Chapter 1

Basic models for light, matter and light-matter interactions

This first chapter will introduce (and essentially remind you of) models to describe light, matter and light-matter interactions. But before overviewing these models, it might be worth taking few lines to explain what a model is, and what to expect from it.

A model is a way to set a problem in order to find an answer to a specific question. Why is the sky blue ? How is the blackbody radiation distributed ? Why do comets have tails ? To answer these questions, we need to turn these situations into seizable descriptions, to give ourselves basic assumptions ruling these descriptions and to see if these assumptions allow us to reach a behavior ressembling our empirical observations.

If you want to calculate the time it takes for an apple to fall, you are used to describing the apple as a mass point with (x,y,z) coordinates ; to assuming that there is a basic force called "gravity" which you can evaluate from the mass and size of the Earth ; and to considering that there is a relation between motion and forces given by Newton's second law. This model allows you to relate the fall time to the height in a single elegant expression $t = \sqrt{2H/g}$. What you have really done here is to create a virtual universe with a moving dot, and claimed that this could be used to account for reality. And it works ! But keep in mind few words of warning about models:

- All models are wrong. The aim of a model is not to give you The Truth, it is to bring a clear answer to a specific question.
- As a rule, a model should be as complicated as needed, but as simple as possible. There is no point in making full relativistic calculations if you want to estimate the fall time of an apple with an accuracy of few miliseconds.
- Advances in science allows to push old models to their limits, where new models are required. It doens't make the old models "wrong" all the sudden, it simply highlights their validity range. In this course, we will often be using outdated models because they can give simple pictures with very good precision as long as they are operated within their validity range.

Warning: easy confusions

- Matter polarization (local density of electric dipole) and light polarization (local direction of the electric field)

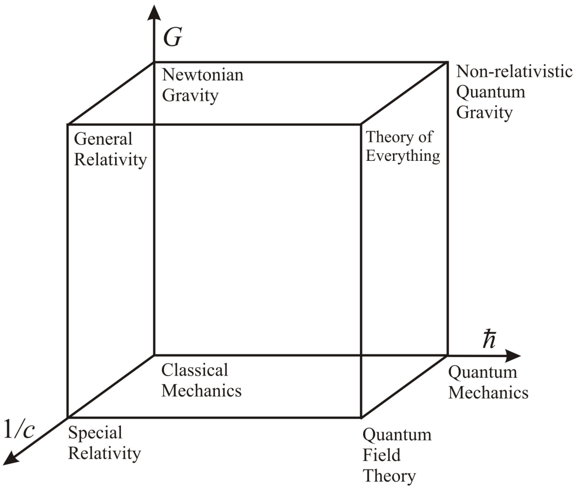
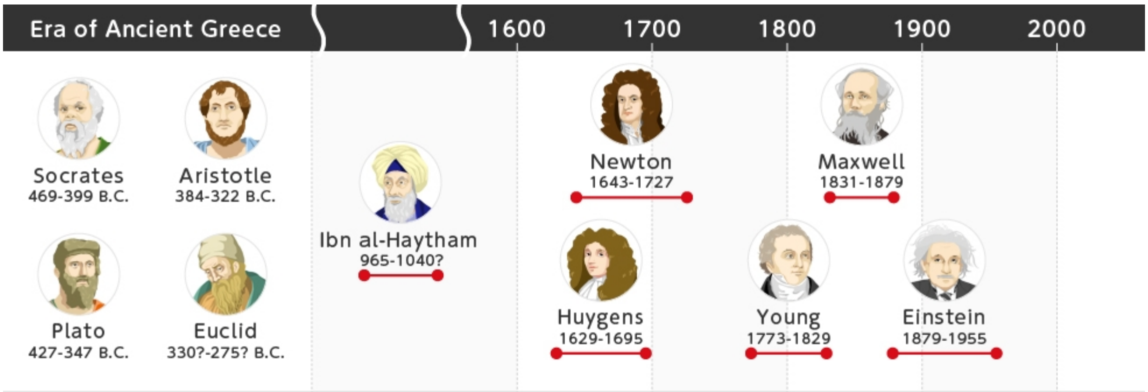


Figure 1.1: Usual framework in physics.

- Electric dipole ($\mathbf{p} = -e\mathbf{r}$) and momentum ($\mathbf{p} = m\mathbf{v}$)
- There might be typos in this text from missing different writings for the electrical charge: e is usually the fundamental charge ($1.6\,10^{-19}$ C) ; but it can (mistakenly) be the charge of the electron ($-1.6\,10^{-19}$ C) and it sometimes include the Coulomb prefactor $\frac{e^2}{4\pi\epsilon_0} \to e^2$.

1.1 Light models

The question "what is light ?" - and the corresponding modelling question "how to account for light ?" - is now well settled, but has been a recurring problem and a raging debate for centuries.



https://photonterrace.net/en/photon/history/

In this course, we will essentially play with classical light as described by Maxwell's theory and with a "semi-quantum" description of photons.

1.1.1 Classical model: electromagnetic wave (reminder from PHY 202)

This is just a reminder, as you have already studied all this extensively.

Maxwell's equations

In a classical picture, light is described by two vector fields $\{\mathbf{E}(\mathbf{r},t), \mathbf{B}(\mathbf{r},t)\}$ obeying the celebrated Maxwell's equations:

$$\begin{aligned} \nabla.\mathbf{E} &= \frac{\rho}{\epsilon_0} & \nabla.\mathbf{B} &= 0 \\ \nabla\times\mathbf{E} &= -\partial_t\mathbf{B} & \nabla\times\mathbf{B} &= \mu_0\left(\mathbf{j}+\epsilon_0\partial_t\mathbf{E}\right) \end{aligned} \tag{1.1.1}$$

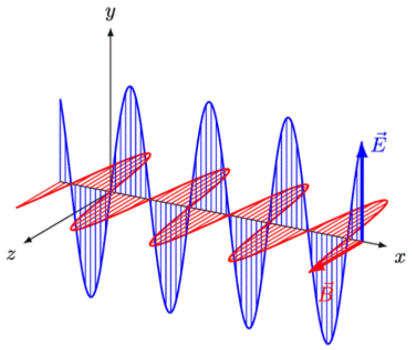
Plane-wave decomposition

Since Maxwell's equations are linear, it is often useful to decompose each field into a sum of monochromatic plane-waves[1] (which corresponds to a time and space Fourier transform):

$$\mathbf{E}(\mathbf{r},t) = \int d\omega \int d\mathbf{k}\, \boldsymbol{\mathcal{E}}(\mathbf{k},\omega)\, e^{i(\mathbf{k}.\mathbf{r}-\omega t)} \tag{1.1.2}$$

The *spectrum* of the field is distribution of the single frequency components $\mathcal{E}(\omega)$ constituting the total field E. In this planewave basis, the relation between electric and magnetic field is straightforward, and leads to the well-known shape of an electromagnetic wave :

$$\boldsymbol{\mathcal{B}} = \frac{\mathbf{k}\times\boldsymbol{\mathcal{E}}}{c} \tag{1.1.3}$$



Dispersion relation

The relation between the wave-vector $\mathbf{k}$ and the frequency ω is called *dispersion relation* and depends on the medium in which the wave is travelling. In vaccum, this relation is very easy:

$$\omega = kc \tag{1.1.4}$$

In general, this relation can be complicated and can depend, for instance, on the field intensity, on the field polarization, or on the location inside the medium (see section 1.3.1)

Energy and intensity

In this model, the directionnal energy flux is given by the Poynting vector

$$\boldsymbol{\Pi} = \frac{\mathbf{E}(t)\times\mathbf{B}(t)}{\mu_0},\ [\Pi] = \mathrm{W/m^2} \tag{1.1.5}$$

and light intensity is given by the mean value of the Poynting vector: $I = \langle\Pi\rangle$. Energy conservation is embedded in Maxwell's equations and can be written as

$$\partial_t u + \mathrm{div}\boldsymbol{\Pi} = -\mathbf{j}.\mathbf{E} \tag{1.1.6}$$

where $u(\mathbf{r},t) = \frac{1}{2}\epsilon_0 E^2 + \frac{1}{2\mu_0}B^2$ is the volumic density of energy.

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[1] Note however that fields can also be decomposed on other basis, which might be more relevant in specific situation (such as in a waveguide).

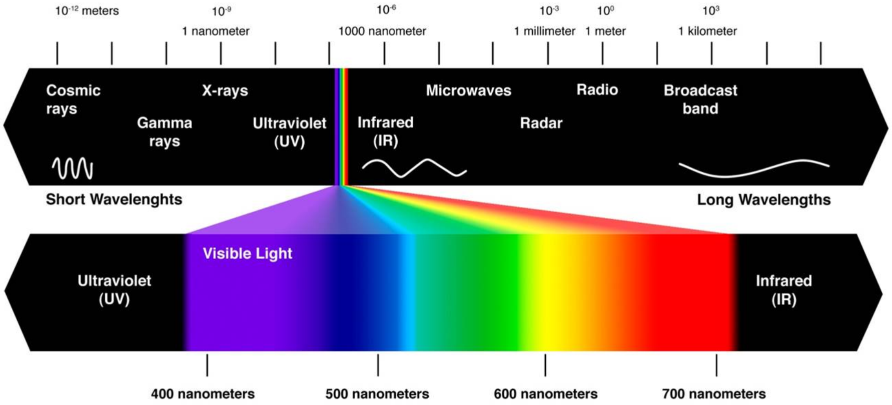


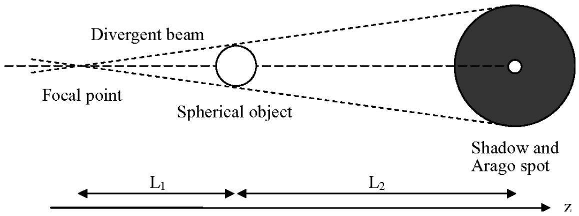
Figure 1.2: The whole spectrum !

For monochromatic planewaves, we get

$$I = \frac{\Re\left(\mathcal{E}^{*}\mathcal{B}\right)}{\mu_0} = \frac{1}{2\mu_0 c}\left|\mathcal{E}\right|^2 \tag{1.1.7}$$

When do we need classical light ?

- Electromagnetic spectrum
- Interferences
  Describing light as a wave highlights its ability to show interference and diffraction features. Besides Young's double slit experiment, the most celebrated signature of this wave nature is certainly the Arago's spot ("tache de Poisson" in French). In 1817, the French Academy of Science decided to award its Mathematics prize to the experimental and theoretical study of diffraction. At this time, the particle or wave nature of light was still fiercly debated ; and Augustin Fresnel, who was then barely 30, submitted a report proposing a wave model of light. Siméon Poisson, one the reviewer who was very much in favour of a particle description, showed that Fresnel's model implied that, in the middle of the shadow casted by an object blocking a light beam, there should be a bright spot. Poisson thought this was non-sense, and that this incorrect prediction prooved the whole theory wrong. However, François Arago, the head of the committee, suggested to perform the experiment and found that, indeed, a bright spot could be found as predicted by the model. Fresnel did win the prize (it seems there were only two candidates that year anyways !).



1.1.2 Quantum model: field operators

This model is out of the scope of this lecture, and will be treated in future quantum optics classes. You don't need to read this paragraph, it's just for your own culture.

In quantum mechanics, a system is described by an appropriate Hilbert space, and its state is given by a wavefunction - ie a vector of this Hilbert space following the Schrodinger equation. To get a quantum description of light, we would need to define a Hamiltonian for light - following the usual procedure, we could start with the classical expression of energy, and turn quantities into operatores:

$$U = \int d^3r\, u(\mathbf{r},t) \Rightarrow \hat{H}_R = \int d^3r \left(\frac{1}{2}\epsilon_0 \hat{\mathbf{E}}^2(\mathbf{r},t) + \frac{1}{2\mu_0}\hat{\mathbf{B}}^2(\mathbf{r},t) \right) \tag{1.1.8}$$

but now we need to define what kind of object a "wavefunction for the field" is, and how the "electric field operator $\hat{\mathbf{E}}^2$ actually acts on this wavefunction. The full quantum treatement is the correct way to introduce the notion of photon, which appear as a quantization of the field.

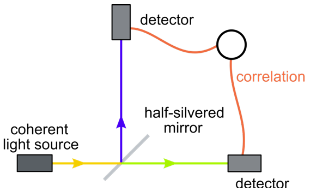
When do we need quantum light?

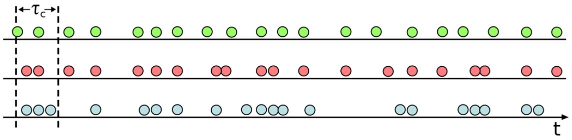
- Spontaenous emission

  Surprising as it might seem, a quantum model for light is required to describe spontaneous emission in a fully rigorous way! We'll discuss this point in future chapters.

- Photon statistics

  Shoot light towards a separating blade, and put two time resolved detectors to monitor when a signal is collected on each of the two arms. Are the two detectors going to "click" simultaneously, non-simultaneously or just randomly ?





Photon detections as function of time for a) antibunched, b) random, and c) bunched light

  Well actually, this is a very tricky question because it really depends on the nature of the light which is being sent. Thermal emission will give a bunched behavior, a single photon source will of course give an anti-bunched signal and laser light will have a random profile. A quantum framework is necessary to fully account for these observations, and it is out of the scope of this lecture.

- Quantum computing

1.1.3 Intermediate model: "Photons"

A somehow intermediate description of light is given by a particle-like picture, where we consider a flow of massless marbles defined by the following relations:

$$\mathbf{p} = \hbar\mathbf{k} \qquad E = \hbar\omega = \hbar k c \tag{1.1.9}$$

We will call these particles “photons”, but bear in mind that the only proper way to introduce photons is the quantum model mentionned above. In this image, light’s spectrum corresponds to the constituting photons’ distributions (ie how many photons with a given energy can be found in this light ?).

A word of warning about this model : this model gives a simplistic vision of light, which can be very convenient (it’s quite easy to picture a bunch of light particles flying in space) and surprisingly powerful, but remember that it is limited and can be misleading. In particular, unlike the previous two models, this picture does not include any notion of phase or coherence in light. Willis Lamb, one of the best spectroscopist ever and Nobel prize in 1955 had quite harsh words about this description of “photons”.

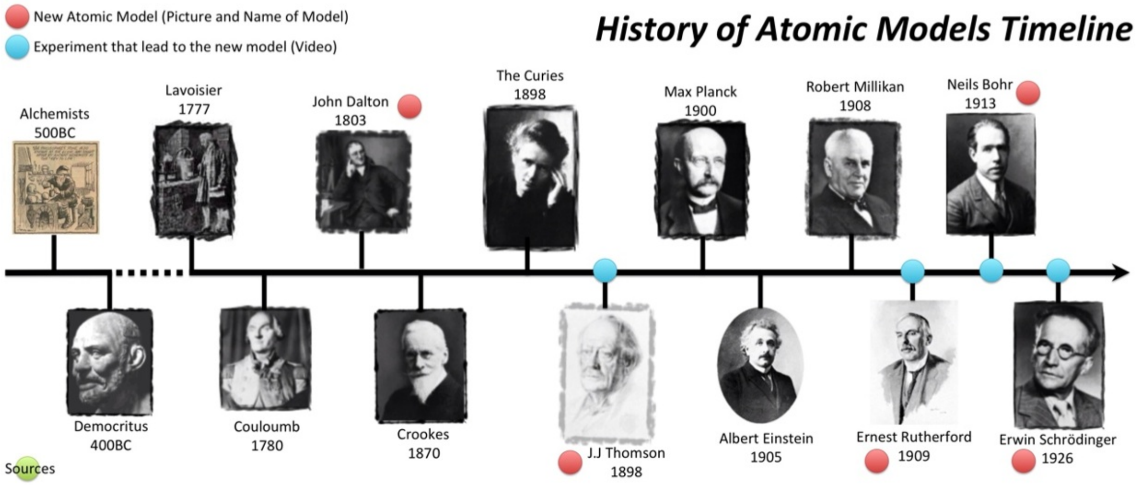
> *“It should be apparent from the title of this article that the author does not like the use of the word "photon", which dates from 1926. In his view, there is no such thing as a photon. Only a comedy of errors and historical accidents led to its popularity among physicists and optical scientists.*
>
> *I suggested that a license be required for use of the word photon, and offered to give such license to properly qualified people.*
>
> *My records show that nobody working [here] in Rochester, and very few other people else where, ever took out a license to use the word "photon". “*
>
> W. E. Lamb, Anti-photon, Appl. Phys. B 60, 77-84 (1995).

When do we need intermediate light?

This model gives a very simple way to account for light-matter interactions with rate equations - we will just have to count how many “photons” are interacting with atoms. It will be used extensively in this course.

1.2 Atomic models

There again, the question “what is matter?” - and the corresponding modelling question “how to account for matter?” - is as old as mankind and remained a bone of contention until the begining of the XXth century.



https://www.thinglink.com/scene/569421147997732866

1.2.1 Classical model: Lorentz oscillator (reminder from PHY 104)

In classical physics, atoms are composed negatively charged marbles (electrons) orbiting around positively charged marbles (protons) under the influence of Coulomb interaction. The state of the system is given by the trajectories (position and velocity) of the marbles, following Newton's second princple. Several approximations are usually made to simplify calculations:

- A phenomenological damping force is often introduced:

$$\mathbf{f} = -m\Gamma\frac{d}{dt}\mathbf{r}_e \tag{1.2.1}$$

- Born-Oppenhiemer approximation: the nucleus is much heavier than electrons, and is assumed to remain still. We can restrict the problem to the study of the electron motion

$$m_e\frac{d^2}{dt^2}\mathbf{r}_e = -m\Gamma\frac{d}{dt}\mathbf{r}_e - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_e^2}\mathbf{u_r} \tag{1.2.2}$$

  It is often useful to introduce the orbital momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$, which is conserved since the force at stake derives from a central potential. The radial equation of motion can then be expressed as

$$\ddot{r} = -\Gamma\dot{r} + \frac{L^2}{m_e r^3} - \frac{Ze^2}{4\pi m_e\epsilon_0}\frac{1}{r^2} \tag{1.2.3}$$

- Elastically bound electrons: consider a stable orbit $\mathbf{r}_e^{(0)}$ satisfying the previous equation. We consider a small perturbation of this stable orbit, such that $\mathbf{r}_e = \mathbf{r}_e^{(0)} + \delta\mathbf{r}_e$ (but the angular momentum is conserved). If we perform a Taylor expansion of eq.(1.2.3) to the first order in $\delta\mathbf{r}_e$, we find:

$$m_e\frac{d^2}{dt^2}\delta\mathbf{r} = -m_e\omega_0^2\delta\mathbf{r} - m_e\Gamma\frac{d}{dt}\delta\mathbf{r} \tag{1.2.4}$$

  with $m_e\omega_0^2 = \frac{1}{L^3}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)$[8] (but what matters most here is not the actual value of ω_0, which will most of the time be determined phenomenologically, but the spring-like form which leads to the notion of resonant frequency).

When do we need classical atoms?

- Optical index (see section 1.3.1 for more details).

  We recall that χ is related to the optical index n by the relation,

$$n^2 = 1 + \chi \tag{1.2.5}$$

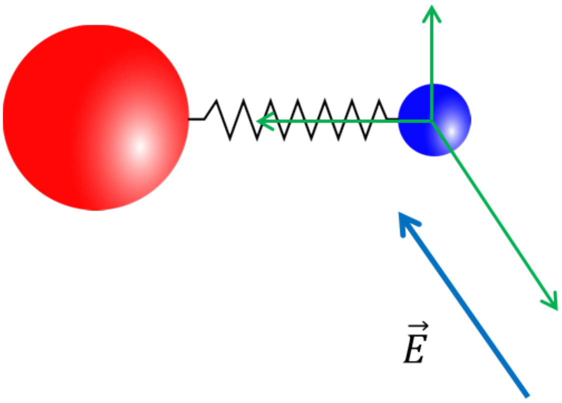
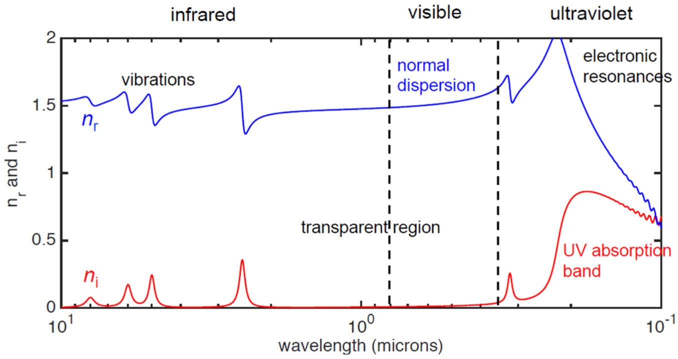


Figure 1.3: The elastically-bound electron model.



1.2.2 Quantum model : Schrödinger model

In basic quantum mechanics, a system is described by a Hamiltonian and the current state of the system is given by a wavefunction following the Schrodinger equation. Here, the relevant Hamiltonian should account for the kinetic and potential energies of the electron :

$$H_0 = \frac{\hat{p}^2}{2m_e} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hat{r}} \tag{1.2.6}$$

A key result of quantum mechanics is that, in a confining potential, the eigen states of the Hamiltonian have discrete energy values (unlike classical physics where all energies can be considered). We will demonstrate in Lecture 6 that energy eigenstates $|\psi_{n,l,m}\rangle$ can here be labelled with an integer numbers (primary quantum number $n \geq 1$, secondary quantum number $0 < l < n$, azimuthal quantum number $-l \leq m \leq +l$), that the n^{th} state is n^2 times degenerate and that the energy values follow the famous scaling law

$$E_n = -\frac{1}{n^2}\underbrace{\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}}_{Ry} \tag{1.2.7}$$

The state of the system can then be described as a linear combination of these eigenstates $|\psi\rangle = \sum\limits_{n,l,m} c_{n,l,m}|\psi_{n,l,m}\rangle$, and the average number of electron in a given state $|\psi_{n,l,m}\rangle$ is $|c_{n,l,m}|^2$. Remember that electron obey the Pauli principle, and two electrons can't share the same state.

When do we need quantum atoms?

- Advanced spectroscopy - if you really want to calculate from scratch where atomic resonance lie, or how they are modified by the presence of an external perturbation, you will need to dive into a proper quantum model.
- Chemistry

1.2.3 Intermediate model : Bohr model

The Bohr model is somehow between both worlds. It is a classical model in the sense that, just like in the Lorentz model, atoms are described as a marble-like electron orbiting around the nucleus according to Newton's law. However, we add on pinch of quantum results : we consider that among all possible orbits, the only allowed trajectories are such that

$$L = n\hbar \tag{1.2.8}$$

where n is integer number. This constraint can be interpreted as follows: if we take the electron as a quantum system for a second, we can attribute it a de Broglie's wavelength $\lambda = h/p$, where p is the momentum of the electron. Orbits should correspond to stationnary waves, meaning that a integer number of wavelength should fit along the orbit. For a circular orbit, this condition reads $2\pi r = n\lambda$, hence the above stated result.

Taking this constraint into account, it is easy to show that the energy of circular orbits take a form similar to that predicted by the full quantum picture:

$$E_n = -\frac{Ry}{n^2} \tag{1.2.9}$$

When do we need intermediate atoms?

Basic spectroscopy: the Bohr model was introduced to give a physical rational to the Rydberg law for the hydrogen spectrum, which calculates the spectral lines as

$$\hbar\omega = Ry\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{1.2.10}$$

1.3 Model for light-matter interactions

Now that we have models for light and models for atoms, we will see how these models connect together, and how to account for interactions between light and atoms in the different descriptions.

1.3.1 Interactions between atoms and a classical field

For all atomic models, the main ideas are always the same :

- The electric field of the light polarises the atom - ie shifts the electron average position resulting in the creation of an electric dipole.
- The atomic polarisation creates a local current and density of charge which changes the dispersion relation for electromagnetic waves, and thus the propagation of light.

Light→Atom

For classical and "intermediate" atoms:

The electron will interact with electric and magnetic fields through the Lorentz force :

$$\mathbf{F} = -e\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right) \tag{1.3.1}$$

Neglecting the magnetic part, we reach the usual expression for the equation of motion:

$$m_e \frac{d^2}{dt^2}\delta\mathbf{r} = -m_e\omega_0^2\delta\mathbf{r} - m_e\Gamma\frac{d}{dt}\delta\mathbf{r} - e\mathbf{E} \tag{1.3.2}$$

Considering a monochromatic light, we introduce complex notations $\mathbf{E} = \mathrm{Re}(\boldsymbol{\mathcal{E}}\, e^{-i\omega t})$ and we will be looking at oscillating solutions to the equation of motion ie $\delta\mathbf{r}(t) = \mathrm{Re}(\delta\mathbf{r_0}e^{-i\omega t})$. The previous equation becomes a forced oscillator:

$$\delta\mathbf{r_0} = -\frac{1}{1-\left(\frac{\omega}{\omega_0}\right)^2 - i\frac{\Gamma}{\omega_0}\left(\frac{\omega}{\omega_0}\right)}\frac{e}{m_e\omega_0^2}\boldsymbol{\mathcal{E}} \tag{1.3.3}$$

and we see that the amplitude of electron oscillations will be very strong if the light frequency is close to the eigenfrequency of the system $\omega \simeq \omega_0$.

We will often have to consider not a single atom, but an actual medium composed of many similar atoms. It will then be useful to define the density of polarization $\mathbf{P}$, which correponds to the density of electric dipole induced by a monochromatic field:

$$\mathbf{P} = -ne\delta\mathbf{r_0} \equiv \epsilon_0\chi\boldsymbol{\mathcal{E}} \tag{1.3.4}$$

where n is the density of atoms and χ is the *susceptibility*. Using the equation of motion derived above, it is straightforward to evaluate the susceptibility for the Lorentz model:

$$\chi_{\text{Lorentz}} = \frac{ne^2}{m\epsilon_0\omega_0^2}\frac{1}{1-\left(\frac{\omega}{\omega_0}\right)^2 - i\frac{\Gamma}{\omega_0}\frac{\omega}{\omega_0}} \tag{1.3.5}$$

For quantum atoms (see chapter 6 for more details)

In a quantum model, the influence of the light on the atom appears as an additionnal term in the Hamiltonian corresponding to the potential energy of the dipole $E_p = -\underbrace{e\,\mathbf{r}}_{\text{dipole}}.\mathbf{E}$, leading to

$$H = \frac{\hat{p}^2}{2m_e} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hat{r}} - e\hat{\mathbf{r}}.\mathbf{E} \tag{1.3.6}$$

Note that the electric field $\mathbf{E} = \mathbf{E_0}\cos\omega t$ is a classical quantity here (not hat), while the electron position and momentum are quantum quantities.

To calculate the susceptibility, keeping the same definition as above, we need to estimate the density of polarization by computing the average value of the dipole:

$$\mathbf{P} = -ne\left\langle\psi\right|\hat{\mathbf{r}}\left|\psi\right\rangle \equiv \epsilon_0\chi\mathbf{E} \tag{1.3.7}$$

Atoms→Light (Reminder from PHY202)

The local density of polarisation $\mathbf{P}$ results in a local density of charge $\rho_p = -\mathrm{div}\mathbf{P}$ and a current density $\mathbf{j}_p = \partial_t \mathbf{P}$, which have to be included as sources in Maxwell equations. In isotropic (ie χ doesn't depend on the light polarization), linear (ie χ doesn't depend on the light intensity) and homogenous (ie χ is the same everywhere in space) media, these terms simply lead to a small change in the dispersion relation, which becomes:

$$\omega = \frac{kc}{n} \tag{1.3.8}$$

where $n \equiv \sqrt{1+\chi}$ is the optical index.

1.3.2 Interactions between atoms and a "intermediate" field

See next section.

1.3.3 Map for light-matter interactions

Table (1.1) summarizes the different models introduced before, and the framework to account for interaction between light and matter in each case.

1.4 Focus on the semi-quantum description

In this section, we consider a semi-quantum description to account for the blackbody radiation - which will allow us to introduce three basic light-matter interaction processes that we will be using the for rest of this course.

Let us go back to 1900, when the description of thermal radiation was a fierce issue[2]. It has been observed that all materials, regardless of their nature, tend to emit a similar radiation which depends only on their temperature. Two phenomenological rules were established by Rayleigh and Jeans and Wien to account for the spectral distribution of this radiation at low and high temperatures respectively

$$u_E(h\nu) \underset{h\nu\to\infty}{\sim} \frac{1}{\pi^2\hbar^3c^3}\,(h\nu)^3 \exp\left(-\frac{E}{k_BT}\right) \quad \& \quad u_E(h\nu) \underset{h\nu\to 0}{\sim} \frac{k_BT}{\pi^2\hbar^3c^3}\,(h\nu)^2 \tag{1.4.1}$$

In 1901, Planck comes with a "deperate move" and proposes the ad-hoc expression which connects the dots between these two models

$$u_E(h\nu) = \frac{1}{\pi^2\hbar^3c^3}\frac{(h\nu)^3}{e^{h\nu/k_BT}-1} \tag{1.4.2}$$

but the numerical description doesn't rely on a clear physical explanation of the processes at stake. In 1917, Einstein offers an elegant microscopic explanation of this model.

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[2] The approach proposed in this section does *not* faithfully follow the historical path. It is a re-interpretation for pedagogical purposes. For instance, we will consider rates based on photon densities because it is easier to picture in comparision to chemical processes. This picture made no sense at the time. Einstein equations were written using energy densities instead.

Interaction map	Classical Lorentz $\mathbf{r}$	Quantum Schrodinger $\|n\rangle$	Intermediate Bohr $(\mathbf{r}, n)$
Classical $\mathbf{E}(\mathbf{r},t) = \mathbf{E_0} e^{i\mathbf{k}.\mathbf{r}-\omega t}$	*"Classical"* Light→Atoms $\begin{array}{rcl} -m_e \frac{d^2}{dt^2}\mathbf{r} & = & -m\omega_0^2\mathbf{r} - \Gamma\frac{d}{dt}\mathbf{r} + \mathbf{F} \\ \text{with } \mathbf{F} & = & q\left(\mathbf{E} + \mathbf{v}\times\mathbf{B}\right) \end{array}$ Atoms→Light $\mathbf{P} = -ne\delta\mathbf{r}_0 = \epsilon_0\chi\mathbf{E}$ ⇒dispersion relation	*"Semi-classical"* Light→Atoms $\begin{array}{rcl} i\hbar\frac{d}{dt}\|\psi\rangle & = & (H_0 + H_D)\|\psi\rangle \\ H_\mathrm{D} & = & -e\hat{\mathbf{r}}.\mathbf{E}(\hat{\mathbf{r}},t) \end{array}$ Atoms→Light $\mathbf{P} = -ne\langle\psi\|\,\hat{\mathbf{r}}\,\|\psi\rangle = \epsilon_0\chi\mathbf{E}$ ⇒dispersion relation	*"Classical +"* Light→Atoms $\begin{array}{rcl} -m_e \frac{d^2}{dt^2}\mathbf{r} & = & -m\omega_0^2\mathbf{r} - \Gamma\frac{d}{dt}\mathbf{r} + \mathbf{F} \\ L & = & n\hbar \\ \text{with } \mathbf{F} & = & q\left(\mathbf{E} + \mathbf{v}\times\mathbf{B}\right) \end{array}$ Atoms→Light $\mathbf{P} = -ne\delta\mathbf{r}_0 = \epsilon_0\chi\mathbf{E}$ ⇒dispersion relation
Quantum $\hat{\mathbf{E}}(\hat{\mathbf{r}})$	-	*"Quantum"* $H = -\hat{\mathbf{D}}.\hat{\mathbf{E}}$	-
Intermediate $\mathbf{p} = \hbar\mathbf{k}$, $E = \hbar\omega$	-	-	*"Semi-quantum"* Light→Atoms $\mathbf{f} = \frac{\Delta\mathbf{p}}{\Delta t}$, Atoms→Light Rate equations

Table 1.1: Light-matter interaction models

1.4.1 Absorption, spontaneous and stimulated emission

The main idea is the following one: this thermal radiation results from the equilibrium between matter on the one hand, and radiation on the other hand.

From matter side, consider atoms decscribed as two levels (Bohr like) systems. At thermal equilibrium, the population ratio is given by

$$\frac{N_e}{N_g} = \exp\left(-\frac{E_e - E_g}{k_B T}\right) \tag{1.4.3}$$

From the radiation perspective, consider an ensemble of photons going in all directions with all possible energies. At the end of the day, we should find that the distribution of these photons $n_\gamma(h\nu)$ is compatible with eq. (1.4.2) - i.e.

$$u_\gamma(h\nu) = E \times n_\gamma(h\nu) \tag{1.4.4}$$

Now the missing point is the interactions between matter and light. Somehow, we expect that electrons can go from the ground state E_g to the excited state E_e by absorbing a photon with the corresponding energy $h\nu = E_e - E_g$, or from E_e to E_g by emitting a similar photon. But more precisely, theses processes should be such that, at equilibrium, both matter and radiation are following their own equilibrium distributions.

First try Let's try and write down the transition rates corresponding to the two basic processes we already mentioned.

- How many *absorption* processes take place every second ? We expect this number to be proportionnal to the spectral density of photons which can be absorbed n_γ and to the number of atoms able to actually absorb these photons (ie atoms in the ground N_g). Absorbtion will remove one atom from the ground state, and add one atom to the excited state. Noting B_{ge} the proportionnality factor, we get

$$\left.\frac{d}{dt}N_g\right|_{\text{abs}} = -B_{ge}N_g n_\gamma \quad \& \quad \left.\frac{d}{dt}N_e\right|_{\text{abs}} = +B_{ge}N_g n_\gamma \tag{1.4.5}$$

- How many *spontaneous emission* processes take place every second ? Assuming that atoms in the excited state have a fixed probability Γ to go back down to the ground state every second[3], we get :

$$\left.\frac{d}{dt}N_e\right|_{\text{spt}} = -\Gamma N_e \quad \& \quad \left.\frac{d}{dt}N_g\right|_{\text{spt}} = +\Gamma N_e \tag{1.4.6}$$

In stationnary state, the rate *going to* any state should be the same as the rate *leaving from* that state (detailled balance condition, see appendix), leading to:

$$B_{ge}N_g n_\gamma = \Gamma N_e \Rightarrow n_\gamma = \frac{\Gamma / B_{ge}}{\exp\left(\frac{\hbar\omega}{k_B T}\right)} \tag{1.4.7}$$

and we see that this form cannot be made to match eq. (1.4.2). It means that somehow, something is missing from our simple model.

---

[3] Γ is often noted A when deriving Einstein coefficient, to remain coherent with the B notation for absorption processes.

Second try This something is what Einstein introduced as the *stimulated emission* : in addition to the spontaneous decay from excited to ground state, which can emit a photon in any direction, atoms can also be pushed back down by an existing photon. In this case, the photon emitted through the process is an exact copy of the photon which triggered the emission.

- How many *stimulated emission* processes take place every second ? This process is actually the inverse of absorption : it take one photon (so we expect the rate to be proportionnal to the spectral density of photons) and one atom in the excited state (so we expect the rate to be proportionnal to the number of atoms in the excited state) to produce one atom in the ground state:

$$\frac{d}{dt}N_e\bigg|_{\text{stim}} = -B_{eg}N_e n_\gamma \quad \& \quad \frac{d}{dt}N_1\bigg|_{\text{stim}} = +B_{eg}N_e n_\gamma \tag{1.4.8}$$

In steady state, a detailled balance now gives

$$n_\gamma = \frac{\Gamma}{B_{ge}\exp\left(\frac{h\nu}{k_B T}\right) - B_{eg}} \tag{1.4.9}$$

Comparing this results with Planck's law gives two very important results :

$$\boxed{B_{eg} = B_{ge}} \tag{1.4.10}$$

which means that stimulated emission has exactely the same coupling as absorption, and

$$\boxed{\frac{\Gamma}{B_{eg}} = \frac{(h\nu)^2}{\pi^2\hbar^3c^3}} \tag{1.4.11}$$

which means that a system isn't able absorb radiation without being also able to emit this same radiation.

1.4.2 Light-matter cross section

In the precious section, we have identified three basic processes for light matter interactions. It is also interesting to interpret these terms from the *radiation* perspective: how are these interactions affecting a light beam passing through atoms ?

Consider an ensemble of atoms, not necessarily in thermal equlibirum - so unlike the previous case, N_e and N_g are not fixed. Instead of the thermal radiation from before, we now consider a beam of photons passing through the atoms.

We will add one techinical difficulty when making this calculation. So far, we have been counting photons, considering all photons had exactly the same energy $h\nu$. When considering real light, of course, the spectrum is never infinitely narrow. So we will make this calculation with spectral quantities instead. The spectral intensity of the beam is $\mathcal{I}(h\nu)$ - ie the power carried by photons with energy between $h\nu$ and $h\nu + d(h\nu)$ is $\mathcal{I}(h\nu)\,d(h\nu)$. In the same was, we will consider the spectral density of photons $\mathcal{N}(h\nu)$ such that the number of photons with energy between $h\nu$ and $h\nu + d(h\nu)$ is $\mathcal{N}(h\nu)\,d(h\nu)$.

From spectral intensity to spectral photon density

Let's first relate the light intensity to the corresponding photon density. To do so, we perform an energy balance over a period dt on the ensemble of the beam's photons with energy $h\nu$ up to $d(h\nu)$ which are going to pass through a control surface dS during this period. The number of considered photons is $\mathcal{N}(h\nu)\, d(h\nu)\, dS\, cdt$, the corresponding energy which will pass through dS during dt is $h\nu \times \mathcal{N}(h\nu)\, d(h\nu)\, dS\, cdt$ - and this is by definition of the intensity equal to $\mathcal{I}(h\nu)\, d(h\nu)\, dSdt$, leading to

$$\mathcal{N}(h\nu) = \frac{1}{c}\frac{\mathcal{I}(h\nu)}{h\nu} \tag{1.4.12}$$

From energy balance to the Beer-Lambert law

We now perform an energy balance on the light beam passing through an infinitesimal slab of atoms of surface dS and thickness dx between t and $t+dt$, considering only photons with energy between $h\nu$ and $h\nu + d(h\nu)$

- Energy entering the slab: $\mathcal{I}(h\nu,\, x)\, d\,(h\nu)\;\, dSdt$
- Energy leaving the slab: $\mathcal{I}(h\nu,\, x+dx)\, d\,(h\nu)\;\, dSdt$
- Energy absorbed from the beam by the atoms: $h\nu \times B_{ge} n_g\, dSdx \times \mathcal{N}(h\nu)\, d(h\nu) \times dt$
- Energy added to the beam by the atoms: $h\nu \times B_{eg} n_e Sdx \times \mathcal{N}(h\nu)\, d(h\nu) \times dt$ (we only take stimulated emission into account ; spontaneous emission can go in all direction and doesn't contribute to the beam)

This balance leads to

$$\frac{1}{c}\frac{d\mathcal{I}}{dt} + \frac{d\mathcal{I}}{dx} = \frac{B_{\text{eg}}}{c}\left(n_e - n_g\right)\mathcal{I} \tag{1.4.13}$$

and in steady state

$$\boxed{\frac{d}{dx}\mathcal{I} = \sigma_{eg}\,\left(n_e - n_g\right)\mathcal{I} \qquad (1.4.14)}$$

where we introduced the interaction cross section $\sigma_{eg} = \frac{B_{\text{eg}}}{c}$ which tells the size of the *target* each atoms represents from the beam perspective. An atom in the ground state is a target which will *remove* energy from the beam by absorbing a photon if "hitted" ; an atom in the excited state will *add* energy to the beam by stimulated emission. We recover here the celebrated Beer Lambert law which accounts for light propagation through a medium and we now interpret it as two contributions : the strength of the coupling (which is the same for absorption and stimulated emission as discussed before) and available populations in the ground and excited states.

Interaction cross-sections

Very importantly, we can re-write the interactions rates for an atom in a light beam using the cross section rather than the B_{eg} coefficient, which is the formalism we will use in most of this lecture. The probability per second for an atom in the ground state to absorb a photon from the beam, which is the same as the probability per second for an atom in the excited state to emit a photon in a stimulated way, can be written as

$$r_{\text{abs}} = r_{\text{stim}} = \int d\,(h\nu)\ B_{eg}\mathcal{N}(h\nu) \tag{1.4.15}$$

$$= \frac{\sigma_{eg} I}{h\nu} \tag{1.4.16}$$

(where we assumed that the B coefficient is the same for all wavelengths with significant spectral intensity, an assumption we will relax in future lectures).

1.5 Take-home messages

The key elements you need to remember from this first chapter are the following ones :

1. You should be able to redraw the model map (classical, quantum and intermediate description of light, matter and their interaction) by yourself
2. Remember the 3 basic processes in the semi-quantum model (absorption, spontaenous emission, stimulated emission) and how they are connected to each other (eq. (1.4.10) and eq. (1.4.11)).
3. Keep in mind the Beer Lamber law eq. (1.4.14) and the interaction cross sections eq.(1.4.15) as it's going to be recurring tools from now on.

1.6 Appendix

1.6.1 Basic accounting

1.6.1.1 How to make a balance ?

State the balance clearly Start by writing explicitely the balance under consideration

What?	We are considering a balance of particles / energy / electric charge / momentum / potatoes /...
When?	bewteen time t and $t + dt$ / between the begining and the end of the interaction / ...
Where?	in the volume betwee x and $x + dx$, y and $y + dy$, z and $z + dz$ / in the slab of section S and thickness dz / ...

To prevent confusion, take the time to write down all ingredients of the balance (examples are given for a 1D problem)

Detail all ingredients

1. Amount inside the system at time t. Usually something like, $n(x,t)Sdx$.
2. Amount entering the system t et $t + dt$. Usually something like, $d\phi_x = j_x(x,t)Sdt$. Voir plus bas.
3. Amount leaving the system$t$ et $t + dt$. Idem. Usually something like, $d\phi_{x+dx} = j_x(x + dx, t)Sdt$. Idem
4. Amount created inside the system$t$ et $t + dt$. Usually something like, $dG = \mathcal{G}(x,t)Sdxdt$
5. Amount destroyed inside the system$t$ et $t + dt$. Usually something like, $dR = \mathcal{R}(x,t)Sdxdt$

6. Amount inside the system at time $t + dt$. Usually something like, $n(x, t + dt)Sdx$.

Use conservation

The balance can then easily be stated as:

$$\begin{aligned}
\begin{matrix}\text{What is insde the system at time } t+dt \\ n(x,t+dt)Sdx\end{matrix} &= \begin{matrix}\text{What was inside at time } t \\ n(x,t)Sdx\end{matrix} \\
&+ \begin{matrix}\text{What got in} \\ j_x(x,t)Sdt\end{matrix} \\
&- \begin{matrix}\text{What got out} \\ j_x(x+dx,t)Sdt\end{matrix} \\
&+ \begin{matrix}\text{What has been created} \\ \mathcal{G}(x,t)Sdxdt\end{matrix} \\
&- \begin{matrix}\text{What has been destroyed} \\ \mathcal{R}(x,t)Sdxdt\end{matrix}
\end{aligned} \tag{1.6.1}$$

Use Taylor-Young formula

Express quantities in $x + dx$ or $t + dt$ as a function of quantities in x or t using a first order development:

$$f(x_0 + dx, y_0, z_0, t_0) \simeq f(x_0, y_0, z_0, t_0) + \frac{\partial f}{\partial x}(x_0, y_0, z_0, t_0)dx$$

.

The balance then becomes

$$\begin{aligned}
\left(n(x,t) + \frac{\partial n}{\partial t}(x,t)dt\right) Sdx &= n(x,t)Sdx \\
&+ j_x(x,t)Sdt \\
&- \left(j_x(x,t) + \frac{\partial j_x}{\partial x}(x,t)dx\right) Sdt \\
&+ \mathcal{G}(x,t)Sdxdt \\
&- \mathcal{R}(x,t)Sdxdt
\end{aligned}$$

Turn it into a nice differential equation

All that remains is to simplify this expression into an elegant form:

$$\frac{\partial n}{\partial t} + \frac{\partial j_x}{\partial x} = \mathcal{G} - \mathcal{R}$$

1.6.1.2 Detailled balance

$$\begin{pmatrix}
\text{Population in state i} \\
\times \\
\sum\limits_{j \neq i} \text{Transition rate from i to j} \\
= \text{Nb of jumps from i per second} \\
= n_i \sum\limits_{j \neq i} r_{i \to j}
\end{pmatrix}
=
\begin{pmatrix}
\sum\limits_{j \neq i} \text{(Population in state j} \\
\times \\
\text{Transition rate from j to i)} \\
= \text{Nb of jumps from j to i per second} \\
= \sum\limits_{j \neq i} n_j r_{j \to i}
\end{pmatrix} \tag{1.6.2}$$

1.6.2 Note on units

Dealing with spectral densities can be tricky. A spectral density gives the amount of particles (or energy) in a very small spectral interval - but that interval can be counted in terms of energy, frequency or wavelength :

- How many photons are there with an energy between E and $E + dE$? → $n_E(E)dE$
- How many photons are there with a frequency between ω and $\omega + d\omega$? → $n_\omega(\omega)d\omega$
- How many photons are there with a wavelength between λ and $\lambda + d\lambda$? → $n_\lambda(\lambda)d\lambda$

Of course these quantities are related, since $E = \hbar\omega = hc/\lambda$; but be careful ! If we just replace the expression of E by hc/λ inside $n_E(E)$, we won't get the correct expression for spectral density in wavelength ! We will still have the spectral density in energy (ie the number photons with an energy between E and $E + dE$). If we want to switch to a spectral density in wavelength, we need to consider the differential element as well:

$$n_E(E)dE = n_\omega(\omega)d\omega = n_\lambda(\lambda)d\lambda \tag{1.6.3}$$

with $dE = \hbar d\omega = \frac{hc}{\lambda^2}d\lambda$, leading to

$u_E(E,\Omega)$	$u_\omega(\omega,\Omega)$	$u_\nu(\nu,\Omega)$	$u_\lambda(\lambda,\Omega)$
$\frac{E^3}{4\pi^3\hbar^3c^3}\frac{1}{\exp\left(\frac{E}{k_BT}\right)-1}$	$\frac{(\hbar\omega)^3}{4\pi^3\hbar^2c^3}\frac{1}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}$	$\frac{(h\nu)^3}{2\pi^2\hbar^2c^3}\frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}$	$\frac{2hc}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1}$
$E_{\text{max}} = 2.82\, k_BT$	$\hbar\omega_{\text{max}} = 2.82\, k_BT$	$h\nu_{\text{max}} = 2.82\, k_BT$	$\lambda_{\text{max}} = 0.2497\, \frac{\mu\text{m eV}}{k_BT}$

1.6.3 Bohr model

Model

Consider an electron submitted to the Coulomb force induced by a nucleus of charge $+Ze$.

We will restric our study to circular orbits for the sake of simplicity. We will note r the radius of the orbit.

Bohr assumption on orbital angular momentum : $\mathbf{L} = \mathbf{r} \times \mathbf{p} = n\hbar\mathbf{u}_z$

De Broglie's interpretation Consider that the electron is described by a wave of wavelength λ. For an orbit to be allowed, a stationnary wave should fit along the perimeter - ie $2\pi r = n\lambda$. Using de Broglie's relation, $\lambda = h/p$, we find easily Bohr's assumption.

Results Radius quantization : the orbit radius can only take values scaling like :

$$r = n^2\frac{\hbar^2}{m}\frac{4\pi\epsilon_0}{Ze^2} \tag{1.6.4}$$

Derivation Using Newton's second law

$$m\frac{d^2}{dt^2}\mathbf{r} = -m\frac{v^2}{r}\mathbf{u_r} = -\frac{Zq^2}{4\pi\epsilon_0}\frac{1}{r^2}u_r \Leftrightarrow v^2 = \frac{Zq^2}{4\pi m\epsilon_0}\frac{1}{r} \tag{1.6.5}$$

and Bohr assumption induces the condition

$$mrv = n\hbar \tag{1.6.6}$$

We deduce the expression of the radius from these two equations.

Energy spectrum : the electron energy can only take values scaling like :

$$E_n = -\frac{1}{n^2}\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \tag{1.6.7}$$

Derivation

- Kinetic energy

$$E_c = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{n\hbar}{mr}\right)^2 = \frac{1}{2n^2}\frac{m}{\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \tag{1.6.8}$$

.

- Potential energy

$$E_p = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r} = -\frac{1}{n^2}\frac{m}{\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \tag{1.6.9}$$