) \tag{2.1.2}$$

Born-van Karman boundary conditions

As the idea is to take $L \to \infty$ in the end, the boundary conditions should not matter so much. So instead of considering $\psi = 0$ at the walls of the box (the so called "Dirichlet conditions"), we will consider that the wave function is periodic (the so called "Born - van Karman conditions"):

$$\psi\left(x + L\right) = \psi(x) \tag{2.1.3}$$

such that the eigenstates are now given by $\mathbb{N}$

$$\phi_{\mathbf{n}}(x) = \sqrt{\frac{1}{L_x L_y L_z}} \exp\left(i\frac{2\pi n_x}{L_x}x\right) \exp\left(i\frac{2\pi n_y}{L_y}y\right) \exp\left(i\frac{2\pi n_z}{L_z}z\right) \tag{2.1.4}$$

$$E_{\mathbf{n}} = \frac{\hbar^2}{2m}\left(\frac{4\pi^2}{L_x^2}n_x^2 + \frac{4\pi^2}{L_y^2}n_y^2 + \frac{4\pi^2}{L_z^2}n_z^2\right) \tag{2.1.5}$$

1. Generally speaking, the relation between the energy E and the momentum $\mathbf{k}$ is called a *dispersion relation*.
2. Yes, this condition is weird. For a quantum physicist, the Universe is a periodic shoe box.
3. At the end of the day, all physical results are independent of the size of the box, or on the boundary conditions. In the following, we will consider $L_x = L_y = L_z = L$.
4. Note that now, we have $n \in \mathbb{Z}$.

One of the main motivation for considering this condition is that the wave vectors $\{|\phi_{\mathbf{n}}\rangle\}$ are "plane waves", ie the eigenvectors of the momentum operator $\mathbf{p} = -i\hbar\boldsymbol{\nabla}$, with eigenvalue $\hbar\mathbf{k}$:

$$\hat{\mathbf{p}}\,|\psi_{\mathbf{k}}\rangle = \hbar\mathbf{k}\,|\psi_{\mathbf{k}}\rangle \qquad \text{with}\, \mathbf{k} = \frac{2\pi}{L}\begin{bmatrix} n_x \\ n_y \\ n_z \end{bmatrix} \tag{2.1.6}$$

Note Since $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$, it is easy to show that $\psi_{\mathbf{k}}(\mathbf{r}) = L^{-3/2}\exp(i\,\mathbf{k}.\mathbf{r})$. These functions are called plane waves because all points in any plane orthogonal to $\mathbf{k}$ have the same phase.

From discrete to continuous

The energy looks very much like that of a massive particle

$$E = \frac{p^2}{2m} \qquad \mathbf{p} = \hbar\begin{pmatrix} \frac{2\pi}{L_x}n_x \\ \frac{2\pi}{L_y}n_y \\ \frac{2\pi}{L_z}n_z \end{pmatrix} \tag{2.1.7}$$

where the momentum $\mathbf{p}$ can only take discrete values, with a step π/L_i in each direction.

However, if L is very large (and we want to take it towards infinity), this step is very small and $\mathbf{p}$ seems almost continuous.

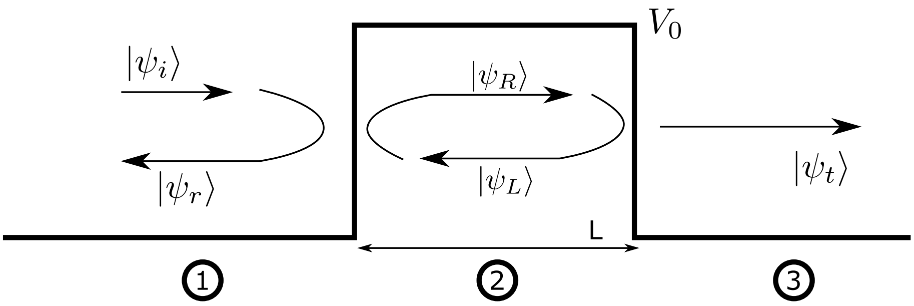
We will now just take some time to play a bit with these plane waves and get more familiar with them

2.2 Tunnel effect

2.2.1 Standard derivation

Note: this textbook exercise is one of the most classical application of basic quantum mechanics.

Let us consider a plane wave of energy E propagating towards a potential barrier of height V_0 and length L. We will restrict the analysis to 1D for the sake of simplicity.



1. In a classical picture, imagine rolling a ball from left to right towards a hill. If the ball initially has enough kinetic energy to pass the top of the hill (ie $E > V_0$), it will keep rolling towards the right side. Otherwise, it will roll back towards the left side.

2. We will first consider the quantum case where $E > V_0$

   (a) Any eigenstate $|\psi\rangle$ of the Hamiltonian should verify $H|\psi\rangle = E|\psi\rangle$ in all three regions of space, ie:

   $$\begin{cases} -\frac{\hbar^2}{2m}\partial_x^2\psi = E\psi & \text{in region 1} \\ -\frac{\hbar^2}{2m}\partial_x^2\psi + V_0\psi = E\psi & \text{in region 2} \\ -\frac{\hbar^2}{2m}\partial_x^2\psi = E\psi & \text{in region 3} \end{cases} \tag{2.2.1}$$

   from which we deduce the form of the wave-function in each region of space

   $$\psi(x) = \begin{cases} A_i \exp(ikx) + A_r \exp(-ikx) & \text{in region 1} \\ A_R \exp(ik'x) + A_L \exp(-ik'x) & \text{in region 2} \\ A_t \exp(ikx) + A_b \exp(-ikx) & \text{in region 3} \end{cases} \tag{2.2.2}$$

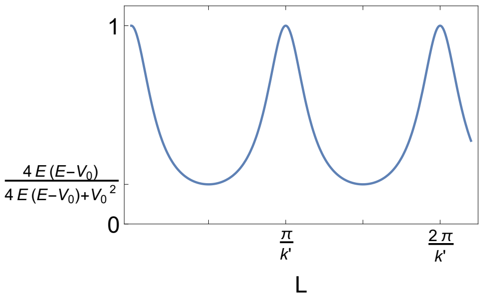
   with $k = \frac{1}{\hbar}\sqrt{2mE}$ and $k' = \frac{1}{\hbar}\sqrt{2m(E - V_0)}$. A spatial dependency $\propto \exp(ikx)$ corresponds to a wave moving from left to right. As there is no contribution coming from the right side of the barrier towards it, we take $A_b = 0$.

   (b) The continuity of ψ and $\partial_x\psi$ leads to 4 equations:

   $$\begin{array}{rcl} A_i + A_r & = & A_R + A_L \\ k(A_i - A_r) & = & k'(A_R - A_L) \end{array} \quad \& \quad \begin{array}{rcl} A_R e^{ik'L} + A_L e^{-ik'L} & = & A_t e^{ikL} \\ k'\left(A_R e^{ik'L} - A_L e^{-ik'L}\right) & = & kA_t e^{ikL} \end{array} \tag{2.2.3}$$

   (c) As we have 5 variables, one more relation would be required to determine the exact value of each amplitude. The normalization of the wave-function could provide such a relation. However, as we are interested in the reflection and transmission coefficients, which are expressed as a ratio of these amplitudes, and we don't need to go through this painful calculation !

$$
\begin{aligned}
T &= \left|\frac{A_t}{A_i}\right|^2 \\
&= \frac{4E(E-V_0)}{4E(E-V_0)+V_0^2\sin^2\left(\frac{1}{\hbar}\sqrt{2m(E-V_0)}.L\right)}
\end{aligned}
$$



Remarkably, this coefficient depends on L and *is not always equal to 1*, even though $E > V_0$! In the quantum world, even if the ball has enough energy to pass over the barrier, it has a non-zero probability of bouncing back, except if the thickness of the barrier takes very specific values ($L = n\pi/k'$). Note that if $E \gg V_0$, the probability of bouncing becomes extremely small.

3. We now consider the case where $E < V_0$

   (a) Just like before, we solve separately the eigenvalue equation in the three regions of space. The only difference is that, since $E < V_0$, the wave-vector in the barrier region is now imaginary, which corresponds to an evanescent wave (and not to a propagating wave anymore). We therefore find:

$$
\psi(x) = \begin{cases} A_i \exp\left(ikx\right) + A_r \exp\left(-ikx\right) & \text{in region 1} \\ A_R \exp\left(-k''x\right) + A_L \exp\left(k''x\right) & \text{in region 2} \\ A_t \exp\left(ikx\right) & \text{in region 3} \end{cases} \tag{2.2.4}
$$

   with $k = \frac{1}{\hbar}\sqrt{2mE}$ and $k'' = \frac{1}{\hbar}\sqrt{2m\left(V_0 - E\right)}$.

   (b) Considering that the wave function ψ and its gradient $\partial_x\psi$ must be continuous at each interface, write 4 equations relating the amplitude of each term of ψ.

$$
\begin{aligned}
A_i + A_r &= A_R + A_L \\
ik\left(A_i - A_r\right) &= k''\left(A_R - A_L\right)
\end{aligned}
\quad \& \quad
\begin{aligned}
A_R e^{k''L} + A_L e^{-k''L} &= A_t e^{ikL} \\
k''\left(A_R e^{k''L} - A_L e^{-k''L}\right) &= i \quad kA_t e^{ikL}
\end{aligned}
\tag{2.2.5}
$$

   (c) From these equations, it can be shown that

$$
T = \left|\frac{A_t}{A_i}\right|^2 = \frac{4E\left(V_0 - E\right)}{4E\left(V_0 - E\right) + V_0^2 \sinh^2\left(\frac{1}{\hbar}\sqrt{2m\left(V_0 - E\right)}.L\right)} \tag{2.2.6}
$$

$$
\simeq 16\,\frac{E \times \left(V_0 - E\right)}{V_0^2}\,\exp\left(-\frac{\sqrt{8m\left(V_0 - E\right)}}{\hbar}L\right) \tag{2.2.7}
$$

   The classical case would simply give $T = 0$: if the particle doesn't have enough energy to climb up the barrier, it has no chance to pass through and will roll back to where it came from. The situation is here completely different: the wave has a non-zero probability to be transmitted, as if it had gone *through* the barrier - hence the celebrated name "tunnel effect".

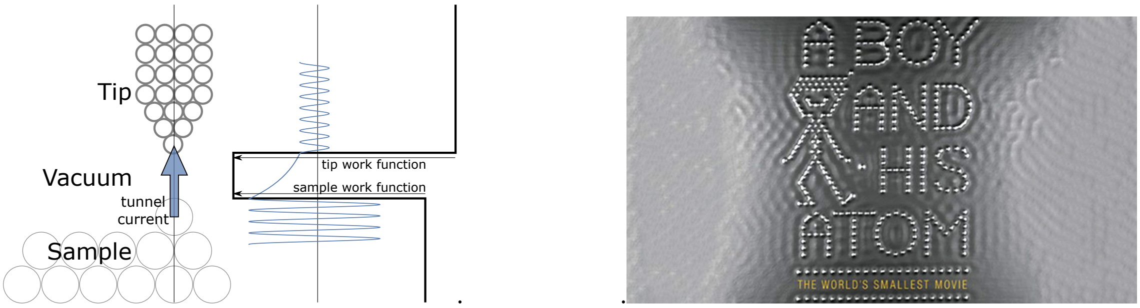
The tunnel effect is a quantum phenomena where a system can access states which would be unreachable because of a too high potential barrier in a classical picture. It is due to the finite penetration of the wave-function inside the barrier, where it behaves as an evanescent wave (see section 1.3.5)

Note that the higher the potential, the larger the barrier and the heavier the particle, the less likely it is to tunnel through the barrier.

2.2.2 Applications

Scanning tunneling microscopy

STM is a electronic microscopy technique which allows a sub-atomic resolution ($\sim 0.01\,\mathrm{nm}$ depth resolution, $\sim 0.1\,\mathrm{nm}$ lateral resolution) of the surface topography of a sample. A tip is brought close to the sample ($\sim 0.3\,\mathrm{nm}$). Electrons, which were confined in the sample by the work-function ϕ of the material, can now tunnel through vacuum to reach the tip. The ensuing electronic flow constitute an electrical current I proportional to the tunneling probability T estimated above[1].



Left: a simple model for STM. Right: This technique has been used by IBM to create "A boy and his atom", a stop-motion movie where each pixel is a single atom (IBM, 2013). It has been recognized by the Guinness Book of World Records as the World's Smallest Stop-Motion Film.

The exponential behavior of the tunneling probability makes this technique extremely sensitive to small variations in the sample's surface. With a typical work-function $\phi \sim 5\,\mathrm{eV}$, the current decreases by a factor 10 if the distance from the tip to the sample's surface changes by $\delta = 0.1\,\mathrm{nm}$:

$$\frac{I(d+\delta)}{I(d)} = \frac{\exp\left(-\frac{\sqrt{8m\phi}}{\hbar}(d+\delta)\right)}{\exp\left(-\frac{\sqrt{8m\phi}}{\hbar}d\right)} = \exp\left(-\frac{\sqrt{8m\phi}}{\hbar}\delta\right) \sim 0.1 \tag{2.2.8}$$

By measuring this tunnel current as the tip is moved across the sample (or alternatively by adjusting the tip height to maintain a constant current), it is thus possible to map the surface with an excellent accuracy.

---

[1] In practice, an external voltage V is applied to prevent electrons from the tip from tunneling to the sample, in order to ensure a non zero electrical current ($I \sim 10\,\mathrm{pA}$).

Alpha decay

The radioactive α decay corresponds to the emission of an α particle (2 protons and 2 neutrons) by an atomic nucleus. In a simple model, the α particle experiences two competing potentials:

- Inside the nucleus, the strong interaction appears as a flat negative potential

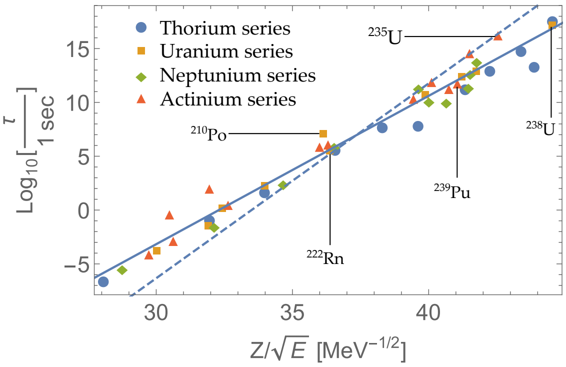
$$V(r < R_N) = -U_0$$

- Outside of the nucleus, the Coulombian interaction due to the Z protons of the nucleus repels the α particle

$$V(r > R_N) = \frac{2Ze^2}{4\pi\epsilon_0 r}$$

Alpha particles have a typical kinetic energy $E \lesssim 10\,\text{MeV}$, while the Coulomb barrier for heavy nucleus ($Z \gtrsim 80$) reaches $V(R_N \sim 10^{-15}\text{m}) \gtrsim 20\,\text{MeV}$, so the particle cannot escape classically from the strong interaction: it has to tunnel through the barrier. Considering that the radioactive lifetime τ of the nucleus is inversely proportional to the tunneling probability, we can recover the phenomenological law of Geiger and Nuttal[2] (1911):

$$\log(\tau) = A - B \times \frac{Z}{\sqrt{E}} \tag{2.2.9}$$



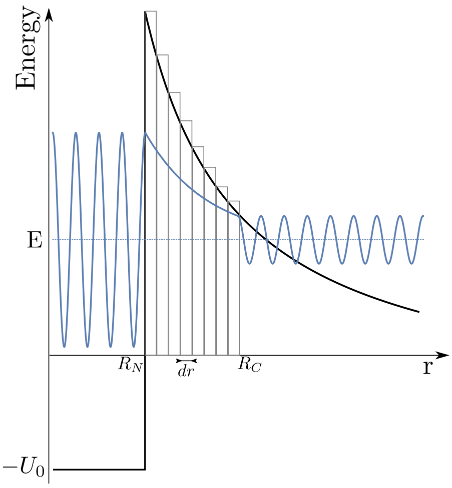
Radioactive lifetime as a function of the charge number of the nucleus and of the kinetic energy of the α particle. Data (Wikipedia) for the Thorium series (circle), Uranium series (square), Neptunium series (diamond) and Actinium series (triangle). The solid line is the best linear fit ($B = 1.4\,\text{MeV}^{-1/2}$) while the dashed line is the estimate from the Gamow model $B = 1.8\,\text{MeV}^{-1/2}$.

To do so, we follow the approach of Gamow, who offered the first derivation of this law in 1928. In order to recover the previous situation, we first decompose the Coulomb barrier into small steps of constant height, and we note T_i the probability of transmission through the i^{th} barrier

$$T_i \simeq \exp\left(-\frac{2}{\hbar}\sqrt{2m(V_i - E)}dx\right)$$

---

[2] This law is remarkable because it provides a correct estimate of the lifetime over 20 orders of magnitude !



Modeling α decay as quantum tunneling through the Coulomb barrier. To perform the calculation, we will approximate the repulsive Coulomb potential as a series of barriers similar to the one studied above.

The probability of passing through the whole barrier can then be expressed as:

$$T_{\text{tot}} = T_1 \times T_2 \times ... \times T_n$$

where the last bit corresponds to the distance R_C where the Coulomb barrier decreases below the kinetic energy of the particle[3]. Expressing the discrete sum as an integral, we get:

$$T_{\text{tot}} \sim \exp\left(-\frac{2}{\hbar}\sqrt{2m}\int_{R_N}^{R_C}\sqrt{V(r)-E dr}\right)$$

This integration can be performed analytically[4] and leads, when considering $R_C \gg R_N$, to the following result:

$$T_{\text{tot}} \sim \exp\left(-\frac{e^2\sqrt{2m}}{2\hbar\epsilon_0}\frac{Z}{\sqrt{E}}\right)$$

Assuming that the lifetime $\tau \propto T_{\text{tot}}^{-1}$, we recover the Geiger and Nuttal law, and we can estimate the slope to $B \sim 1.8\,\text{MeV}^{-1/2}$. As shown above, this rough estimate is in remarkable agreement with the experimental data !

2.3 Density of states (DOS)

2.3.1 Problem

What matters most is the energy of a state - quite often, all states with the same energy will behave in the same way. So we need to know how many states have any given energy - which is hard in the general case. But what we can easily know is how many states have a given *momentum* **p**.

In the discrete perspective, **p** can only take given values $\frac{2\pi\hbar}{L}\left(n_x, n_y, n_z\right)$ and the energy can therefore only take given values $E = E_0\left(n_x^2 + n_y^2 + n_z^2\right)$.

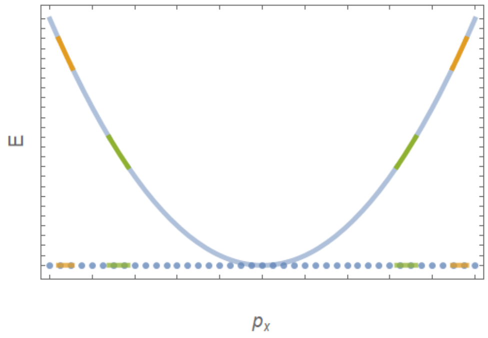
---

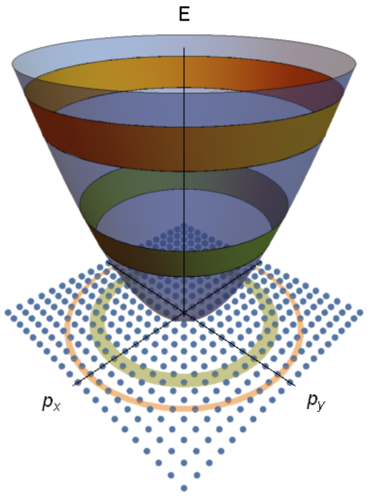
[3] In the classical picture, this distance corresponds to the closest point that a α particle with energy E could reach if it was sent towards the nucleus from infinity.

[4] or at least approximated using $\int_{x_0}^{x_1}\sqrt{\frac{x_1}{x}-1dx} \simeq x_1\int_0^1\sqrt{u^{-1}-1du} = x_1\frac{\pi}{2}$

In a continuous perspective, **p** can take any value, and the energy can therefore take any value as well. The question that makes sense is thus the following:

How many states is there with an energy between E and $E + dE$?





2.3.2 Definition

The density of state $D(E)$ is the number of states per energy interval, ie

$$\boxed{\text{There are } D(E)\,dE \text{ states with an energy between } E \text{ and } E + dE.}$$

Note: be careful with units ! If E is expressed in eV / Hz / nm, $D(E)$ is in eV^{-1}/ Hz^{-1}/ nm^{-1}.

Note From discrete to continuous description

$$\boxed{\sum_{\mathbf{p}} \rightarrow \left(\frac{L}{2\pi\hbar}\right)^3 \int d^3\mathbf{p}}$$

2.3.3 Strategy

The strategy to calculate the DOS is always the same

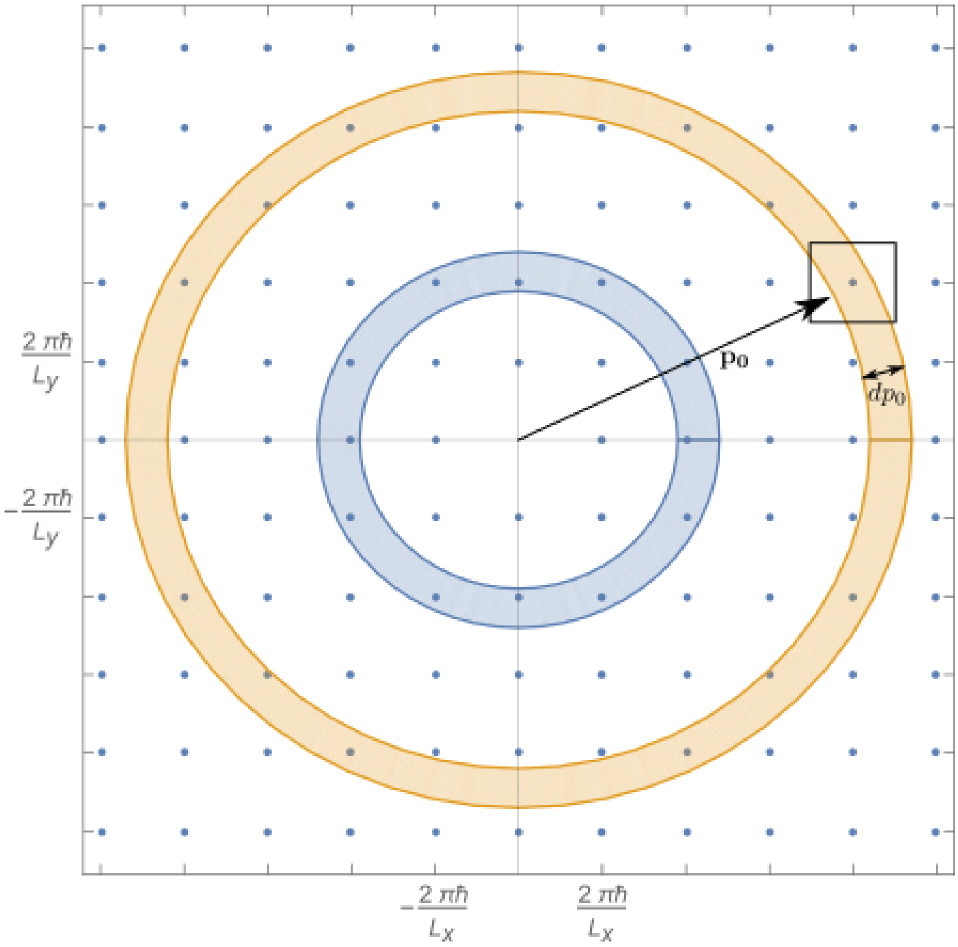
Step 1 We want to count energy states, but what we can easily do is to count momentum states. So let's translate the problem in terms of momentum.

All states with energy between E_0 and $E_0 + dE_0$ have a momentum with modulus between p_0 and $p_0 + dp_0$.

$$\underbrace{D(p_0)\,dp_0}_{\text{nb of states with momentum of modulus } p_0 \text{ up to } dp_0} = \underbrace{D(\mathrm{E}_0)\,dE_0}_{\text{nb of states with energy } E_0 \text{ up to } dE_0} \tag{2.3.1}$$

Note that here, p_0 (resp $p_0 + dp_0$) is the modulus of momentum corresponding to the energy E_0 (resp $E_0 + dE_0$). The differential elements dp_0 and dE_0 are related - and their relation is given by the dispersion relation $E_0 = f(p_0)$ which we calculated before.

So we now need to calculate $D(p_0)dp_0$.



Step 2 To do so, we first calculate the volume in momentum space where the corresponding states can be found. These states are located on the shell between the sphere of radius p_0 and the sphere of radius $p_0 + dp_0$. The volume of this shell depends on the dimension of the problem

$$dV^{3D}_{\text{shell}} = \frac{4}{3}\pi\left(p_0 + dp_0\right)^3 - \frac{4}{3}\pi p_0^3 = 4\pi p_0^2\, dp_0 \tag{2.3.2}$$

$$dV^{2D}_{\text{shell}} = \pi\left(p_0 + dp_0\right)^2 - \pi p_0^2 = 2\pi p_0\, dp_0 \tag{2.3.3}$$

$$dV^{1D}_{\text{shell}} = \left(p_0 + dp_0\right) - p_0 = dp_0 \tag{2.3.4}$$

Step 3 Finally, we will consider that momentum states are uniformly distributed in momentum space. In 3D, the momentum is quantified $\mathbf{p} = \frac{2\pi\hbar}{L}\left(n_x, n_y, n_z\right)$, so around any state, there is a small unoccupied volume $\left(\frac{\pi\hbar}{L}\right)^3$ in momentum space. The density of state in momentum space is thus

$$D^{3D}(\mathbf{p_0}) = \left(\frac{2\pi\hbar}{L}\right)^{-3} \tag{2.3.5}$$

and the number of states with momentum of modulus p_0 up to dp_0 is thus $D^{3D}(\mathbf{p_0}) \times$

dV^{3D}_{shell}, i.e.:

$$D^{3D}(p_0) = \left(\frac{2\pi\hbar}{L}\right)^{-3} 4\pi p_0^2 \, dp_0 \tag{2.3.6}$$

and we can rewind the calculation to reach $D(\mathrm{E}_0)$ (fiou !)

2.3.4 Calculations

For 3D massive free particles (detailed calculation)

As calculated before, the dispersion relation is

$$E = \frac{1}{2m} p^2 \tag{2.3.7}$$

which we differentiate to

$$dE = \frac{1}{m} p \, dp \tag{2.3.8}$$

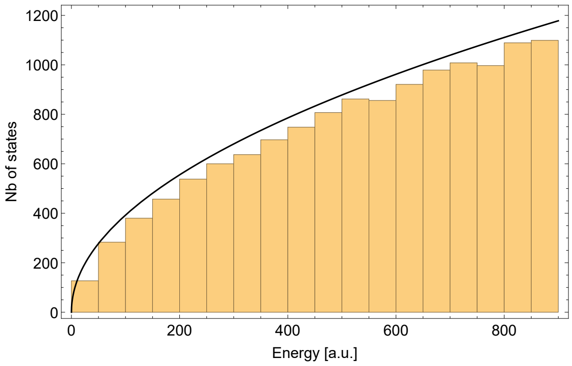
Eq. (2.3.1) can then be written as

$$\begin{aligned} \left(\frac{2\pi\hbar}{L}\right)^{-3} 4\pi p^2 dp &= D(E)\, dE \qquad (2.3.9)\\ &= D(E)\, \frac{1}{m}\, p\, dp \qquad (2.3.10)\end{aligned}$$

and we find

$$\boxed{D(E) = \left(\tfrac{L}{2\pi\hbar}\right)^3 4\pi m\, p = \left(\tfrac{L}{2\pi\hbar}\right)^3 4\pi\sqrt{2m^3} \times \sqrt{E}}$$

Note The density of state grows with the energy. This is basically saying that, for two shells with the same thickness dE_0, the larger one contains more states than the small one. Be careful, this result is not as intuitive as it might seem (cf DOS in 2D and 1D) !



Other useful cases

2D and 1D massive particles

The dispersion relation remains the same as above $dE = \frac{1}{m}\, p\, dp$, but we should now consider

$$\begin{aligned} D^{2D}(\mathbf{p_0}) &= \left(\tfrac{2\pi\hbar}{L}\right)^{-2} \\ dV^{2D}_{\text{shell}} &= 2\pi p_0\, dp_0 \end{aligned} \qquad \begin{aligned} D^{1D}(\mathbf{p_0}) &= \left(\tfrac{2\pi\hbar}{L}\right)^{-1} \\ dV^{1D}_{\text{shell}} &= dp_0 \end{aligned}$$

The relation $D(E)dE = D(\mathbf{p_0}) \times dV_{\text{shell}}$ thus becomes

$$\begin{aligned} D^{2D}(E) &= \left(\frac{2\pi\hbar}{L}\right)^{-2} 2\pi p \frac{dp}{dE} \\ &= \left(\frac{L}{2\pi\hbar}\right)^{2} 2\pi m \end{aligned} \qquad \begin{aligned} D^{1D}(E) &= \left(\frac{2\pi\hbar}{L}\right)^{-1} \frac{dp}{dE} \\ &= \left(\frac{L}{2\pi\hbar}\right) \sqrt{\frac{m}{2}} \times \frac{1}{\sqrt{E}} \end{aligned}$$

3D photons

The dispersion relation of mass-less particles such as photons is $E = \hbar kc = pc$, leading to $dE = c\,dp$. The distribution of **p** vectors is the same as for massive 3D particles. We find therefore:

$$D(E) = \left(\frac{2\pi\hbar}{L}\right)^{-3} 4\pi p^2 \frac{dp}{dE} \tag{2.3.11}$$

$$= \left(\frac{L}{2\pi\hbar}\right)^{3} \frac{4\pi}{c^3} \times E^2 \tag{2.3.12}$$

Including Spin

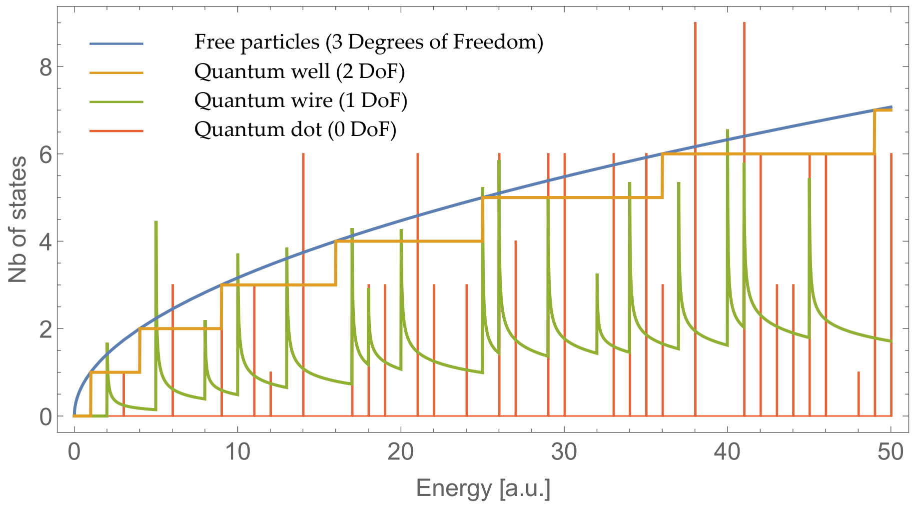
Unlike momentum, spin is a discrete property: a particle with spin s can access $(2s+1)$ states, from $S_z = +\hbar s$ to $S_z = -\hbar s$ by steps of $\hbar$. The total density of states should therefore be multiplied by $\times(2s+1)$.

With nano-structures

In nano-structures, particles are confined along some directions of space (1 direction in a quantum well, 2 in a quantum wire and 3 in a quantum dot), and remain free in the other directions. To describe the existing states in such systems, we need to merge the results obtained in the previous chapter on quantum confinement, and in this chapter for free particles.

	Well	Wire	Dot
Confinement	1D	2D	3D
Corresponding DoS	$\delta(E - E_0 n_x^2)$	$\delta(E - E_0 \left(n_x^2 + n_y^2\right))$	$\delta(E - E_0 \left(n_x^2 + n_y^2 + n_z^2\right))$
Degree of freedom	2	1	0
Corresponding DoS	indep E	$\propto 1/\sqrt{E}$	-

The total density of state is the product of these two contributions:



2.3.5 Summary on density of states

	Free massive part. 3D	Free massive part. 2D	Free massive part. 1D	Photon
$d^n\mathbf{p}$	$4\pi p^2\,dp$	$2\pi p\,dp$	dp	$4\pi p^2 dp$
$D(\mathbf{p})$	$1/\left(\frac{2\pi\hbar}{L}\right)^3$	$1/\left(\frac{2\pi\hbar}{L}\right)^2$	$1/\left(\frac{2\pi\hbar}{L}\right)$	$1/\left(\frac{2\pi\hbar}{L}\right)^3$
E	$\frac{p^2}{2m}$	$\frac{p^2}{2m}$	$\frac{p^2}{2m}$	$p\,c$
dE	$\frac{1}{m}\,p\,dp$	$\frac{1}{m}\,p\,dp$	$\frac{1}{m}\,p\,dp$	$c\,dp$
$D(E)$	$4\pi\sqrt{2m^3}/\left(\frac{2\pi\hbar}{L}\right)^3\times\sqrt{E}$	$2m\pi/\left(\frac{2\pi\hbar}{L}\right)^2$	$\sqrt{m}/\left(\sqrt{2}\frac{2\pi\hbar}{L}\right)\times\frac{1}{\sqrt{E}}$	$4\pi/\left(\frac{2\pi\hbar c}{L}\right)^3\times E^2$

with spin s: $D\rightarrow D\times(2s+1)$

2.4 Take home message

- Plane waves are very often used to describe or at least label quantum states.
- The evanescent behavior of plane waves penetrating a potential barrier provides a non-zero probability for a quantum particle to *tunnel* through the barrier.
- The density of states counts the number of quantum states with a given energy: there are $D(E).dE$ states with an energy between E and $E+dE$.
- The expression of the density of states depends on the dispersion relation (massive or massless particles ?) and on the dimensionality of the problem.

Chapter 3

Occupation factor

3.1 Occupation number

So far, we have discussed which states were accessible to the system - this means that we can prepare the system and put it in any of these states. But what if we don't prepare it, and just let it go to its "natural" equilibrium state. Which state would that be ?

An equivalent way to state this question is:

What is the probability of finding the system in any given state ?

What is the average number of particle in any given state ?

Note 1 This question is not specific to quantum mechanics. We could basically ask the same question concerning the molecules in this room: what the probability of finding a molecule traveling at 10 m/s towards the window ?

Note 2 The notion of "natural equilibrium" would require much more development than what we will do here. Roughly speaking, it corresponds to a thermal state, characterized by the thermodynamical potential of the system being minimal. We won't go further into the details.

We will accept the following key results:

- The average number of particles occupying any given state only depends on the energy of this state and on the quantum nature of particles (electrons are *fermions*, photons and phonons are *bosons*).
- The probability distribution is entirely determined by two parameters: the temperature T and the chemical potential μ

$$f(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon-\mu}{k_B T}\right) + \alpha} \text{ with } \alpha = \begin{cases} +1 & \text{Fermions} \rightarrow \text{Fermi Dirac distribution} \\ 0 & \text{Classical} \rightarrow \text{Maxwell Boltzmann distribution} \\ -1 & \text{Bosons} \rightarrow \text{Bose Einstein distribution} \end{cases}$$

where $k_B = 10^{-23}\,\text{J.K}^{-1}$ is the Boltzmann constant.

Note 3 The chemical potential is probably not as usual to you as the temperature, but it plays a similar role. Roughly speaking, temperature is related to the amount of energy stored in the system ; the chemical potential is related to the amount of particles stored in the system[1]. A qualitative picture takes the chemical potential as the quantity of work required to add one additional particle to the system - or equivalently the amount of work gathered when extracting a particle from the system.

Two systems who can share energy will converge towards the same temperature ; two systems who can share particles will converge towards the same chemical potential.

Note 4 We introduced here two types of particles. Fermions have half-integer spins (electrons, holes, nucleons, quarks, neutrinos...), while bosons have integer spins (photons, phonons). When considering an ensemble of indistinguishable particles, the former interfere destructively, while the latter interfere constructively (and classical particles don't interfere at all). This difference results from very fundamental properties of symmetry groups, which will not be discussed here.

Note 5 If $-\mu \gg k_B T$ (which happens at high temperatures), the distribution function f is the same for Fermions, Bosons or classical particles.

Note 6 The Greek letter μ is used both for the chemical potential (in J) and for the mobility of carriers (in $\text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$). To avoid confusion, the chemical potential of Fermions is often referred to as *Fermi energy* and noted E_F, for reasons that should become clear by the end of this lecture.

First application

With a simple accounting, we get the total number of particles and total energy of the system:

$$\boxed{\begin{aligned} N &= \int d\epsilon\, D(\epsilon)\, f(\epsilon) \\ E &= \int d\epsilon\, \epsilon\, D(\epsilon)\, f(\epsilon) \end{aligned}}$$

Note If N is fixed, then μ has the change with the temperature such that $\int d\epsilon\, D(\epsilon).f(\epsilon)$ remains constant.

Note While energy is the most useful way to label states, it is always possible to consider counting states by momentum, for instance: $E = \int d^3\mathbf{p}\, \epsilon(\mathbf{p})\, D(\mathbf{p})\, f(\epsilon(\mathbf{p}))$.

3.2 Maxwell Boltzmann distribution - equipartition theorem

We first consider a classical gas, like air in this room. We describe it as N classical massive free particles in 3D, at a temperature T.

1. The density of state for 3D massive free particles is given by $D(E) = \gamma\sqrt{E}$, and classical particles are populating energy states according to the Maxwell Boltzmann distribution.

---

[1] Be careful with this rough picture: both the energy and the number of particles are actually related to T and μ.

2. The chemical potential μ is such that the total number of particles is equal to N:

$$N = \gamma \exp\left(\frac{\mu}{k_B T}\right) \times \underbrace{\int d\epsilon \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{k_B T}\right)}_{\frac{\sqrt{\pi}}{2}(k_B T)^{3/2}} \Rightarrow \exp\left(\frac{\mu}{k_B T}\right) = \frac{N}{(k_B T)^{3/2}} \frac{2}{\gamma\sqrt{\pi}}$$

   We see here that the chemical potential, the temperature and the number of the system are related.

3. To estimate the average energy per particle, we calculate the total energy E, and use the previous expression to replace the chemical potential by the number of particles:

$$E = \gamma \exp\left(\frac{\mu}{k_B T}\right) \times \underbrace{\int d\epsilon\, \epsilon \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{k_B T}\right)}_{\frac{3\sqrt{\pi}}{4}(k_B T)^{5/2}} \Rightarrow \frac{E}{N} = \frac{3}{2} \times k_B T$$

4. The same calculation can be performed in 1D and 2D, where $D(E) = \gamma$ and $D(E) = \gamma/\sqrt{E}$ respectively:

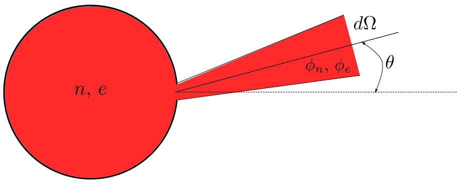
$$\begin{aligned} \exp\left(\frac{\mu_{2D}}{k_B T}\right) &= \frac{N}{k_B T}\frac{1}{\gamma} \\ \frac{E}{N} &= k_B T \end{aligned} \qquad\qquad \begin{aligned} \exp\left(\frac{\mu_{1D}}{k_B T}\right) &= \frac{N}{\sqrt{k_B T}}\frac{1}{\sqrt{\pi}\gamma} \\ \frac{E}{N} &= \frac{1}{2} \times k_B T \end{aligned}$$

   This result illustrate the celebrated *equipartition theorem*: each degree of freedom of an ideal gas contribute to the average energy of the particles by a factor $\frac{1}{2} \times k_B T$.

Useful integrals: $\int_0^\infty dx\, x\sqrt{x}\, e^{-x} = \frac{3\sqrt{\pi}}{4}$, $\int_0^\infty dx\, x\, e^{-x} = 1$, $\int_0^\infty dx\, \sqrt{x}\, e^{-x} = \frac{\sqrt{\pi}}{2}$, $\int_0^\infty dx\, \frac{1}{\sqrt{x}} e^{-x} = \sqrt{\pi}$

3.3 Bose Einstein distribution - black-body radiation

We will now describe the light emitted by the Sun - which will be most useful for solar cells ! To do so, we will consider the sun as a closed box ("cavity") in which an ensemble of photons (mass-less bosons) are at equilibrium at a temperature $T_\odot$ and at zero chemical potential. We will then estimate the flux exiting through a hole drilled in the wall of the box.



Let us first determine the properties of the photon gas inside the cavity, assumed to be of size $L \times L \times L$.

1. The density of state for 3D mass-less free particles is given by $D(E) = \left(\frac{L}{2\pi\hbar}\right)^3 \frac{4\pi}{c^3} \times E^2$, and bosons are populating energy states according to the Bose-Einstein distribution.

2. By definition of the density of state, the number of photons with an energy between E and $E + dE$ is given by $D(E)dE$. The spatial density of photons is simply that value divided by

the volume of the box L^3, ie:

$$dn(E) = \frac{E^2}{\pi^2\hbar^3c^3}\frac{1}{\exp\left(\frac{E}{k_BT}\right)-1}\,dE \tag{3.3.1}$$

3. We now consider a small hole of surface dS drilled in the wall of the cavity. The hole is small enough for the photon distribution to remain unperturbed inside the cavity. All photons that can escape the cavity through this hole in the direction Ω over a duration dt initially occupy a volume $dV = cdt\,\cos\theta dS$. Within this volume, there are $dn(E)dV$ photons with energy between E and $E + dE$. And as their momentum is isotropically distributed, only a fraction $d\Omega/4\pi$ is going in the Ω direction up to $d\Omega$. This simple accounting allows us to estimate the flux of photons with an energy between E and $E + dE$ escaping the cavity in a direction given by a solid angle between Ω and $\Omega + d\Omega$ during a duration dt:

$$dN_{\text{out}}(E,\Omega) = \frac{d\Omega}{4\pi}\times dn(E)\times cdt\,\cos\theta dS \tag{3.3.2}$$

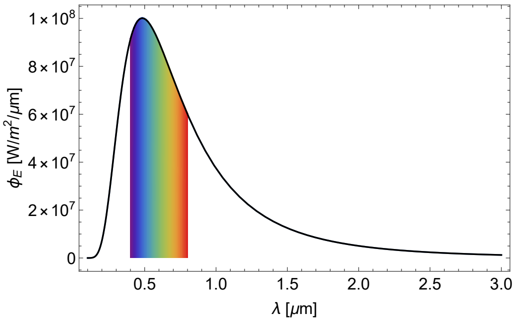
$$\tag{3.3.3}$$

4. To obtain the Planck law, we first have to integrate over all possible angles (to obtain the total number of photon escaping per second and per surface unit)

$$d\phi_N(E) = \frac{E^2}{\pi^2\hbar^3c^2}\frac{1}{\exp\left(\frac{E}{k_BT}\right)-1}dE \times \underbrace{\int_{\theta=0}^{\pi/2}\int_{\varphi=0}^{2\pi}\cos\theta\frac{\sin\theta d\theta d\varphi}{4\pi}}_{1/4} \tag{3.3.4}$$

Considering that each of these photons carries an energy E, we recover the celebrated Planck's law expressing the spectral intensity of radiation:

$$\begin{aligned}\phi_E(E) &= E\times\frac{d\phi_N(E)}{dE}\\ &= \frac{1}{4\pi^2\hbar^3c^2}\times\frac{E^3}{\exp\left(\frac{E}{k_BT}\right)-1}\end{aligned}$$



Spoiler alert: in solar cell physics, we will consider a radiation with a non zero chemical potential !

From this relation, several key results can be reached.

1. The Planck law can be expressed with different units, keeping in mind that the density of photons should be adapted

$$\begin{gathered}u(E)dE = u(\omega)d\omega = u(\lambda)d\lambda\\ E = \hbar\omega = hc/\lambda\end{gathered}$$

Energy	Angular frequency	Frequency	Wavelength
$\frac{E^3}{4\pi^3\hbar^3c^3}\frac{1}{\exp\left(\frac{E}{k_BT}\right)-1}$	$\frac{(\hbar\omega)^3}{4\pi^3\hbar^2c^3}\frac{1}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}$	$\frac{(h\nu)^3}{2\pi^2\hbar^2c^3}\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}$	$\frac{2hc}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1}$
$E_{\text{max}} = 2.82\,k_BT$	$\hbar\omega_{\text{max}} = 2.82\,k_BT$	$h\nu_{\text{max}} = 2.82\,k_BT$	$\lambda_{\text{max}} = 0.2497\,\frac{\bar{}\mathrm{m\,eV}}{k_BT}$

2. The average energy per photon is

$$\langle\hbar\omega\rangle = \frac{\int \frac{E^3}{\exp\left(\frac{E}{k_BT}\right)-1}dE}{\int \frac{E^2}{\exp\left(\frac{E}{k_BT}\right)-1}dE} = \frac{\pi^4}{30\,\zeta(3)} = 2.7\,k_BT \tag{3.3.5}$$

A simple estimate ($\langle\hbar\omega\rangle = 3\,k_BT$) can be found by neglecting the -1 in the denominator.

3. The spectral intensity is maximum for

$$0 = \frac{d}{d\lambda}\frac{\lambda^{-5}}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1} = \frac{-5\lambda^{-6}}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1} - \frac{\lambda^{-5}\times\exp\left(\frac{hc}{\lambda k_BT}\right)\times\left(-\frac{hc}{\lambda^2k_BT}\right)}{\left(\exp\left(\frac{hc}{\lambda k_BT}\right)-1\right)^2}$$

$$\Leftrightarrow 5 = \frac{\exp\left(\frac{hc}{\lambda k_BT}\right)}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1}\times\left(\frac{hc}{\lambda k_BT}\right)$$

and solving numerically $x\times\frac{e^x}{e^x-1} = 5$ for $x \simeq 4.96$, we recover the Wien's displacement law:

$$\lambda_{\text{max}}T \simeq 2.9\,10^{-3}\,\text{m.K} \tag{3.3.6}$$

4. The total power emitted per surface unit is given by the Stefan law

$$P = \frac{1}{4\pi^2\hbar^3c^2}\times\int\frac{E^3}{\exp\left(\frac{E}{k_BT}\right)-1}dE = \sigma T^4 \tag{3.3.7}$$

where we introduced the Stefan constant (memo hint: σ value is 5-6-7-8 in standard units)

$$\sigma = \frac{\pi^2k_B^4}{60\hbar^3c^2} \simeq 5.67\times10^{-8}\,\text{W.m}^{-2}.\text{K}^{-4} \tag{3.3.8}$$

3.4 Fermi Dirac distribution - Fermi level

We finally turn to the description of an ensemble of free spin 1/2 fermions in 3D. This situation will notably help us understand how electrons behave in a solid.

1. The density of state for 3D massive particles is $D(E) = 2\times4\pi\left(\frac{L}{2\pi\hbar}\right)^3\sqrt{2m^3}\sqrt{E}$ and fermions obey the Fermi-Dirac distribution f_{FD}. Since exp > 0, the number of fermions occupying any energy state is $f_{FD} < 1$, which is compatible with the Pauli exclusion principle: two fermions can never be found in the same state.

2. At $T\to0$, $\exp\left(\frac{E-\mu}{k_BT}\right)\to\begin{cases}+\infty & \text{if } E>\mu\\ 0 & \text{if } E<\mu\end{cases}$ and the Fermi-Dirac distribution can therefore be

approximated by a step-function $f_{FD}(E) = \theta\left(\mu - E\right)$ with a threshold given by the chemical potential μ. In this situation ($T = 0$), the chemical potential is called the *Fermi energy* and noted E_F.

3. An ensemble of Fermions is correctly described by such a step-function distribution as long as $T \ll T_F = E_F/k_B$.

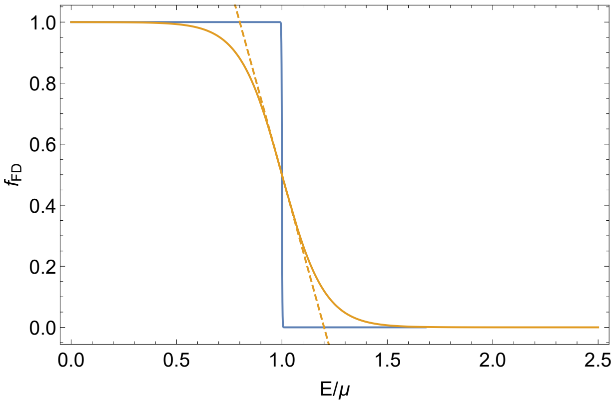
4. Considering that the ensemble contains N fermions, the Fermi energy has to be such that

$$\begin{aligned} N &= \int d\epsilon\, D(\epsilon).f(\epsilon) \\ &= 8\pi \left(\frac{L}{2\pi\hbar}\right)^3 \sqrt{2m^3} \int_0^{E_F} \sqrt{\epsilon} d\epsilon \\ \Rightarrow n &= \frac{N}{L^3} = \frac{8}{3}\pi \left(\frac{\sqrt{2m}}{2\pi\hbar}\right)^3 E_F^{3/2} \end{aligned}$$

	n	m	E_F	T_F
Nucleus	$\sim 10^{44}\,\mathrm{m}^{-3}$	$1.6 \times 10^{-27}\,\mathrm{kg}$	$\sim 50\,\mathrm{MeV}$	$10^9\mathrm{K}$
Atom	$\sim 10^{31}\,\mathrm{m}^{-3}$	$9 \times 10^{-31}\,\mathrm{kg}$	$\sim 200\,\mathrm{eV}$	$10^6\,\mathrm{K}$
Metal	$\sim 10^{29}\,\mathrm{m}^{-3}$	$9 \times 10^{-31}\,\mathrm{kg}$	$\sim 10\,\mathrm{eV}$	$10^5\,\mathrm{K}$

$$\boxed{E_F = \frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3}}$$

Numerical applications for nuclear, atomic and condensed matter physics show that the ambient temperature is well below the Fermi temperature. This means that fermions in these systems are well in the quantum regime (they are *degenerated*) and that Pauli principle is apparent. The Fermi energy gives a typical scale, and it is often useful to approximate the Fermi-Dirac distribution "around" the Fermi energy (i.e. for energies E such that $|E - E_F| \ll E_F$:



- Around the Fermi level
$$f_{FD} \simeq \frac{1}{2} - \frac{1}{4} \times \frac{E - \mu}{k_B T}$$
- Well above the Fermi level
$$f_{FD} \simeq \exp\left(-\frac{E - \mu}{k_B T}\right)$$
- Well below the Fermi level
$$f_{FD} \simeq 1$$

5. The total amount of energy stored in the ensemble is

$$E = \int d\epsilon\, \epsilon.D(\epsilon).f(\epsilon) = 4\pi \left(\frac{L}{2\pi\hbar}\right)^3 \sqrt{2m^3} \int_0^{E_F} \epsilon\sqrt{\epsilon} d\epsilon = \frac{3}{5}\, N\, E_F$$

It is important to see that the Fermi energy is *not* the average energy per particle (that would be $3\,E_F/5$), nor the total energy carried by the fermions !

Application to astrophysics (just for fun, no use for STEEM):

A white dwarf is a dead star where two competing forces are balanced:

1. Gravity tends to collapse the star, as the gravitational energy decreases if the radius of the star decreases, following
$$U = -\frac{3GM^2}{5R}$$
where R is the radius of the star, M is its mass and $G = 6.67 \times 10^{-11}\, m^3\, \mathrm{kg}^{-1}\, \mathrm{s}^{-2}$ is the Cavendish constant (demonstration in any undergrad textbook).

2. Pauli principle forbids two electrons to be in the same state, and the internal energy increases with the density
$$E = \frac{3}{5} N\, E_F = \frac{3}{40} \left(\frac{9}{4\pi^2}\right)^{2/3} \frac{h^2}{m_e} \frac{N^{5/3}}{R^2} \tag{3.4.1}$$

The radius of the white dwarf has to minimize the total energy of the star

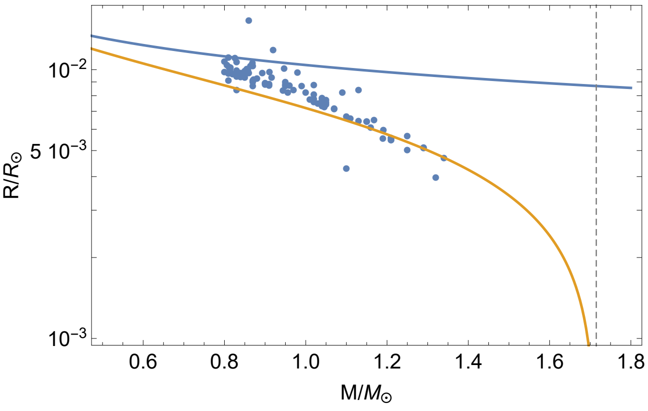
$$0 = \frac{\partial}{\partial R}(U + E) = \frac{3GM^2}{5R^2} - \frac{6}{40}\left(\frac{9}{4\pi^2}\right)^{2/3} \frac{h^2}{m_e}\frac{N^{5/3}}{R^3} \tag{3.4.2}$$
$$\Rightarrow R = \frac{N^{5/3}}{m_e M^2} \frac{2h^2}{8G} \left(\frac{9}{4\pi^2}\right)^{2/3} \tag{3.4.3}$$

The mass of the star is essentially given by the number of nucleons (proton and neutron) ; and each proton is accompanied by one electron. The mass of the star is thus proportional to the number of electrons, and we write:

$$M = \gamma N \tag{3.4.4}$$

On average, for light elements, atoms have as many neutrons as protons, and we take $\gamma \sim 2m_p$. We therefore find that, the heavier the star, the smaller its radius

$$R = \frac{1}{\gamma^{5/3} m_e} \frac{2h^2}{8G} \left(\frac{9}{4\pi^2}\right)^{2/3} \frac{1}{M^{1/3}} \tag{3.4.5}$$



Radius of white dwarfs as a function of their mass. Data from "A catalogue of isolated massive white dwarfs", M. Nalezyty & J. Majed, A&A ***420****, 507–513 (2004). The blue line is the theoretical value derived above. It gives a very good estimate for white drawfs lighter than the sun. For heavier stars, electrons become relativistic and the classical dispersion relation* $E = p^2/2m$ *should be replaced by* $E = \sqrt{p^2c^2 + m^2c^4}$ *(yellow line). The dashed line is the Chandrasekhar limit. Note that the theoretical estimate has no free parameter !*

We can go one step further and consider a star in which all electrons are ultra-relativistic. This situation can be described by considering free 3D particles with a dispersion relation $E = pc$ (just like photons), but following a Fermi-Dirac distribution (unlike photons). We therefore find:

$$\begin{aligned} N &= 2 \times \left(\tfrac{L}{hc}\right)^3 \int_0^{E_F} E^2 dE & \qquad E &= 2 \times \left(\tfrac{L}{hc}\right)^3 \int_0^{E_F} E^3 dE = \tfrac{3}{4}\, N\, E_F \\ &= \tfrac{32\pi^2}{9} \tfrac{R^3}{h^3 c^3} E_F^3 & &= \tfrac{3}{8} \left(\tfrac{3}{2\pi}\right)^{2/3} \tfrac{hc}{R} N^{3/4} \end{aligned}$$

This time, the total energy has no local minimum as a function of R:

$$E + U = \left(\frac{3hc}{8} \left(\frac{3}{2\pi} \right)^{2/3} \left(\frac{M}{\gamma} \right)^{4/3} - \frac{3GM^2}{5} \right) \frac{1}{R}$$

and such a star can only be stable if the pre-factor is 0, i.e.

$$M = \frac{1}{\gamma^2} \left(\frac{15hc}{24G} \right)^{3/2} \simeq 1.7\, M_\odot$$

This is the known as the Chandrasekhar limit (vertical line in the above figure), which sets the upper limit for white dwarfs. In any star heavier than this limit, Pauli principle is not sufficient to balance the gravitational collapse and the density increases until electrons and protons merge to become neutrons - hence forming a neutron star, where gravity is balanced by the degeneracy pressure of *neutrons.* The same calculation as before can be performed for neutron stars, basically by replacing $m_e \to m_n$ and $\gamma \to m_n$. This time, if gravity becomes too strong even for neutrons, the neutron star collapses and form a black hole.

3.5 Take home message

- The probability distribution is entirely determined by two parameters: the temperature T and the chemical potential μ

$$f(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + \alpha} \text{ with } \alpha = \begin{cases} +1 & \text{Fermions} \to \text{Fermi Dirac distribution} \\ 0 & \text{Classical} \to \text{Maxwell Boltzmann distribution} \\ -1 & \text{Bosons} \to \text{Bose Einstein distribution} \end{cases}$$

- A simple accounting gives

$$\begin{aligned} N &= \int d\epsilon\, D(\epsilon).f(\epsilon) \\ E &= \int d\epsilon\, \epsilon.D(\epsilon).f(\epsilon) \end{aligned}$$

- For classical particles, the MB distribution leads to the equipartition theorem: each degree of freedom contributes as $k_B T/2$ to the average energy per particle.
- For Fermions, the FD distribution leads to the exclusion principle (two fermions cannot share the same quantum state). At low temperatures, Fermions fill all available states starting from low energy states. The chemical potential corresponds to the energy of the last particle.

- For Bosons, the BE distribution notably leads to the properties of the black-body radiation. It also allows a phase transition towards a Bose-Einstein condensate, where all particles are accumulated in the same quantum state. This transition was not discussed here.

Chapter 4

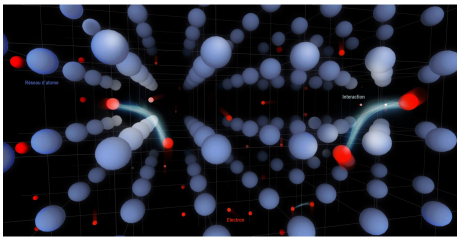
Basic semiconductor physics

4.1 Introduction

4.1.1 Aim and scope

We want to describe the behavior of materials. The whole quantum description is a nightmare:

$$\begin{aligned} H = &\sum_{\text{atoms}} \frac{1}{2M}\mathbf{P}_i^2 + \sum_{\text{electrons}} \frac{1}{2m}\mathbf{p}_i^2 \\ &+ \frac{Z^2}{2} \sum_{\text{at.}-\text{at.}} V_c\left(\mathbf{R}_i - \mathbf{R}_j\right) \\ &+ Z \sum_{\text{at.}-\text{el.}} V_c\left(\mathbf{r}_i - \mathbf{R}_j\right) \\ &+ \frac{1}{2} \sum_{\text{el.}-\text{el.}} V_c\left(\mathbf{r}_i - \mathbf{r}_j\right) \end{aligned}$$



so we will consider several simplifications. We assume that atoms are distributed periodically, forming a lattice. We assume that they don't move (Born Oppenheimer approximation), and we will only consider the dynamics of electrons. We assume that all electron experience the same potentials, due to the atomic lattice and to the other electrons (mean field approximation).

With theses approximations, each electron can be taken independently from the others, and the Hamiltonian can be written as the independent terms

$$H \simeq \sum_{\text{electrons}} \frac{1}{2m}\mathbf{p}_i^2 + V_{\text{eff}}(\mathbf{r}_i) \tag{4.1.1}$$

where the effective potential contains all information about what the electron is experiencing.

4.1.2 A first simple example

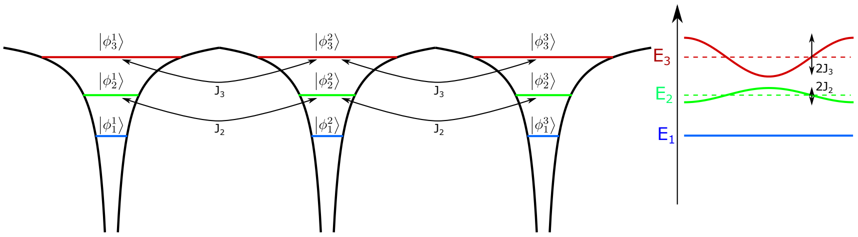
We will first consider a simple 1D model, to highlight the key properties of electrons in a periodic potential. We will generalize these results in the next section.

Let us consider N atoms regularly spaced with a distance a - which is a generalization of the double well situation discussed in the first chapter. We will note $h_0^{(n)}$ the Hamiltonian corresponding to the n^{th} atom alone. The eigenstates of $h_0^{(n)}$ are noted $\left|\phi_i^{(n)}\right\rangle$ with energies E_i - so each ϕ_i^n is the same function simply centered around the n^{th} atom

$$\phi_i^n(x) = \phi_i(x + na) \tag{4.1.2}$$

$$h_0\phi_i = E_i\phi_i \tag{4.1.3}$$

Because of the tunnel effect, an electron can jump from one atom to the next one. We note J_i the coupling strength between the i^{th} energy state of two neighboring atoms - and we assume that the electron can only jump to its nearest neighbor, and cannot jump from from one energy state to another.



Reminder

- In the presence of a trapping potential, the Hamiltonian eigenstates take discrete energy values, and can be labeled by an integer number n.
- Any coupling between states tends to lift degeneracies. The eigenstates are then delocalized. The resulting energy splitting is larger if the coupling is stronger.

Like in chapter 1, $H = H_0 + V$ with

$$H_0 |\phi_i^n\rangle = E_i |\phi_i^n\rangle \tag{4.1.4}$$

$$V |\phi_i^n\rangle = -J_i \left(\left|\phi_i^{n-1}\right\rangle + \left|\phi_i^{n+1}\right\rangle \right) \tag{4.1.5}$$

We look for eigenstates of the total Hamiltonian H as linear combinations of the eigenstates of H_0 (we know we can do this because $\{|\phi_i^n\rangle\}$ is a basis). Justify that we can restrict to the same energy levels on all sites

$$|\psi_i\rangle = \sum_n c_i^n |\phi_i^n\rangle \qquad \& \qquad H|\psi_i\rangle = E|\psi_i\rangle \tag{4.1.6}$$

which leads to

$$E\, c_i^n = E_i\, c_i^n - J_i \left(c_i^{n-1} + c_i^{n+1} \right) \tag{4.1.7}$$

Due to the lattice symmetry, the Bloch theorem (see below) implies that eigenstates have to obey

$$\psi_j(x + a) = e^{ika}\psi_j(x) \tag{4.1.8}$$

$$\Rightarrow \sum_n c_j^n \phi_j^n(x + a) = \sum_n c_j^n e^{ika} \phi_j^n(x) \tag{4.1.9}$$

where $k = \frac{2p\pi}{N\,a}$, $p \in \mathbb{Z}$ to satisfy the boundary conditions. As $N \gg 1$, we will treat k as a continuous quantity. Using eq.(4.1.2), we identify

$$c_j^{n+1} = c_j^n e^{ika} \Rightarrow c_j^n = c_j^0 e^{i\,n\,k\,a} \tag{4.1.10}$$

and this relation allows us to solve eq.(4.1.7) and to obtain the dispersion relation

$$E = E_i - 2J_i \cos(ka) \tag{4.1.11}$$

From this finding, several key results should be highlighted

Energy bands

In the double well situation, the energy E_0 was split in two discrete values, $E_0 + J$ and $E_0 - J$. In this case, each energy E_i is split into a continuum of energies distributed between $E_i + 2J_i$ and $E_i - 2J_i$. These values form an *energy band* allowed for the electron. The situation is midway between trapped electrons (the state of which is defined by a discrete number n, corresponding to discrete energies E_n) and that of free electrons (the state of which is defined by a momentum $\mathbf{p}$, corresponding to a continuous energy $E = p^2/2m$). Here, the electron state is defined by a discrete number (describing in which band is the electron) *and* a continuous quantity k (describing where is electron located within the band).

Energy gaps

Just like for trapped electrons, some energies corresponds to no states, and can there not be reached. This is the case for all energies between the top of one band ($E_i + 2J_i$) and the bottom of the following one ($E_{i+1} - 2J_{i+1}$). These energies form a *forbidden band,* and the corresponding width is called the *energy gap.*

Folding of the band structure

Considering that k always appears in periodic functions, all quantities are unchanged if we change $k \rightarrow k + p\frac{2\pi}{a}$. So rather than consider $k \in [-\infty, +\infty]$, we will only consider the interval $\left[-\frac{\pi}{a}, +\frac{\pi}{a}\right]$, and reduce any value of k to that interval by adding or subtracting $2\pi/a$ to it an integer amount of times.

Number of states

Considering that $k = \frac{2p\pi}{Na}$, $p \in \mathbb{Z}$ and the previous point, we see that there are N different states (remember that N is the number of atoms in the chain). Since electrons have spin 1/2, there are $2N$ electronic states per energy band. For all practical cases, as $N \gg 1$, we will consider k to be continuous. But we can now understand that if each atom brings two electrons per energy state, all the existing states will be filled.

4.1.3 Generic results

This first example was intended to give some global ideas about how electrons behave in a solid. We will now give strong and generic results. We will not go into the details of the demonstrations.

1. Lattice structure

   In our simplified example, we considered a 1D periodic system. In the general case of a 3D system, a crystalline structure can be defined with two ingredients:

   (a) A Bravais lattice - ie an infinite array of points obtained with a translation $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where $\mathbf{a}_i$ are the *primitive vectors* of the lattice.

   The Bravais lattice holds *quantity* of information on the properties of the system, because it defines the symmetry of the system. Two of the key notions associated to the Bravais lattice are:

   i. The reciprocal lattice
      is essentially the Fourier transform of the direct lattice. It is defined as the ensemble of points **K** such that $\exp(i\,\mathbf{K}.\mathbf{R}) = 1$, where $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ is any given point of the direct lattice. The reciprocal lattice is also a Bravais lattice.
   ii. The Brillouin zone
      is the region of the reciprocal lattice closer to the origin than to any other point of the lattice. It is the extension of the interval $\left[-\frac{\pi}{a}, +\frac{\pi}{a}\right]$ which played a major role in our simple example
   (b) A motif - ie an ensemble of atoms occupying each point of the lattice.

2. Bloch Theorem is one of the most important result for electrons in a solid. Let's state it first, we will discuss its interpretation just below.

   Because the lattice potential is periodic, the eigenstate of the Hamiltonian take the form:

   $$H\psi_{n,\mathbf{k}} = E_{n\,\mathbf{k}}\psi_{n,\mathbf{k}} \tag{4.1.12}$$
   $$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} \times u_{n,\mathbf{k}}(\mathbf{r}) \tag{4.1.13}$$

   where $u_{n,\mathbf{k}}(\mathbf{r})$ is has the same periodicity as the lattice - i.e.

   $$u_{n,\mathbf{k}}\left(\mathbf{r} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3\right) = u_{n,\mathbf{k}}(\mathbf{r})$$

   This theorem is a very deep result, coming from the symmetry properties of the lattice. It justifies the form of the coefficients $c_j^{(n)}$ chosen above.

   Note **k** is the "crystal momentum" or "quasi-momentum". *It does NOT give the total momentum of the electron*

   $$\begin{aligned}\langle\mathbf{p}\rangle_{n,\mathbf{k}_0} &= \langle\psi_{n,\mathbf{k}_0}|-i\hbar\boldsymbol{\nabla}\,|\psi_{n,\mathbf{k}_0}\rangle \\ &= \hbar\mathbf{k}_0 + \int u^*_{n,\mathbf{k}_0}(\mathbf{r})\boldsymbol{\nabla}u_{n,\mathbf{k}_0}(\mathbf{r})d^3\mathbf{r} \neq \hbar\mathbf{k}_0\end{aligned}$$

   The total momentum of the electron is instead given by

   $$\boxed{\langle\mathbf{p}\rangle_{n,\mathbf{k}_0} = m\,\langle\mathbf{v}\rangle_{n,\mathbf{k}_0} = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}}E_{n,\mathbf{k}_0}} \tag{4.1.14}$$

   where the first equality comes from Ehrenfest theorem and the second equality is demonstrated in appendix.

   Remarkably (and counter intuitively), this result means that *electrons have a well-defined time-independent velocity* despite the potential potential which surrounds them. Unlike what could be expected in a classical picture, electrons are *not colliding* with the lattice.

3. Energy bands and energy gaps

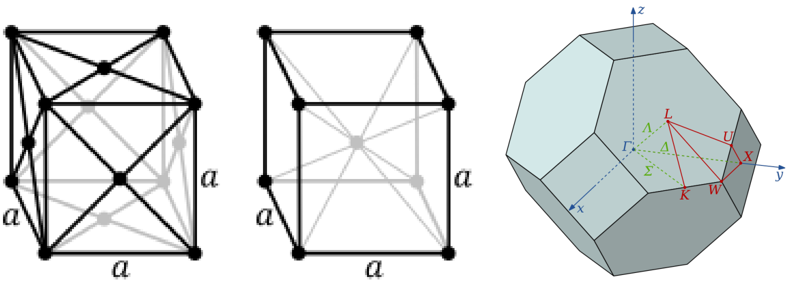
   Just like in our simple example, the situation is mid-way between electrons in a potential well (where states are labeled by a discrete number n) and free electrons (where states are labeled by a wave vector **k**). Here, electrons are labeled by an energy level (actually, an energy band) *and* a wave vector within this energy level. This means that two electrons with the same energy band can have different energies (if they have different **k**) ; and that two electrons with the same **k** can have different energies (if they have different n).

This also means that some energies are accessible to the electrons (energy bands), and some may not be (energy gaps between the bands). Note that in 2D and 3D, there might be *no energy gap* between two energy bands, if the bottom of the upper band has less energy than the top of the lower one.

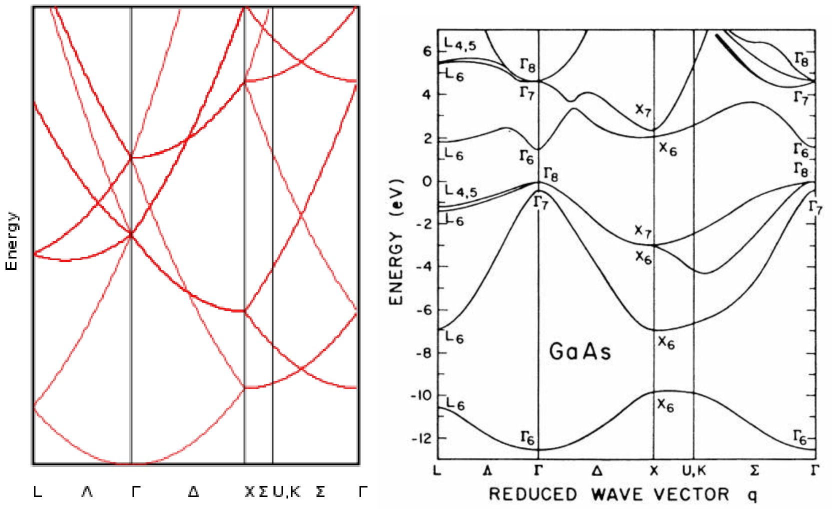
4. Band folding and Brillouin zone

Just like in our simple example, the periodicity of the potential implies that it is sufficient to consider **k** within the first Brillouin zone. The whole dispersion relation (which expresses the energy E as a function of the quasi momentum **k** and the energy band n) can be pictured within this region.

However, this folding is more complicated to picture than in our simple example - simply because we consider a 3D situation. Usually, the dispersion relation is plotted along specific directions given by the symmetries of the lattice.



Direct lattice (FCC), Reciprocal lattice (BCC), Brillouin zone (truncated octahedron)



Band structure of free electrons and GaAs (FCC lattice).

5. Phonons

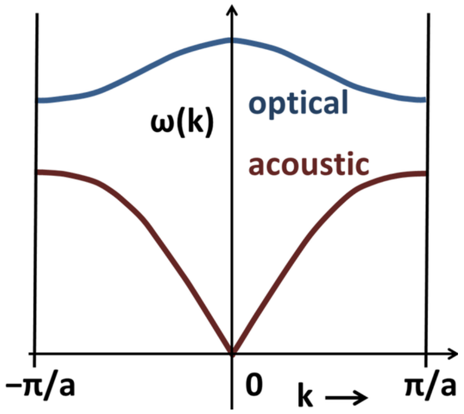
So far we assumed that the atomic lattice was still, and only considered the behavior of the electrons. We can also take into account the small vibrations of the lattice, which we picture as *phonons*. The coupling between electrons and phonons means that, somehow, the electrons can either set the atomic lattice on motion (thereby creating a phonon) or take energy from the shaking of the lattice (thereby absorbing a phonon).

Phonons could be the topic of a whole lecture. We will just flash three results here:

(a) Phonon eigenmodes can be described as plane-waves - ie any vibration of the lattice can be described as a sum of exp $\left(i\mathbf{k}_{ph}.\mathbf{r}\right)$. Just like for electrons, the challenge is to find the dispersion relation - ie the relationship between the momentum $\mathbf{k}_{ph}$ of the phonon and its energy. Just like for electrons, the momentum of the phonon can only take discrete values (multiples of $\frac{2\pi}{Na}$), which we assume to be continuous if $N \gg 1$.

(b) If the motif of the crystalline lattice has p atoms (usually, $p = 1$ or 2), then there are p phonon modes - each mode is like a band for the electrons. Usually, one mode has $E(\mathbf{k}_{ph} = 0) = 0$ (and is called acoustic phonon), and one mode has $E(\mathbf{k}_{ph} = 0) \neq 0$ (and is called optical phonon).

(c) On top of that, the lattice oscillation can occur along the propagation direction (one longitudinal mode) or perpendicular to it (two transverse mode)



4.2 Band filling

Let's add the content of the third lecture to this model !

4.2.1 Metal, insulator and semiconductors

We now know which states are accessible to electrons in a solid, but not how electrons are distributed among these states. From Fermi Dirac distribution, we know that electrons will stack starting from low energy states. At ambient temperature, we can consider that $T \ll T_F$ (as shown in the previous chapter) and that all states below the Fermi level are filled. Three types of material can be considered depending on where the Fermi level is located. We will see later that the response of the system to any stimulation essentially depends on electrons around the Fermi level - hence on the location of the Fermi level.

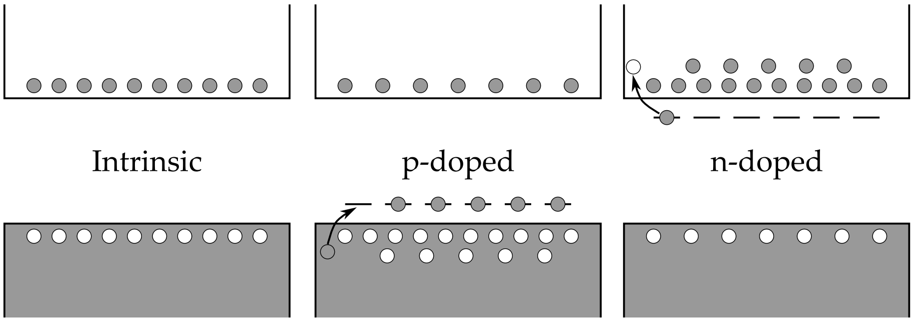
- Metals have their Fermi level somewhere in the middle of an energy band. Consequently, some empty states are available at arbitrary low energies above the Fermi level.

- Insulator and semiconductors have their Fermi level somewhere in the middle of an energy gap. The last band below the Fermi level (which is occupied) is called the *valence band*, the first band above the Fermi level (which is empty) is called the *conduction band.* The only difference between an insulator and a semiconductor is the value of the energy gap. A semiconductor has a gap small enough such that, at ambient temperature (remember that the step-like distribution functions spreads a little bit with the temperature), some carriers are present in the conduction band.

During the STEEM program, you will mostly work with semiconductor, so we will focus on these materials. We will now highlight two concepts of major importance to understand the behavior of semiconductors.

4.2.2 Electrons, holes and doping

At $T = 0$, all states below the Fermi level are filled, all states above are empty. If a carrier is transferred from the valence band to the conduction band, an empty state will appear below the Fermi level - exactly like a bubble appears if you remove water from a tank. These empty states can be described as *holes* in the filled band. Since the probability of finding an electron at an energy E is given by $f_{\mathrm{FD}}(E)$, the probability of finding a hole (ie of not finding an electron) is $1 - f_{\mathrm{FD}}(E)$. Usually, the density of electrons in the conduction band is labeled n, and that of holes in the valence band is p. We will see that holes contribute to the electrical current as much as electrons !



In addition to the thermal electrons spontaneously populating the conduction band, it is possible to add minute quantities of matter, impurity atoms, to "dope" the semiconductor - *i.e.* to modify carriers concentration.

- If we add atoms with more electrons than that of the lattice (donor impurities), and with a highest occupied orbit just below the conduction band, we will increase the density of electrons in the conduction band. In such n-type semiconductor, the density of electrons in the conduction band is essentially given by the density of donor impurities: $n \simeq N_D$.

  Example: phosphorus (P) or arsenic (As) in silicon.

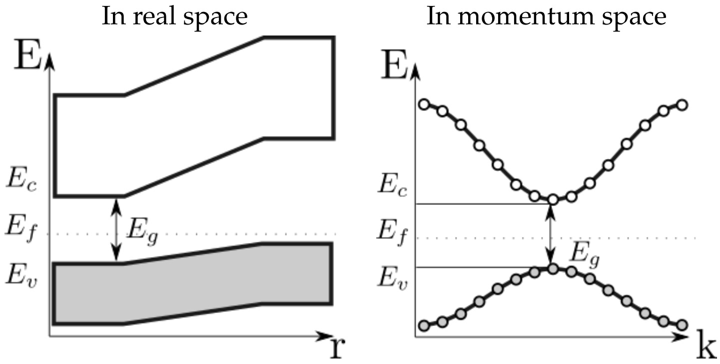
- If we add atoms with less electrons than that of the lattice (acceptor impurities), and with a lowest unoccupied orbit just above the valence band, we will increase the density of holes in the valence band. In such p-type semiconductor, the density of holes in the valence band is essentially given by the density of acceptor impurities: $p \simeq N_A$.

  Example: boron (B) or aluminum (Al) in silicon.

- By contrast, an undoped semiconductor is called *intrinsic.*

4.2.3 Graphical representations

- How to picture semiconductors (in real space and in momentum space):


In real space
In momentum space

Fermi level	Yes	Yes
Gradient of Fermi level	Yes	No
Conduction / valence band	Yes	Yes
Energy gap / energy band	Yes	Yes (too much ?)
Occupied / empty states	Yes	Yes
Junction btw materials	Yes	No
Dispersion relation	No	Yes
Direct / indirect gap	No	Yes

- We will see below that a gradient in the Fermi level corresponds to an electrical current. So at equilibrium, the Fermi level should be perfectly flat in real space.

- The closer the Fermi level is to the bottom of the conduction band, the more electrons there are in the conduction band.

4.3 Effective mass

4.3.1 Definition

As mentioned above, what matters most for the response of the system are carriers close to the Fermi level. For semiconductor, the Fermi level lies within the energy gap. The carriers closest to the Fermi level are therefore around the maximum of the valence band and the minimum of the conduction band. Around any extremum $\mathbf{k_0}$ of a band n, we have $E_n'(\mathbf{k_0}) = 0$ by definition (we will not pay much effort to define this derivative properly). So if we expand the dispersion relation around $\mathbf{k_0}$, we find

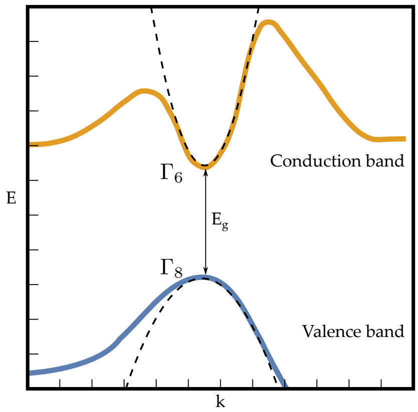
$$E_n(\mathbf{k}) \simeq E_n(\mathbf{k_0}) + \frac{1}{2} E_n''(\mathbf{k_0}) (\mathbf{k} - \mathbf{k_0})^2$$

which is pretty similar to the dispersion relation of free carriers $E = \frac{\hbar^2 k^2}{2m}$, considering an effective mass such that $E_n''(\mathbf{k_0}) = \frac{\hbar^2}{m_{eff}}$.

Let's sumarize this key result:

The behavior (and the density of states) of carriers at the bottom of the conduction band or the top of the valence band can be accounted for by free carriers with an effective mass $m_{\text{eff}} = \hbar^2 \left(E_n''(\mathbf{k_0})\right)^{-1}$.

All information about the shape of the lattice, the strength of the interactions between atoms and carriers (or even between carriers) is included in this effective mass.



Note The effective mass depends on band considered: it is for instance not the same in the valence band and in the conduction band (see figure above).

Note Properly speaking, the effective mass also depends on the *direction* considered - and a proper definition would be $\left(m_{\text{eff}}^{-1}\right)_{\alpha,\beta} = \hbar^{-2}\partial_{k_\alpha}\partial_{k_\beta}E_n$. For the sake of simplicity, we will only consider isotropic effective masses.

4.3.2 Effective density of states

In a semiconductor, the Fermi energy lies somewhere between the valence and conduction band. As the temperature is not 0 K , some electrons will be promoted from the valence band to the conduction band. Considering that the distance between any band and the Fermi level is much larger than thermal energy $k_B T$, the density of electrons thermally promoted to the conduction band is

$$n = \int\limits_{\text{CB}} D(E)\, f_{FD}(E)\, dE \simeq \int\limits_{\text{CB}} D(E)\, e^{\frac{E_F - E}{k_B T}}\, dE$$

Rembering that there are no states in the band gap, we can re-write with a simple variable change

$$\boxed{n = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right)}$$

where $N_C = \int\limits_{\text{CB}} D(E)\, e^{\frac{E_C - E}{k_B T}}\, dE$ is called the *effective density of states in the valence band*. Assuming a parabolic dispersion relation (ie we accept the effective mass approximation at the bottom of the band, and consider that electrons never explore high energies), we can easily[1] estimate

$$N_V \simeq \left(\frac{1}{2\pi\hbar}\right)^3 4\pi \sqrt{2m_{\text{eff},CB}^3} \int\limits_0^{+\infty} \sqrt{E}\, e^{\frac{-E}{k_B T}}\, dE = 2\left(\frac{m_{\text{eff},CB}k_B T}{2\pi\hbar^2}\right)^{3/2} \tag{4.3.1}$$

---

[1] if you remember that $\int\limits_0^\infty dx\, \sqrt{x}\, e^{-x} = \frac{\sqrt{\pi}}{2}$!

In the same way, it is possible to estimate the number of holes depleted in the valence band as

$$p = \int_{\mathrm{VB}} D(E)\,(1 - f_{FD}(E))\,dE \simeq \int_{\mathrm{VB}} D(E) \times e^{\frac{E-E_F}{k_B T}}\,dE$$

and we find a similar expression

$$\boxed{p = N_V\ \exp\left(\frac{E_V - E_F}{k_B T}\right)}$$

where the effective density of state in the conduction band is given by

$$N_V \simeq \left(\frac{1}{2\pi\hbar}\right)^3 4\pi\sqrt{2m_{\mathrm{eff},VB}^3} \int_{-\infty}^{0} \sqrt{-E} \times e^{\frac{E}{k_B T}}\,dE = 2\left(\frac{m_{\mathrm{eff},VB}\,k_B T}{2\pi\hbar^2}\right)^{3/2} \tag{4.3.2}$$

We can use these results to demonstrate two important properties of carriers in a semiconductor:

Law of mass action

Remarkably, the product $n \times p$ does not depend on the position of the Fermi level, but only on the value of the gap

$$\boxed{n\,p = N_C N_C\ \exp\left(-\frac{E_g}{kT}\right) \equiv n_i^2 \qquad (4.3.3)}$$

This product is therefore independent of the doping of the material (which translates into a shift of the Fermi level). It can be understood in the following way: starting from an intrinsic material ($n = p = n_i$), we add some acceptor impurities and increase the density of holes in the valence band ($p \to N_D \gg n_i$). As there are now more holes, an electron in the conduction band is more likely to recombine and decay towards the valence band. As a result, the density of electrons decreases.

A complementary picture is the following: at equilibrium, the number of thermal excitation promoting electrons from conduction band to the valence band has to balance the number of spontaneous decay from the conduction band to the valance band. The excitation rate only depends on the temperature and is unaffected by the doping. The decay process can be treated as an interaction between an electron and a hole, and its rate thus scales with the product of the concentration of the reactant. For the decay rate to be independent of doping, $n \times p$ has to be independent of the doping as well.

Note that this property *only holds at thermal equilibrium* - which is in particular not the case for a system under illumination.

Position of the Fermi level

- In an intrinsic semiconductor, charge neutrality implies $n = p \equiv n_i$ and hence

$$E_F^{(i)} = \frac{E_C + E_V}{2} + \frac{3}{4} kT \times \ln \frac{m_{\mathrm{eff},VB}}{m_{\mathrm{eff},CB}}$$

If $m_{\mathrm{eff},VB} = m_{\mathrm{eff},CB}$, then the Fermi levels is at the middle of the gap.

- In a n-doped semiconductor, $n = N_D$ and $p = n_i^2/N_D$ according to the law of mass action. Assuming $m_{\text{eff},VB} = m_{\text{eff},CB}$ for simplicity, we easily find

$$E_F^{(n)} = E_F^{(i)} + kT \times \ln \frac{N_D}{n_i}$$

- Similarly, for a p-doped semiconductor, we get

$$E_F^{(p)} = E_F^{(i)} - kT \times \log \frac{N_A}{n_i}$$

4.4 Elements of response theory

The goal of all this is to be able to describe / predict how the material will behave when submitted to an external stimulation. This will be the object of your following courses through the STEEM program. Here, we will give a brief introduction to two standard stimulation: an external electric field, and an external illumination.

4.4.1 Electronic transport

In a classical picture, when a voltage is applied to a semiconductor material, carriers are accelerated by the potential difference and their transport forms an electrical current $\mathbf{j}$. The proper way to treat this situation in our quantum description would be to add the corresponding energy $\sum_i - e\phi(\mathbf{r}_i)$ to the Hamiltonian. However, this is quite cumbersome, and we will rather use a semi-classical model, where the electrical current can still be estimated by a simple accounting of carriers:

$$\mathbf{j} = \sum_{\text{occupied states}} \text{carrier charge} \times \text{carrier velocity} \tag{4.4.1}$$

As mentioned before, within the wave-packet approximation (see appendix), the velocity of a carrier in the band n with crystalline momentum $\mathbf{k}_0$ is given by$\mathbf{v}_n(\mathbf{k}_0) = \frac{1}{\hbar}\partial_{\mathbf{k}} E_n(\mathbf{k}_0)$. From these results, we can already derive two major properties of electronic transport:

Filled bands are inert

This is a surprising yet crucial result:

> A band that is completely filled with carriers cannot contribute to the electrical current.

Let us demonstrate this property for a 1D system, and accept its generalization. The current contribution of the band n, assumed to be completely filled, is given by:

$$\begin{aligned} \mathbf{J}_n &= \sum_{\text{full band}} (-e) \times v_n(k) = -e\frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk\, \partial_k E_n(k) \\ &= -e\frac{L}{2\pi}\left[E_n\left(\frac{\pi}{a}\right) - E_n\left(-\frac{\pi}{a}\right)\right] = 0 \end{aligned}$$

Note This property justifies how previous assumption that only the energy bands close to the Fermi level are relevant. Any other band is either completely full or completely empty, and has therefore no contribution to the total current.

Holes contribution to the current

The concept of holes that we introduced before is actually particularity useful to estimate the contribution to current of almost full bands (typically, the valence band), owing to the following result:

$$\boxed{\text{It is equivalent to consider that the charge current results either from the motion of negatively charged electrons or of positively charged holes.}}$$

This rule comes from the previous property:

$$\mathbf{J}_n = -e \sum_{\text{filled}} v_n(k) = -e \left(\underbrace{\sum_{\text{full band}} v_n(k)}_{=0} - \sum_{\text{unfilled}} v_n(k) \right) = +e \sum_{\text{unfilled}} v_n(k) \tag{4.4.2}$$

We now consider what happens when we actually apply a voltage.

Carriers dynamics

We will accept[2] that the dynamics of a carrier is simply given by

$$\hbar \frac{d}{dt}\mathbf{k} = \mathbf{F}_{\text{ext}} \tag{4.4.3}$$

$$\frac{d}{dt}\mathbf{v}_n = \frac{1}{m_{\text{eff}}}\mathbf{F}_{\text{ext}} \tag{4.4.4}$$

where $\mathbf{F}_{\text{ext}} = e\boldsymbol{\nabla}\phi = -e\boldsymbol{\mathcal{E}}$ is the external force applied to the carrier (in this case, it is due to the electric field resulting from the applied bias).

Note We see here the difference between **p** and $\hbar\mathbf{k}$. The *total momentum* **p** of an electron changes under the influence of the *all forces* (ie interactions with the lattice *and* external forces). The *crystalline momentum* $\hbar\mathbf{k}$ already includes lattice effects, and is modified by the application of external forces only.

Note We also see the effective mass appearing again, playing a role similar to the real mass in Newton's second law.

Ideal systems: Bloch oscillations

Let's consider for now the ideal system we have developed so far, in which the lattice is perfectly periodic, without any impurity. According to eq.(4.4.3), the crystalline momentum increases linearly over time[3], as $\mathbf{k}(t) = \mathbf{k}_0 - \frac{e\boldsymbol{\mathcal{E}}}{\hbar}t$. This is in stark contrast with the behavior of a free gas, in which the *total momentum* would increase. The difference is striking when considering the velocity of the carriers:

$$\mathbf{v}_n\left(\mathbf{k}(t)\right) = \frac{1}{\hbar}\partial_{\mathbf{k}} E_n \left(\mathbf{k}_0 - \frac{e\boldsymbol{\mathcal{E}}}{\hbar}t\right)$$

---

[2] This actually comes from adding $-e\phi$ to the Hamiltonian, and estimating the perturbation induced on the previous eigenstates.

[3] In this case, we cannot use eq.(4.4.4) because, as **k** changes, the effective mass changes as well and the equation is a nightmare to integrate.

As $E_n(\mathbf{k})$ is periodic, this means that the velocity of carriers (and hence the electrical current) is periodic - *i.e. carriers are oscillating back and forth under the influence of a fixed DC voltage !* The extremely surprising result is called *Bloch oscillations*. It is easily destroyed by non-idealities, and therefore extremely hard to see in real solid state systems - but it can be experimentally observed in cold atoms experiments !

Non-ideal systems: mobility

Let's now consider a less exotic case, where carriers are likely to collide with impurities, or interact with phonons. We will accept that these effects can be accounted by a viscous force $\mathbf{F}_{\text{coll}} = -\frac{m_{\text{eff}}}{\tau}\mathbf{v}$, where τ is the typical time between two collisions. Using eq.(4.4.4), it is straightforward to show that the steady-state velocity reaches the value

$$\boxed{\mathbf{v} = \underbrace{\frac{-e\tau}{m_{\text{eff}}}}_{\mu}\boldsymbol{\mathcal{E}}}$$

where we introduced the mobility $\mu = \frac{-e\tau}{m_{\text{eff}}}$ - a key property that you will often meet in future lectures.

Notes for the future

Drift and diffusion

In this subsection, we considered the motion of particles induced by a potential gradient $\mathbf{v} = -\mu\boldsymbol{\nabla}\phi$ (with $\boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}\phi$). This motion leads to an electrical current $\mathbf{j}_{\text{drift}} = ne\mu\boldsymbol{\nabla}\phi$ which is called a *drift* current. In addition to it, a *diffusion* current can be due to a concentration gradient. The Fick law provides an expression for this current: $\mathbf{j}_{\text{diff}} = -eD\nabla n$ where D is the diffusion constant of the electrons.

Note that a mobility and diffusion coefficient can also be defined for holes.

Einstein relation

A remarkable result from statistical physics (the fluctuation-dissipation theorem) allows to relate the diffusion coefficient D and the mobility μ of carriers in the so-called Einstein relation:

$$\frac{D}{\mu} = \frac{k_B T}{e}$$

Total current

Considering these two results, and remembering that the effective density of states at a position x in the material is given by $n(x) = N_C \exp\left(\frac{E_F(x)-E_C(x)}{kT}\right)$ (with $E_C(x) = E_C - eV(x)$), we can express the total current induced in the material as

$$\mathbf{J}_{\text{tot}} = \mathbf{j}_{\text{drift}} + \mathbf{j}_{\text{diff}} = -n\mu\boldsymbol{\nabla}E_F \tag{4.4.5}$$

In other words, the electrical current appears as a gradient of the Fermi level throughout the material.

4.4.2 Absorption and emission of light

Shining light on a material essentially means adding an electromagnetic wave to the problem $\boldsymbol{\mathcal{E}} = \mathcal{E}_0 \left(e^{i\omega t}\right)$. The field can either provide energy to a carrier, promoting it from a lower to a higher energy state (absorption), or gather energy from a carrier as the particle decays from a higher to a lower energy state (emission). The problem then becomes:

If an electron is initially is a state $|\psi_i\rangle$, how likely is it to evolve towards a state $\left|\psi_f\right\rangle$ under the influence of illumination ?

Just like for the voltage, the influence of an illumination should be considered by including in the Hamiltonian an additionnal term corresponding to the light-matter interaction. There are basically two ways to do this, which are equivalent. The easiest (but least intuitive) way[4] is simply to change $\mathbf{p} \to \mathbf{p} - q\mathbf{A}$, where $\mathbf{A}$ is the magnetic vector potential[5], leading to

$$h = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + V_{\text{eff}}(\mathbf{r}) \simeq h_0 + \frac{e}{m}\mathbf{p}.\mathbf{A} \tag{4.4.6}$$

Provided that the field is weak enough, the second term can be treated perturbatively. The Fermi Golden Rule (see chapter 1) then relates the transition rate from $|\psi_i\rangle$ to $\left|\psi_f\right\rangle$ to the matrix element $\left|\left\langle \psi_f\right| \mathbf{p}.\mathbf{A} \left|\psi_i\right\rangle\right|^2$. By studying this term, we can infer most properties of light absorption and emission. A full quantum treatment would underline the existence of three contributions: absorption, spontaneous emission and stimulated emission. We will not perform the derivation here, but simply accept the following results.

Energy and momentum conservation

As always in Physics, total energy has to be conserved throughout the process. For an absorption (resp. emission) process, this condition translates as:

$$E_i \pm \hbar\omega = E_f \tag{4.4.7}$$

In the same way, the total momentum has to be conserved. Remarkably, because of the periodicity of the lattice, it can be shown that, actually, *the momentum has to be conserved.* Furthermore, since the dispersion relation for light is $q = \omega/c$, we can assume $q \ll k_{i,f}$ and we finally get the condition:

$$\mathbf{k}_i \pm \underbrace{\mathbf{q}}_{\simeq 0} = \mathbf{k}_f \tag{4.4.8}$$

In other words, direct optical transitions cannot alter the quasi-momentum of carriers (see "indirect transitions" below).

Absorption coefficient

As light propagates through a uniform absorbing medium, its intensity decreases following the Beer-Lambert law

$$I(x) = I_0\, e^{-a\,x} \tag{4.4.9}$$

where $a(\hbar\omega)$ is the absorption coefficient.

---

[4] For the record, the second option is to introduce the dipole operator $\hat{\mathbf{d}} = -e\hat{\mathbf{r}}$, and to consider the field-dipole interaction $-\mathbf{d}.\boldsymbol{\mathcal{E}}$.

[5] which is defined as $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, and $\mathbf{B}$ is related to $\boldsymbol{\mathcal{E}}$ by $\mathbf{B} = \frac{\mathbf{q}\times\boldsymbol{\mathcal{E}}}{\omega}$. All this result from Maxwell equations.

The capacity of a slab of material to absorb light will depend not only on the ability of one carrier to absorb a photon, but also on the number of carriers in the valence band available to undergo the transition, and on the number of empty state in the conduction band to welcome them. It can be shown that, assuming all possible transitions have the same probability, the absorption coefficient of the material scales as

$$a(\hbar\omega)[\mathrm{L}^{-1}] \propto \sqrt{\hbar\omega - E_g} \tag{4.4.10}$$

This expression emphasizes that no absorption is possible if the light frequency is small than the gap.

Quasi Fermi levels

Under the influence of light, the density of electrons in the conduction band increases and so does the density of holes in the valence band. Remember that the density of electrons / holes is related to the position of the Fermi level. In order to increase both densities, we have to start considering *two different Fermi levels*, one to describe the population of electrons in the conduction band, one to describe the population of holes in the valence band. We then talk about "quasi Fermi levels". This is a very strong result that will play a major role in PV physics:

> Under illumination, electrons and holes are described by two different quasi Fermi levels, usually denoted $E_{F,n}$ and $E_{F,p}$.

Considering that the Fermi energy is the thermodynamic potential of carriers, as an electron is extracted from the conduction band and injected in the valence band, the maximal amount of work gathered during this transformation is given by the quasi-Fermi levels splitting (see below). To rephrase it,

> The electrical voltage (as measured with a volt-meter) at the output terminals of the device is nothing but the quasi-Fermi levels splitting.
>
> $$qV = E_{F,n} - E_{F,p}$$

Recombination rate

Conversely, it is often important to estimate how quickly carriers in the conduction band recombine spontaneously with holes from the valence band. The full calculation is a bit long, and leads to the van Roosbroeck - Shockley relation:

$$\begin{aligned} R_{\mathrm{spont}}(\hbar\omega)[\mathrm{L}^{-3}.\mathrm{s}^{-1}] &= a(\hbar\omega)\,\frac{(\hbar\omega)^2}{\pi^2\hbar^3c^3}\,\frac{1}{\exp\left(\frac{\hbar\omega-\left(E_{F,n}-E_{F,p}\right)}{k_BT}\right)-1} \\ &\simeq B(\hbar\omega)\times n.p \end{aligned}$$

The first equation shows that, the larger the quasi Fermi level splitting $E_{F,n} - E_{F,p}$, the stronger the recombination rate. The second equation is an approximation which will be most often used in PV physics.

Indirect transition

While direct transitions have to preserve the crystalline momentum, it is also possible to consider phonon-assisted transitions. In this case, as carriers interact with the photon, they also absorb or emit a phonon which has very little influence in terms of energy, but carriers a significant momentum. Energy and momentum conservation then becomes:

$$E_i \pm \hbar\omega \pm \underset{\simeq 0}{E_{\text{phonon}}} = E_f \tag{4.4.11}$$

$$\mathbf{k}_i \pm \underset{\simeq 0}{\mathbf{q}} \pm \mathbf{q}_{\text{phonon}} = \mathbf{k}_f \tag{4.4.12}$$

When both direct and indirect transitions are possible, indirect transitions are much less likely to happen than direct transition because they require a 3 body interaction. But sometimes (the case in point being Silicon), only indirect transitions are possible. The main difference is then that, summing over all possible phonons, the absorption coefficient now scales as

$$a_{\text{indirect}}(\hbar\omega)[\mathrm{L}^{-1}] \propto \left(\hbar\omega - E_g\right)^2 \tag{4.4.13}$$

4.5 Take home message

1. Most fundamental properties of a solid result from the symmetry of the atomic lattice.
2. The behavior of electrons in a solid is very close to that of free electrons, except that
    - Free electronic states are defined by a wave vector **k**; electronic states in a solid a define by a wave factor **k** *and* a quantum number n
    - Free electronic states can be found for all energy ; some energies are forbidden in a solid
    - Free electrons have a mass $m_e = 9.11 \times 10^{-31}$ kg ; electrons in a solid have an effective mass (which can depend on the directions considered) which accounts for its interactions with both atoms and other electrons (mean field approach)
3. The chemical potential is a critical parameter to understand the behavior of carriers
    (a) Its position with respect to the energy bands determines the nature of the material (metal, insulator, semiconductor)
    (b) Any electrical current corresponds to a gradient of the Fermi level
    (c) A voltage between two points corresponds to a difference between the Fermi levels at these two points
4. Electronic Transport:
    - A band that is completely filled cannot contribute to the electrical current.
    - It is equivalent to consider that the charge current results either from the motion of negatively charged electrons or of positively charged holes.
    - Electrical current has two contributions:
        - Drift is due to an electric potential gradient and is characterized by mobility $\mathbf{v} = \mu\boldsymbol{\mathcal{E}}$

  - Diffusion is due to a concentration gradient and is characterized by diffusion coefficient $\mathbf{j}_{\text{diff}} = -eD\nabla n$
  - Drift and diffusion are related by the Einstein relation $\frac{D}{\mu} = \frac{k_B T}{e}$

5. When carriers are injected (e.g. under illumination), electrons and holes are described by two different quasi Fermi levels, usually denoted $E_{F,n}$ and $E_{F,p}$.

   The electrical voltage (as measured with a volt-meter) at the output terminals of the device is nothing but the quasi-Fermi levels splitting $qV = E_{F,n} - E_{F,p}$.

Chapter 5

Appendix

5.1 References to go further

Solid-state physics

- N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, 1^{st} edition, Thomson Press, 2003.
- C. Kittel, *Introduction to Solid State Physics*, 8^{th} edition, Wiley, 2004.

The "Ashcroft and Mermin" and "Kittel" are the two most celebrated textbooks on basic solid-state physics. These are the books to read if you want to know more about Brillouin zones, phonons and Bloch electrons.

Semiconductors

- S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices*, Wiley-Interscience, 2006.

A comprehensive and understable reference on how to use semiconductors to produce working devices. This is where you will find everything you need about pn or tunnel junctions, laser diodes and so on...

Solar cells

- J. Nelson, *The physics of solar cells*, ICP, 2003.
- https://www.pveducation.org/, https://www.pvlighthouse.com.au/

Dedicated to solar energy, the book by Nelson provides clear and rigorous derivation of key results of PV physics. PV Education and PV Lighthouse websites offer useful reminders and interactive applets to get familiar with basic properties of solar cells.

5.2 Reference values for semiconductor materials

You will often have to use numerical values of key parameters (effective masses of electrons or holes, mobilities...). Besides the short and incomplete table below, a good reference is provided by the Ioffe Institute (http://www.ioffe.ru/SVA/NSM/Semicond/index.html)

	n_i @300K	E_g	N_C	N_V	m_e	m_h	μ_n	D_n	μ_p	D_p
	cm^{-3}		cm^{-3}	cm^{-3}	m_0	m_0	cm$^2 V^{-1} s^{-1}$	cm^2/s	cm$^2 V^{-1} s^{-1}$	cm^2/s
Ge	2.4×10^{13}	0.66	1.04×10^{19}	6×10^{18}	0.55	0.37	$4\,10^3$	101	$2\,10^3$	50
Si	1.5×10^{10}	1.12	2.8×10^{19}	1.04×10^{19}	1.08	0.56	$1.5\,10^3$	36	$4.5\,10^2$	12
GaAs	1.8×10^{6}	1.424	4.7×10^{17}	7×10^{18}	0.07	0.5	$8.5\,10^3$	200	$4\,10^2$	10
AlAs	4×10^{1}	2.17	1.5×10^{19}	1.6×10^{19}	0.7	0.75	$1.9\,10^2$	5	$1.4\,10^2$	4
InAs	1×10^{15}	0.36	9×10^{16}	6.6×10^{18}	0.023	0.41	$4\,10^4$	1000	$5\,10^2$	13
InP	1.3×10^{7}	1.35	5.7×10^{17}	1.1×10^{19}	0.08	0.6	$5.4\,10^3$	130	$2\,10^2$	5
GaP		2.26	1.8×10^{19}	1.9×10^{19}	1.12	0.8	$2.5\,10^2$	6.5	$1.5\,10^2$	4
CdTe		1.44								

5.3 Orders of magnitude

Conversion efficiencies

Steam turbine	Mechanical W	Electrical W	40 %	Combustion engine	Chemical Q	Mechanical W	10 – 50 %
Wind turbine	Mechanical W	Electrical W	(< 59 %)	Electric engine	Electrical W	Mechanical W	30 – 90 %
Water turbine	Mechanical W	Electrical W	90 %	Photosynthesis	Solar Q	Chemical Q	5 %
Solar cell	Solar Q	Electrical W	(<33 %)	Muscles	Chemical Q	Mechanical W	20 %

Energy and power

Energy (J)	
Ambient temperature	10^{-21}
Electron volt	10^{-19}
Visible photon	$2\,10^{-19}$
Binding energy per nucleon	10^{-10}
Daily nutritional need	10^{7}
Gasoline in a car tank	10^{9}
Lightning	10^{9}
1 ton of TNT	$5\,10^{9}$
1 ton of oil	$4.2\,10^{10}$
1 gram of Uranium	10^{11}
Tropical cyclone	10^{12}
Hiroshima bomb	10^{13}
Krakatoa Volcano	10^{17}
Tsar bomba	10^{17}
Valdivia Earthquake	10^{20}
World TPES in 2014	10^{20}

Power (W)	
Wind turbine (per m^2)	2
Human body (heat)	100
Computer	100
Solar panel (per m^2)	20
Conso per cap. (Bengladesh)	300
Sprinter	700
Conso per cap. (World, China)	$2\,10^3$
Conso per cap. (Europe)	$5\,10^3$
Conso per cap. (US)	10^4
Car	10^5
Conso per cap. (Qatar)	$3\,10^5$
Nuclear plant	10^9
Total world consumption	10^{13}
Lightning	10^{14}
Solar flux on Earth	10^{17}
Total solar flux	$4\,10^{26}$

5.4 Basic differential equations

5.4.1 First order

First order differential equations usually take the form :

$$\partial_t f + \Gamma f = A \tag{5.4.1}$$

The solution starts at $f(0)$ and converges as an exponential towards A/Γ

$$f(t) = f(0)e^{-\Gamma t} + \frac{A}{\Gamma}\left(1 - e^{-\Gamma t}\right) \tag{5.4.2}$$

5.4.2 Second order

- Two situations should be *very* familiar :

$$\partial_t^2 f + \omega_0^2 f = 0 \Rightarrow f(t) = A\cos(\omega_0 t) + B\sin(\omega_0 t) \tag{5.4.3}$$

$$\partial_t^2 f - \omega_0^2 f = 0 \Rightarrow f(t) = Ae^{\omega_0 t} + Be^{-\omega_0 t} \tag{5.4.4}$$

  and integration constants A and B are fixed by initial conditions.

- Another familiar situation is provided by forced oscillations :

$$\partial_t^2 f - \Gamma\partial_t f + \omega_0^2 f = A\cos(\omega t) \tag{5.4.5}$$

  In this case, we are usually not looking for the full time evolution of the system, but only its stationnary behavior. As the system is driven at a frequency ω, we will be looking for solutions oscillating at this same frequency :

$$f = \Re\left(f_0 e^{i\omega t}\right) \tag{5.4.6}$$

  Owing to the linearity of the equation, we can estimte the amplitude and dephasing of this oscillation as :

$$f_0 = \frac{A}{\omega_0^2 - \omega^2 - i\Gamma\omega} \tag{5.4.7}$$

5.5 Demonstration of the Fermi Golden Rule

At equilibrium, the system is described by a Hamiltonian H_0, associated to a set of eigenstate $\{|\psi_n\rangle\}$ with energies $E_n^{(0)}$. If the system is prepared in any of these states, for instance in $|\psi_i\rangle$, it will stay in this state forever.

We now apply a time dependent perturbation $W(t)$. Note that *all* perturbations are time dependent, would it be only because you have to switch it on, at some point. Because of this perturbation, the system will not stay in $|\psi_i\rangle$ forever, but can evolve towards other states - this is because $|\psi_i\rangle$ is not an eigenstate of the whole Hamiltonian $H = H_0 + W(t)$ anymore. The Fermi Golden Rule gives an estimation of the departure rate from the initial state.

As we are interested in time evolution of the wave-function, we should consider the Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)\,|\psi(t)\rangle \tag{5.5.1}$$

Taking advantage of the spectral theorem, we can decompose any wave function as a sum over all eigenstates of the Hamiltonian H_0:

$$|\psi(t)\rangle = \sum c_n(t)\,|\psi_n\rangle \tag{5.5.2}$$

Following a standard trick, we will re-write the coefficients of the linear combination as

$$c_n(t) = \exp\left(-i\frac{E_n}{\hbar}t\right)\tilde{c_n}(t) = \exp\left(-i\omega_n t\right)\tilde{c_n}(t) \tag{5.5.3}$$

leading, after few lines of development, to

$$\frac{\partial\tilde{c_n}(t)}{\partial t} = \frac{1}{i\hbar}\sum_k \exp\left(-i\omega_{nk}t\right)\,\tilde{c_k}(t)\,W_{nk}(t) \tag{5.5.4}$$

where $\hbar\omega_{nk} = E_n - E_k$ and $W_{nk}(t) = \langle\psi_n|\,W(t)\,|\psi_k\rangle$.

We will now make two assumptions to reach a usable expression:

1. The system is initially in an eigenstate $|\psi_i\rangle$ of H_0, ie

$$c_n(0) = \delta_{n,i} \tag{5.5.5}$$

2. We are only considering short term variations, such that the system is more likely to stay in the initial state than to evolve towards any other state:

$$\left|c_{n\neq i}(t)\right| \ll 1 \tag{5.5.6}$$

With these two assumptions, which correspond to a first order perturbation theory, one term prevails in the right hand side of eq.(5.5.4):

$$\frac{\partial\tilde{c_n}(t)}{\partial t} \simeq \frac{1}{i\hbar}\exp\left(-i\omega_{ni}t\right)\,W_{ni}(t) \tag{5.5.7}$$

which we can integrate to

$$\tilde{c_n}(t) = \frac{1}{i\hbar}\int_0^t dt'\,e^{-i\omega_{ni}t'}\,W_{ni}(t') \tag{5.5.8}$$

The probability of finding the system in any state $\left|\psi_f\right\rangle$ after a time t is thus given by

$$P_{i\to f}(t) = \left|c_f(t)\right|^2 = \frac{1}{\hbar^2}\left|\int_0^t dt'\,e^{-i\omega_{fi}t'}\,W_{fi}(t')\right|^2 \tag{5.5.9}$$

To further simplify this expression, let's assume that the perturbation is switched on at $t = 0$

and takes a sine form afterwards

$$W(t>0) = 2W\cos(\omega t) = W\left(e^{i\omega t} + e^{-i\omega t}\right) \tag{5.5.10}$$

Equation (5.5.9) then reduces to

$$P_{i\to f}(t) = \frac{\left|\left\langle \psi_f \right| W \left|\psi_i\right\rangle\right|^2}{\hbar^2} \left| \frac{e^{i\left(\omega-\omega_{fi}\right)t}-1}{i\left(\omega-\omega_{fi}\right)} + \frac{e^{i\left(\omega+\omega_{fi}\right)t}-1}{i\left(\omega+\omega_{fi}\right)} \right|^2 \tag{5.5.11}$$

Assuming that the excitation is close to the resonant frequency $\omega_{fi} \sim \omega$, we will neglect the second term which corresponds to a non resonant contribution[1]. We then recover an expression close to the previous one:

$$P_{i\to f}(t) = \frac{\left|\left\langle \psi_f \right| W \left|\psi_i\right\rangle\right|^2}{\hbar^2} f\left(\omega_{if} - \omega,\, t\right) \tag{5.5.12}$$

where $f(\omega,\, t) = \frac{\sin^2\left(\frac{\omega t}{2}\right)}{\left(\frac{\omega t}{2}\right)^2}$ has a sharp peak around 0.

Transition towards continuum

So far, we considered the probability of finding the system in any given final state $\left|\psi_f\right\rangle$ knowing that it was initially in the state $\left|\psi_i\right\rangle$. What we are actually interesting in is the departure rate from $\left|\psi_i\right\rangle$, *regardless of the final state*. So we should sum all possible contributions

$$P_{i\to}(t) = \sum_{\psi_f} P_{i\to f}(t) = \int dE_f\, D(E_f)\, \frac{\left|\left\langle \psi_f \right| W \left|\psi_i\right\rangle\right|^2}{\hbar^2} f\left(\frac{E_{if}}{\hbar} - \omega,\, t\right)$$

where $D(E)$ is the density of state (this transition from a discrete sum to an integral is detailed in chapter 2). Assuming that the density of state is much less sharp than f, we will replace it by its resonant value[2] leading to

$$P_{i\to}(t) = \frac{2\pi}{\hbar} \left|\left\langle \psi_f \right| W \left|\psi_i\right\rangle\right|^2 D(E_f = E_i) \tag{5.5.13}$$

where we used $\int f(\omega,\, t)\, d\omega = 2\pi t$.

5.6 Demonstration of Bloch theorem

The potential V_{eff} experienced by the electrons is periodic with a period a:

$$V(x+a) = V(x)$$

Let us introduce a translation operator $\hat{T}_a$, such that for any function f,

$$\left(\hat{T}_a f\right)(x) = f(x+a)$$

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[1] This approximation is known as the *rotating wave approximation.*

[2] $\int f(x)g(x)\, dx \simeq g(x_0) \int f(x)\, dx$ if f is sharply peaked around x_0. Another way to see this is to consider that $f(x) \simeq A \times \delta(x - x_0)$, and the amplitude $A = \int f(x)dx$ can be estimated by integrating both sides of this equation.

1. This translation operator is unitary (ie $\hat{T}_a^\dagger \hat{T}_a = 1$). This implies that all its eigenvalues have a modulus equal to 1. We can choose to write these values as e^{ika}.

2. This translation operator commutes with $\hat{H}$. This implies we can chose a basis of shared eigenvectors $\{\psi\}$ such that

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle$$
$$\hat{T}_a\,|\psi\rangle = e^{ika}\,|\psi\rangle$$

Bloch function

Let us consider $u(x) = e^{-ikx}\psi(x)$. We can easily show that u is periodic with a period a:

$$u(x+a) = e^{-ik(x+a)}\psi(x+a) = e^{-ikx}e^{-ika}\left(\hat{T}_a\psi\right)(x) = e^{-ikx}\psi(x)$$

Quantification of k

Finally, ψ has to be $N \times a$ periodic, ie

$$\psi(x+Na) = \psi(x)$$

which implies

$$k = \frac{2p\pi}{N \times a}$$

5.7 Group velocity of Bloch electrons

Considering a Taylor expansion, the energy of an electron in the n^{th} band at quasi-momentum $\mathbf{k_0} + \mathbf{q}$ can be related to the energy at quasi-momentum $\mathbf{k_0}$ in the same band through

$$E_n(\mathbf{k}_0 + \mathbf{q}) = E_n(\mathbf{k}_0) + \boldsymbol{\nabla}_k E_n(\mathbf{k_0}).\mathbf{q} + ... \qquad (5.7.1)$$

This energy $E_n(\mathbf{k}_0 + \mathbf{q})$ is also the eigenvalue associate to the Bloch function $\psi_{n,\,\mathbf{k_0}+\mathbf{q}}$:

$$\left(\frac{p^2}{2m} + V(\mathbf{r})\right)\underbrace{u_{n,\,\mathbf{k_0}+\mathbf{q}}(\mathbf{r})e^{i(\mathbf{k_0}+\mathbf{q}).\mathbf{r}}}_{\psi_{n,\,\mathbf{k_0}+\mathbf{q}}} = E_n(\mathbf{k_0}+\mathbf{q})u_{n,\mathbf{k_0}+\mathbf{q}}(\mathbf{r})e^{i(\mathbf{k_0}+\mathbf{q}).\mathbf{r}} \qquad (5.7.2)$$

$$\underbrace{\left(\frac{1}{2m}\left(\mathbf{k}_0 + \mathbf{q} - i\nabla\right)^2 + V(\mathbf{r})\right)}_{H_{\mathbf{k_0}+\mathbf{q}}}u_{n,\mathbf{k_0}+\mathbf{q}}(\mathbf{r}) = E_n(\mathbf{k_0}+\mathbf{q})u_{n,\mathbf{k_0}+\mathbf{q}}(\mathbf{r}) \qquad (5.7.3)$$

and we can easily show that

$$H_{\mathbf{k}+\mathbf{q}} = H_{\mathbf{k}} + \frac{\hbar^2}{m}\left(\mathbf{k} - i\nabla\right).\mathbf{q} + \frac{\hbar^2}{2m_0}q^2 \qquad (5.7.4)$$

For small values of $\mathbf{q}$, the eigenvalues of $H_{\mathbf{k}+\mathbf{q}}$ can be related to those of $H_{\mathbf{k}}$ through perturbation theory:

$$E_n(\mathbf{k_0}+\mathbf{q}) = E_n(\mathbf{k_0}) + \left\langle u_{n,\mathbf{k_0}}\right| \left(\frac{\hbar^2}{m}\left(\mathbf{k}-i\nabla\right).\mathbf{q} + \frac{\hbar^2}{2m_0}q^2\right)\left|u_{n,\mathbf{k_0}}\right\rangle + ... \tag{5.7.5}$$

$$= E_n(\mathbf{k_0}) + \left\langle u_{n,\mathbf{k_0}}\right| \left(\frac{\hbar^2}{m}\left(\mathbf{k}-i\nabla\right)\right)\left|u_{n,\mathbf{k_0}}\right\rangle .\mathbf{q} + O(q^2) \tag{5.7.6}$$

$$= E_n(\mathbf{k_0}) + \left\langle \psi_{n,\mathbf{k_0}}\right| \left(\frac{\hbar^2}{m}\left(-i\nabla\right)\right)\left|\psi_{n,\mathbf{k_0}}\right\rangle .\mathbf{q} + O(q^2) \tag{5.7.7}$$

$$\simeq E_n(\mathbf{k_0}) + \frac{\hbar}{m}\left\langle \mathbf{p}\right\rangle_{n,\mathbf{k}_0} .\mathbf{q} + ... \tag{5.7.8}$$

and we identify with the first expression

$$\boldsymbol{\nabla}_k E_n(\mathbf{k_0}) = \frac{\hbar}{m}\left\langle \mathbf{p}\right\rangle_{n,\mathbf{k}_0} = \hbar\left\langle \mathbf{v}\right\rangle_{n,\mathbf{k}_0} \tag{5.7.9}$$

where the last equality stems from Ehrenfest theorem

$$\left\langle \mathbf{v}\right\rangle_{n,\mathbf{k}_0} \equiv \dot{\mathbf{r}} = \frac{1}{i\hbar}\left[\mathbf{r}, H\right] = -\frac{1}{m}i\hbar\nabla \equiv \frac{1}{m}\left\langle \mathbf{p}\right\rangle_{n,\mathbf{k}_0}$$