Phenomenological models of light-matter interaction

September 20, 2022

Contents

The propagation of electromagnetic waves in matter leads to phenomena such as reflection, transmission and absorption. These quantities can be expressed as a function of the linear dielectric susceptibility $\tilde{\chi}(\omega)$ that connects the applied electric field $\mathbf{E}$ and the polarization $\mathbf{P}$.

$$\mathbf{P}(\omega) = \varepsilon_0 \tilde{\chi}(\omega)\,\mathbf{E}(\omega)$$

The polarization $\mathbf{P}$ arises from the interactions between $\mathbf{E}$ and electric charges in matter. Modeling these interactions is necessary to express the dependency of $\tilde{\chi}$ with ω. In this first chapter, we will review two historical and phenomenological models of light-matter interaction.

1 Classical model of an atomic dipole - Drude-Lorentz model

We consider a one-electron atom where both the electron and the nucleus are supposed to be point particles. Because of the large difference in their masses, we make the assumption that the nucleus is to be at rest while the electron is bound to the nucleus by an elastic force:

$$\mathbf{F} = -m\omega_0^2 \mathbf{r}$$

where m is the electron mass, ω_0 is the natural angular frequency of the oscillator and $\mathbf{r}$ the displacement of the electron from its equilibrium position. The system is equivalent to the spring problem in mechanics. The corresponding atomic dipole $\mathbf{p}$ is given by:

$$\mathbf{p} = q\mathbf{r}$$

where q the electronic charge.

1.1 Free evolution

At zero electric field, the classical equation of motion is:

$$m\ddot{x} = -m\omega_0^2 x - 2m\gamma\dot{x}$$

the term $-2m\gamma\dot{x}$ is an effective viscous friction that describes the damping of the dipole that can occur by collisions, interaction with other dipoles or radiation (coupling to external fields).

$$q\ddot{x} + 2\gamma q\dot{x} + q\omega_0^2 x = 0$$

$$\ddot{p} + 2\gamma\dot{p} + \omega_0^2 p = 0$$

The characteristic polynomial of this equation is:

$$\lambda^2 + 2\gamma\lambda + \omega_0^2$$

$$\Delta = 4\gamma^2 - 4\omega_0^2$$

We assume that $\gamma < \omega_0$ so $\Delta < 0$ and:

$$\lambda = -\gamma \pm i\sqrt{\omega_0^2 - \gamma^2}$$

$$p = A\ e^{-\gamma t}\ e^{+i\sqrt{\omega_0^2-\gamma^2}\ t} + B\ e^{-\gamma t}\ e^{-i\sqrt{\omega_0^2-\gamma^2}\ t}$$

p must be real so $B = A^*$

$$\begin{aligned} p &= e^{-\gamma t} \left[A\ e^{+i\sqrt{\omega_0^2-\gamma^2}\ t} + A^*\ e^{-i\sqrt{\omega_0^2-\gamma^2}\ t}\right] \\ &= e^{-\gamma t}\ 2\,\mathrm{Re}\left(A\ e^{+i\sqrt{\omega_0^2-\gamma^2}\ t}\right) \\ &= 2\left|A\right|\ e^{-\gamma t} \cos\left(\sqrt{\omega_0^2-\gamma^2}\ t + \varphi\right) \end{aligned}$$

If $\gamma \ll \omega_0$:

$$\boxed{p \simeq p_0\ e^{-\gamma t} \cos\left(\omega_0\ t + \varphi\right)}$$

The dipole oscillates at a frequency close to the natural frequency ω_0 and is damped with a characteristic parameter that is the inverse of a time.

1.2 Forced motion

In the presence of a sinusoidal electric field $E\left(t\right) = E_0 \cos\omega t$, the dipole equation becomes:

$$\ddot{p} + 2\gamma\dot{p} + \omega_0^2 p = \frac{q^2 E_0}{m} \cos\omega t$$

Given that the wavelength of light is large compared to the characteristic dimensions of atoms, we neglect the spatial dependence of the field and look for the solution in the form:

$$p\left(t\right) = \Re\left(\not{p}\left(\omega\right) e^{-i\omega t}\right)$$

$$\not{p}(\omega)\, e^{-i\omega t}\left(-\omega^2 - 2i\gamma\omega + \omega_0^2\right) = \frac{q^2 E_0}{m} e^{-i\omega t}$$

The dependence of the atomic dipole with ω is given by

$$\not{p}(\omega) = \frac{q^2}{m}\frac{1}{\left(\omega_0^2 - \omega^2 - 2i\gamma\omega\right)} E_0$$

With N atoms per unit-volume, the macroscopic polarization is:

$$\mathscr{P}\left(\omega\right) = N\frac{q^2}{m}\frac{1}{\left(\omega_0^2 - \omega^2 - 2i\gamma\omega\right)} E_0$$

On the other hand, the complex linear susceptibility $\tilde{\chi}$ is defined by:

$$\mathscr{P}\left(\omega\right) = \varepsilon_0 \tilde{\chi}\left(\omega\right) E_0$$

$$\tilde{\chi}\left(\omega\right) = \frac{Nq^2}{\varepsilon_0 m\omega_0^2}\frac{\omega_0^2}{\left(\omega_0^2 - \omega^2 - 2i\gamma\omega\right)} = \chi\left(0\right)\frac{\omega_0^2}{\left(\omega_0^2 - \omega^2 - 2i\gamma\omega\right)}$$

As expected, $\tilde{\chi}$ is a complex number:

$$\tilde{\chi} = \chi' + i\chi'' = \left|\tilde{\chi}\right| e^{-i\varphi}$$

The fact that we choose a minus sign in the argument of the complex exponential enable us to write

$$P\left(t\right) = \varepsilon_0 \left|\tilde{\chi}\right| E_0 \cos\left(\omega t + \varphi\right)$$

The modulus and the argument of $\tilde{\chi}$ are easy to calculate:

$$\begin{aligned}
\left|\tilde{\chi}\right| &= \chi\left(0\right)\frac{\omega_0^2}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2}} \\
\tan\varphi &= -\frac{\chi''}{\chi'} = -\frac{2\gamma\omega}{\omega_0^2 - \omega^2}
\end{aligned}$$

These two quantities are ploted in the figure 1. When $\omega = \omega_0$, the amplitude is maximum and the dipole oscillates in quadrature with the field. This is the resonance phenomenon.

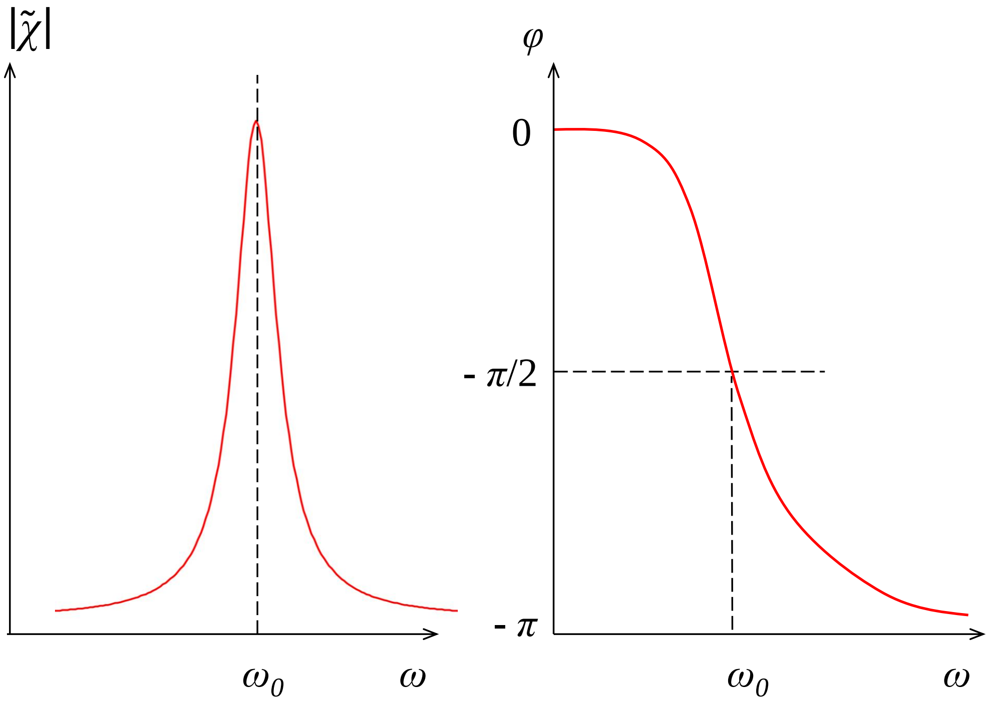


Figure 1: Amplitude and phase shift of the forced motion of the atomic dipole.

1.3 Study of the real and imaginary parts of $\tilde{\chi}$

In this paragraph, we study in detail the real and imaginary parts of χ.

$$\tilde{\chi}(\omega) = \underbrace{\chi(0)\frac{\omega_0^2\left(\omega_0^2-\omega^2\right)}{\left(\omega_0^2-\omega^2\right)^2+4\gamma^2\omega^2}}_{\chi'} + i\underbrace{\chi(0)\frac{2\gamma\omega_0^2\omega}{\left(\omega_0^2-\omega^2\right)^2+4\gamma^2\omega^2}}_{\chi''}$$

$$\frac{\mathrm{d}\chi'}{\mathrm{d}\omega} = 2\chi(0)\,\omega_0^2\omega\frac{\left(\omega_0^2-\omega^2\right)^2-4\gamma^2\omega_0^2}{\left[\left(\omega_0^2-\omega^2\right)^2+4\gamma^2\omega^2\right]^2}$$

The derivative is zero when:

$$\left(\omega_0^2-\omega^2+2\gamma\omega_0\right)\left(\omega_0^2-\omega^2-2\gamma\omega_0\right)=0$$

The roots are:

$$\omega_{1,2}=\omega_0\sqrt{1\pm2\frac{\gamma}{\omega_0}}$$

if $\gamma \ll \omega_0$, the Taylor expansion $(1+x)^\alpha = 1 + \alpha x$ gives:

$$\omega_{1,2} \simeq \omega_0 \pm \gamma$$

we subsitute ω by $\omega_{1,2}^2 = \omega_0^2 \pm 2\gamma\omega_0$ in the expression of χ'

$$\chi'(\omega_1) = \chi(0)\,\omega_0^2 \frac{\left(\omega_0^2 - \omega^2\right)}{\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2}$$

$$\begin{aligned}
\chi'(\omega_1) &= \chi(0)\,\omega_0^2 \frac{2\gamma\omega_0}{\left(2\gamma\omega_0\right)^2 + 4\gamma^2\left(\omega_0^2 - 2\gamma\omega_0\right)} \\
&= \chi(0)\,\omega_0^2 \frac{2\gamma\omega_0}{4\gamma^2\omega_0^2 + 4\gamma^2\omega_0^2 - \underbrace{8\gamma^3\omega_0}_{\text{third order in } \gamma}} \simeq \chi(0)\,\omega_0^2 \frac{2\gamma\omega_0}{4\gamma^2\omega_0^2 + 4\gamma^2\omega_0^2} \\
&= \chi(0)\,\frac{\omega_0}{4\gamma}
\end{aligned}$$

The same calcultion with ω_2 gives:

$$\chi'(\omega_2) = -\chi(0)\,\frac{\omega_0}{4\gamma}$$

Imaginary part

$$\chi''(\omega) = \chi(0)\,\omega_0^2 \frac{2\gamma\omega}{\left(\omega_0^2 - \omega^2\right)^2 + 4\gamma^2\omega^2}$$

When ω is close to ω_0 and $\gamma \ll \omega_0$:

$$\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \simeq -2\omega_0(\omega - \omega_0)$$

$$\begin{aligned}
\chi''(\omega) &= \chi(0)\,\omega_0^2 \frac{2\gamma\omega_0}{4\omega_0^2(\omega - \omega_0)^2 + 4\gamma^2\omega_0^2} \\
&= \chi(0)\,\frac{2\gamma\omega_0}{4(\omega - \omega_0)^2 + 4\gamma^2} = \frac{\chi(0)}{2}\frac{\gamma\omega_0}{(\omega - \omega_0)^2 + \gamma^2}
\end{aligned}$$

$$\chi''(\omega) = \underbrace{\chi(0)\,\frac{\omega_0}{2\gamma}}_{\chi''(\omega_0)} \frac{1}{1 + \left(\dfrac{\omega - \omega_0}{\gamma}\right)^2}$$

Around ω_0, $\chi''(\omega)$ has a lorentzian shape centered at ω_0. The function has its maximum divide by 2 when:

$$\chi''(\omega) = \frac{\chi''(\omega_0)}{2}$$

This condition is satisfied when

$$\omega = \omega_0 \pm \gamma$$

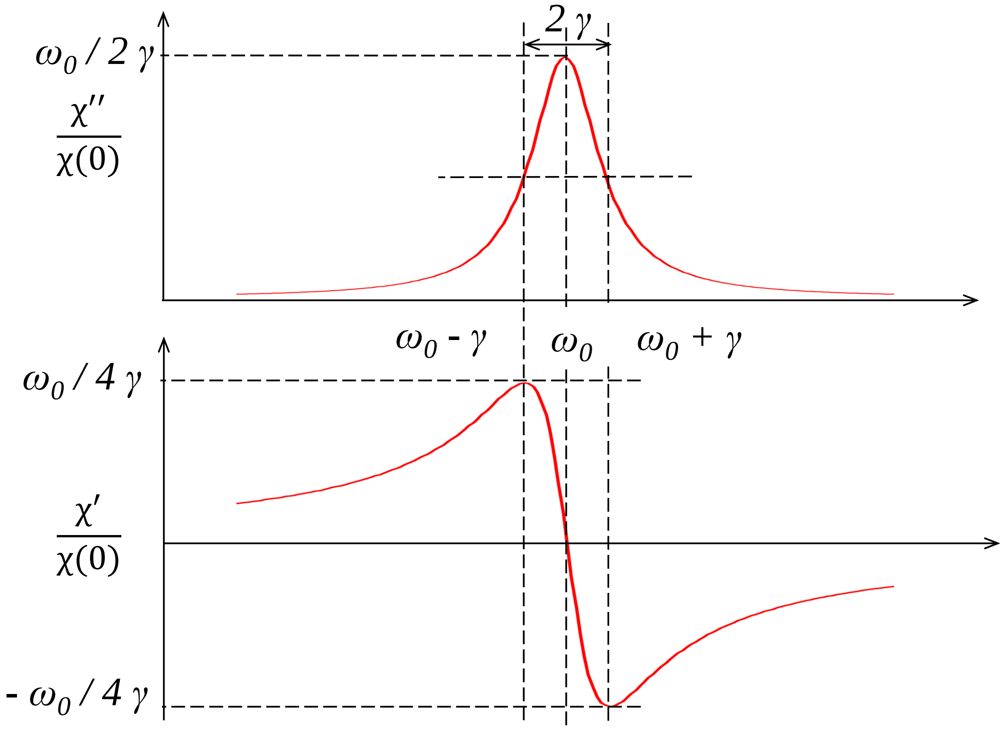


Figure 2: Diagram of the imaginary (top) and real (bottom) parts of the dielectric susceptibility.

1.4 Refractive index

We remind that

$$\tilde{\varepsilon}_r(\omega) = 1 + \tilde{\chi}(\omega) = \tilde{n}^2$$

The real and imaginary parts of ε_r are

$$\begin{cases} \varepsilon_r' = n^2 - \kappa^2 \\ \varepsilon_r'' = 2n\kappa \end{cases}$$

Solving this system allows to extract the real and imaginary parts of:

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$$

We can then model the coefficients of reflection $R(\omega)$ and reflection $T(\omega)$ of a material in the vicinity of a resonance thanks to the Fresnel relation.

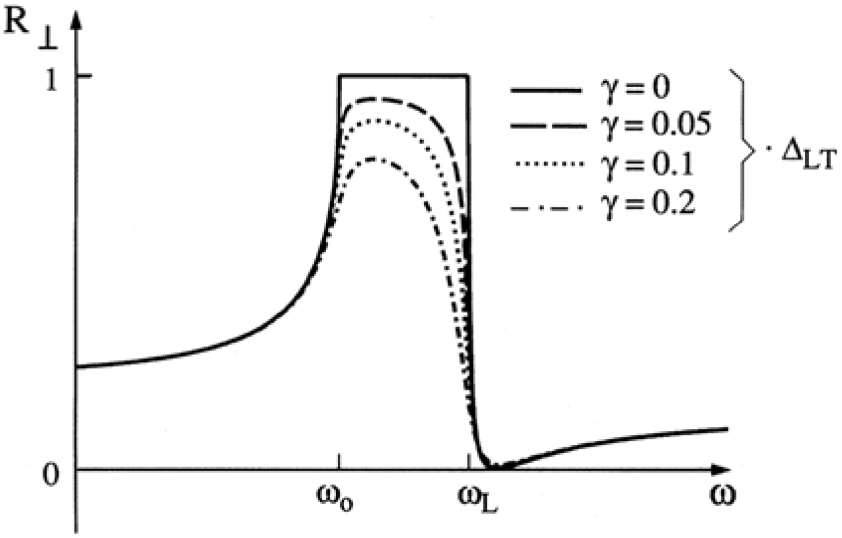


Figure 3: The reflection spectrum of a single resonance with zero and finite damping for normal incidence.

1.5 Energy transfer

In this part, we describe how the energy from the field is used in matter. We start from the Maxwell-Ampère equation in matter:

$$\nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t}$$

with $\mathbf{H} = \dfrac{\mathbf{B}}{\mu_0} - \mathcal{M}$ and $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$. We express the dot product $\mathbf{E} \cdot \mathbf{j}$ which has the dimension of a power per unit-volume:

$$\mathbf{E} \cdot \mathbf{j} = \mathbf{E} \cdot \nabla \times \mathbf{H} - \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t}$$

We use the vectorial relation:

$$\nabla \cdot (\mathbf{A} \times \mathbf{B}) = (\nabla \times \mathbf{A}) \cdot \mathbf{B} - \mathbf{A} \cdot (\nabla \times \mathbf{B})$$

$$\mathbf{A}\cdot(\nabla\times\mathbf{B}) = (\nabla\times\mathbf{A})\cdot\mathbf{B} - \nabla\cdot(\mathbf{A}\times\mathbf{B})$$

$$\mathbf{E}\cdot(\nabla\times\mathbf{H}) = (\nabla\times\mathbf{E})\cdot\mathbf{H} - \nabla\cdot(\mathbf{E}\times\mathbf{H})$$

We obtain:

$$\mathbf{E}\cdot\mathbf{j} = (\nabla\times\mathbf{E})\cdot\mathbf{H} - \nabla\cdot(\mathbf{E}\times\mathbf{H}) - \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}$$

By using the Maxwell-Faraday equation, we find:

$$\mathbf{E}\cdot\mathbf{j} = \frac{\partial\mathbf{B}}{\partial t}\cdot\mathbf{H} - \nabla\cdot(\mathbf{E}\times\mathbf{H}) - \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}$$

Let's rewrite each term:

$$\begin{aligned}\mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t} = \mathbf{E}\cdot\frac{\partial}{\partial t}(\varepsilon_0\mathbf{E}+\mathbf{P}) &= \varepsilon_0\mathbf{E}\cdot\frac{\partial\mathbf{E}}{\partial t} + \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}\\ &= \frac{\varepsilon_0}{2}\frac{\partial\mathbf{E}^2}{\partial t} + \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}\end{aligned}$$

$$\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} = \frac{\mathbf{B}}{\mu_0}\cdot\frac{\partial\mathbf{B}}{\partial t} = \frac{1}{2\mu_0}\cdot\frac{\partial\mathbf{B}^2}{\partial t} = \frac{\varepsilon_0 c^2}{2}\cdot\frac{\partial\mathbf{B}^2}{\partial t}$$

The product $\mathbf{E}\times\mathbf{H}$ is the Poynting vector. In a non-magnetic material, it becomes:

$$\mathbf{E}\times\mathbf{H} = \frac{1}{\mu_0}\mathbf{E}\times\mathbf{B} = \varepsilon_0 c^2\mathbf{E}\times\mathbf{B}$$

$$\mathbf{E}\cdot\mathbf{j} = -\frac{\varepsilon_0}{2}\frac{\partial\mathbf{E}^2}{\partial t} - \frac{\varepsilon_0 c^2}{2}\cdot\frac{\partial\mathbf{B}^2}{\partial t} - \nabla\cdot\left(\varepsilon_0 c^2\mathbf{E}\times\mathbf{B}\right) - \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}$$

$$\boxed{\frac{\partial}{\partial t}\frac{\varepsilon_0}{2}\left[\mathbf{E}+c^2\mathbf{B}\right] = -\mathbf{E}\cdot\mathbf{j} - \nabla\cdot\left(\varepsilon_0 c^2\mathbf{E}\times\mathbf{B}\right) - \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}}$$

let's analyze each of these terms:

- $\frac{\partial}{\partial t}\frac{\varepsilon_0}{2}\left[\mathbf{E}+c^2\mathbf{B}\right]$ is the time derivative of the electromagnetic energy per unit volume.
- $\mathbf{E}\cdot\mathbf{j}$ is the power given to free charges.
- $\nabla\cdot(\varepsilon_0 c^2\mathbf{E}\times\mathbf{B})$ is the power radiated through the surface Σ that encloses the considered volume.
- $\mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}$ is the power needed to modify the polarization.

Let calculate the time average of $\mathbf{E}\cdot\dfrac{\partial \mathbf{P}}{\partial t}$. We write the field and the polarization in complex notation:

$$\mathbf{E}(t)=\frac{\mathbf{E}_0}{2}e^{-i\omega t}+c.c. \text{ et } \mathbf{P}(t)=\frac{\mathscr{P}(\omega)}{2}e^{-i\omega t}+c.c.$$

$$\frac{\partial \mathbf{P}}{\partial t}=-\frac{i\omega}{2}\mathscr{P}(\omega)e^{-i\omega t}+\frac{i\omega}{2}\mathscr{P}^*(\omega)e^{i\omega t}$$

$$\mathbf{E}\cdot\frac{\partial \mathscr{P}}{\partial t}=-\frac{i\omega}{4}\mathbf{E}_0\mathscr{P}(\omega)e^{-2i\omega t}+\frac{i\omega}{4}\mathbf{E}_0^*\mathscr{P}^*(\omega)e^{2i\omega t}-\frac{i\omega}{4}\mathbf{E}_0^*\mathscr{P}(\omega)+\frac{i\omega}{4}\mathbf{E}_0\mathscr{P}^*(\omega)$$

When we calculate the time average, the terms in 2ω have a zero contribution, so we have:

$$\begin{aligned}\left\langle \mathbf{E}\cdot\frac{\partial \mathbf{P}}{\partial t}\right\rangle &=\frac{i\omega}{4}\mathbf{E}_0\mathscr{P}^*-\frac{i\omega}{4}\mathbf{E}_0^*\mathscr{P}=2\,\mathrm{Re}\left\{\left(\frac{i\omega}{4}\mathbf{E}_0\mathscr{P}^*\right)\right\}\\ &=2\,\mathrm{Re}\left\{\left(\frac{i\omega}{4}\mathbf{E}_0\varepsilon_0\left(\chi'-i\chi''\right)\mathbf{E}_0^*\right)\right\}\end{aligned}$$

$$\boxed{\left\langle \mathbf{E}\cdot\frac{\partial \mathbf{P}}{\partial t}\right\rangle=\frac{1}{2}\varepsilon_0\omega\chi''\left|\mathbf{E}_0\right|^2}$$

The power transferred to the medium to modify the volume polarization is proportional to the imaginary part of the dielectric susceptibility.

1.6 Propagation and attenuation

Let us now calculate the mean value of the Poynting vector. As we are interested in propagation, we write the field with its spatial dependence:

$$\tilde{\mathbf{E}}=\mathbf{E}_0\ e^{ikz}\ e^{-i\omega t}$$

The real field is:

$$\mathbf{E}=\frac{1}{2}\left(\tilde{\mathbf{E}}+\tilde{\mathbf{E}}^*\right)$$

With $k=\dfrac{\omega}{c}\tilde{n}$:

$$\tilde{\mathbf{E}}=\mathbf{E}_0\ \exp\left\{\left(-\frac{\omega}{c}\kappa z\right)\right\}\ \exp\left\{\left[-i\omega\left(t-n\frac{z}{c}\right)\right]\right\}$$

A calculation identical to that carried out previously with the complex expressions of the fields gives us:

$$\mathbf{S}=\epsilon_0c^2\left\langle \mathbf{E}\times\mathbf{B}\right\rangle=\frac{\epsilon_0c^2}{2}\,\mathrm{Re}\left(\tilde{\mathbf{E}}\times\tilde{\mathbf{B}}^*\right)$$

We then use the Maxwell-Faraday equation:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

which gives, for monochromatic plane-waves :

$$i\mathbf{k} \times \tilde{\mathbf{E}} = i\omega \tilde{\mathbf{B}}$$

hence the expression for $\tilde{\mathbf{B}}$:

$$\tilde{\mathbf{B}} = \frac{\mathbf{k}}{\omega} \times \tilde{\mathbf{E}}$$

$$\langle \mathbf{S} \rangle = \frac{\epsilon_0 c^2}{2\omega} \operatorname{Re}\left[\tilde{\mathbf{E}} \times \left(\mathbf{k} \times \tilde{\mathbf{E}}\right)^*\right] = \frac{\epsilon_0 c^2}{2\omega} \operatorname{Re}\left[\left(\tilde{\mathbf{E}} \cdot \tilde{\mathbf{E}}^*\right) \mathbf{k}^* - \left(\tilde{\mathbf{E}} \cdot \mathbf{k}^*\right) \tilde{\mathbf{E}}\right]$$

$$\langle \mathbf{S} \rangle = \frac{\epsilon_0 c^2}{2\omega} \mathbf{E}^2 \operatorname{Re}(\mathbf{k}) = \frac{\epsilon_0 c^2}{2\omega} \mathbf{E}^2 \frac{n\omega}{c} \mathbf{u}$$

where n is the real part of the refractive index and $\mathbf{u}$ a unit vector.

$$\boxed{\langle \mathbf{S} \rangle = n\frac{\epsilon_0 c}{2} \mathbf{E}_0^2 \ \exp\left\{\left(-2\frac{\omega}{c}\kappa z\right)\right\} \mathbf{u} = \langle \mathbf{S}_0 \rangle \ \exp\left\{\left(-2\frac{\omega}{c}\kappa z\right)\right\} \mathbf{u}}$$

We write that the energy radiated by the field is damped according to the law:

$$\langle \mathbf{S} \rangle = \langle \mathbf{S}_0 \rangle \ \exp\{(-\alpha z)\} \mathbf{u}$$

where α is the absorption coefficient. When the angular frequency ω of the field is resonant with the natural frequency of the atomic dipole:

$$\tilde{\chi} \simeq \chi''(\omega_0)$$

We also recall that:

$$\tilde{\varepsilon}(\omega) = 1 + \tilde{\chi}(\omega) = \tilde{n}^2$$

we have:

$$\begin{cases} \varepsilon_r' = n^2 - \kappa^2 \\ \varepsilon_r'' = 2n\kappa \end{cases}$$

We deduce that

$$\alpha = 2\frac{\omega}{c}\kappa = 2\frac{\omega}{c}\frac{\varepsilon_r''}{2n} = \frac{\omega}{c}\frac{\chi''}{n}$$

at the resonance:

$$\chi''(\omega_0) = \chi(0)\frac{\omega_0}{2\gamma} = \frac{Nq^2}{\varepsilon_0 m\omega_0^2}\frac{\omega_0}{2\gamma} = \frac{1}{2}\frac{Nq^2}{\varepsilon_0 m\omega_0\gamma}$$

hence the absorption coefficient:

$$\alpha = \frac{1}{2}\frac{Nq^2}{\varepsilon_0 mnc\gamma}\frac{\omega}{\omega_0}$$

1.7 Conclusion

This simple model, when it is compared with experiments, is in good agreement with measurements (for the modeling of the refractive index, the reflectance and absorption coefficients...). The agreement can be very good if :

- ω_0 is a frequency resonance that is determined experimentally
- the susceptibility is multiplied by an adjustable dimensionless parameter called ”oscillator strength” and if the expressions related to the different resonance frequency of the atom are summed. We obtain a phenomenological expression of $\chi(\omega)$:

$$\tilde{\chi}(\omega) = \frac{Nq^2}{\varepsilon_0 m} \sum_i \frac{f_i}{\omega_i^2 - \omega^2 - 2i\gamma\omega}$$

2 Einstein coefficients

The Einstein model of light-matter interaction is a phenomenological model that describes the radiation at the thermal equilibrium. Based on thermodynamical arguments, it predicts the stimulated emission of light which enables the amplification of a light field in matter and, hence, the laser effect. Einstein coefficients are a simple limiting case of the semiclassical model of light-matter interaction.

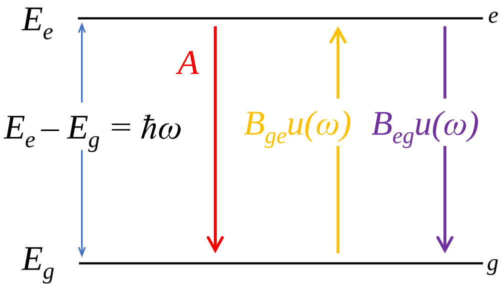


Figure 4: Two level system.

2.1 Rate equations

We suppose that the field is contained in a box. We will neglect any coherence or phase information of the radiation and assume it presents a broad thermal spectrum. The spectral density is denoted $u(\omega)$. $u(\omega)\,\mathrm{d}\omega$ is the energy per unit-volume between ω and $\mathrm{d}\omega$. The energy density is assumed to be uniform across the volume of the box. The total electromagnetic energy per unit-volume is:

$$u = \int_0^{+\infty} u(\omega)\,\mathrm{d}\omega$$

The density of photons in the frequency band between ω and $d\omega$ is $\dfrac{u(\omega)}{\hbar\omega}$. The light-field interacts with atoms with two discrete levels $|e\rangle$ and $|g\rangle$ with energies E_e and E_g, respectively. Because of the coupling to the electromagnetic field, an atom can absorb one photon and goes from the ground state $|g\rangle$ to the excited state $|e\rangle$, or emit one photon to relax from the excited state $|e\rangle$ to the ground state $|g\rangle$. The model is a classical set of rate equation with an *adhoc* quantization of the radiation. Three different processes are are involved:

Spontaneous emission

The atom decays spontaneously from the excited state $|e\rangle$ to the ground state $|g\rangle$ by emitting a photon. This emission does not require the presence of the external applied field to occur and, consequently, does not depend on $u(\omega_0)$.

$$\left.\frac{\mathrm{d}N_e}{\mathrm{d}t}\right|_{spon} = -AN_e$$

A is a probability per unit time.

Absorption

The atom absorbs radiation at frequency ω_0 and makes a transition from $|g\rangle$ to $|e\rangle$:

$$\left.\frac{\mathrm{d}N_e}{\mathrm{d}t}\right|_{abs} = B_{ge}u(\omega_0)\,N_g$$

The absorption probability is proportionnal to the spectral density at the atomic frequency ω_0. B_{ge} is in $\mathrm{J}^{-1}.\mathrm{m}^3.\mathrm{s}^{-2}$.

Stimulated emission

This process was introduced by Einstein to take into account the thermal equilibrium of the atom with the radiation field. An incoming photon induces the desexcitation from $|e\rangle$ to $|g\rangle$ and therefore, the emission of another photon with frequency ω_0.

$$\left.\frac{\mathrm{d}N_e}{\mathrm{d}t}\right|_{stim} = -B_{eg}u\left(\omega_0\right)N_e$$

As for absorption, the probability of stimulated emission is proportionnal to the spectral density at the atomic frequency ω_0.

Taking into account the three different processes, the rate equations writes:

$$\begin{cases}\dfrac{\mathrm{d}N_e}{\mathrm{d}t} = -AN_e - B_{eg}u\left(\omega_0\right)N_e + B_{ge}u\left(\omega_0\right)N_g \\ N_e + N_g = 1\end{cases}$$

2.2 Relations between coefficients

In the stationnary régime $\frac{\mathrm{d}N}{\mathrm{d}t} = 0$.

$$0 = -AN_e - B_{eg}u\left(\omega_0\right)N_e + B_{ge}u\left(\omega_0\right)N_g$$

and:

$$\frac{N_e}{N_g} = \frac{B_{ge}u\left(\omega_0\right)}{A + B_{eg}u\left(\omega_0\right)}$$

The populations of the two levels are in thermal equilibrium and must obey the Boltzmann law:

$$\frac{N_e}{N_g} = \exp\left\{\left(-\frac{E_e - E_g}{k_BT}\right)\right\} = \exp\left\{\left(-\frac{\hbar\omega_0}{k_BT}\right)\right\}$$

where k_B is the Boltzmann constant. Concerning the spectral density, it is given by the Planck law:

$$u\left(\nu_0\right) = \frac{8\pi h\nu_0^3}{c^3}\frac{1}{\exp\{(h\nu_0/k_BT)\} - 1}\ (\mathrm{J.m^{-3}})$$

$$u\left(\omega_0\right) = \frac{1}{2\pi}\frac{8\pi h}{c^3}\left(\frac{\omega_0}{2\pi}\right)^3\frac{1}{\exp\{(\hbar\omega_0/k_BT)\} - 1} = \frac{\hbar\omega_0^3}{\pi^2c^3}\frac{1}{\exp\{(\hbar\omega_0/k_BT)\} - 1}$$

At high temperatures $k_BT \gg \hbar\omega_0$ and $e^{\hbar\omega_0/k_BT} \simeq 1$: The population ratio given by the Boltzmann law becomes:

$$\frac{N_e}{N_g} = \exp\left\{\left(-\frac{\hbar\omega_0}{k_BT}\right)\right\} \simeq 1$$

and:

$$\frac{1}{e^{h\nu_0/k_BT}-1}$$

tends to very large values because the denominator is close to zero. The consequence is $A \ll B_{eg}u\left(\omega_0\right)$ and $A \ll B_{ge}u\left(\omega_0\right)$. We can write:

$$\frac{N_e}{N_g} \simeq \frac{B_{ge}u\left(\omega_0\right)}{B_{eg}u\left(\omega_0\right)} \simeq 1$$

We conclude that

$$\boxed{B_{ge} = B_{eg} = B}$$

Going back to the general case:

$$\frac{N_g}{N_e} = \frac{A + B\ u\left(\omega_0\right)}{B\ u\left(\omega_0\right)} = \exp\left\{\left(\frac{\hbar\omega_0}{k_BT}\right)\right\}$$

$$A = B\ u\left(\omega_0\right)\left[\exp\left\{\left(\frac{\hbar\omega_0}{k_BT}\right)\right\} - 1\right]$$

$$u\left(\omega_0\right) = \frac{A}{B}\frac{1}{\exp\left\{\left(\frac{\hbar\omega_0}{k_BT}\right)\right\} - 1}$$

by equaling this expression with the general expression of $u\left(\omega_0\right)$ given by the Planck's law, we find:

$$u\left(\omega_0\right) = \frac{\hbar\omega_0^3}{\pi^2c^3}\frac{1}{\exp\{(\hbar\omega_0/k_BT)\} - 1} = \frac{A}{B}\frac{1}{\exp\{(\hbar\omega_0/k_BT)\} - 1}$$

We deduce that:

$$\boxed{\frac{A}{B} = \frac{\hbar\omega_0^3}{\pi^2c^3}}$$

2.3 Time evolution of populations

Because the system is closed we have $N_e + N_g = N$ and:

$$\frac{\mathrm{d}N_e}{\mathrm{d}t} = -AN_e - Bu\left(\omega_0\right)N_e + Bu\left(\omega_0\right)\left(N - N_e\right)$$

$$\frac{\mathrm{d}N_e}{\mathrm{d}t} + \left(A + 2Bu\left(\omega_0\right)\right)N_e = NBu\left(\omega_0\right)$$

It can be integrated by multiplying by $e^{(A+2Bu(\omega_0))t}$

$$\frac{\mathrm{d}N_e}{\mathrm{d}t}e^{(A+2Bu(\omega_0))t} + (A + 2Bu\left(\omega_0\right)) N_e e^{(A+2Bu(\omega_0))t} = NBu\left(\omega_0\right) e^{(A+2Bu(\omega_0))t}$$

$$N_e\ e^{(A+2Bu(\omega_0))t} = NBu\left(\omega_0\right) \frac{e^{(A+2Bu(\omega_0))t}}{A+2Bu\left(\omega_0\right)} + \mathcal{C}$$

$$N_e = N\frac{Bu\left(\omega_0\right)}{A+2Bu\left(\omega_0\right)} + \mathcal{C}e^{-(A+2Bu(\omega_0))t}$$

We make the assumption that, at $t = 0$, the system is in the ground state:

$$0 = N\frac{Bu\left(\omega_0\right)}{A+2Bu\left(\omega_0\right)} + \mathcal{C}$$

$$\mathcal{C} = -N\frac{Bu\left(\omega_0\right)}{A+2Bu\left(\omega_0\right)}$$

and:

$$\boxed{N_e(t) = N\frac{Bu\left(\omega_0\right)}{A+2Bu\left(\omega_0\right)}\left[1 - e^{-(A+2Bu(\omega_0))t}\right]}$$

When $t \to +\infty$, the system reaches a steady state and:

$$N_e(t) \to N\frac{Bu\left(\omega_0\right)}{A+2Bu\left(\omega_0\right)} = N\frac{u\left(\omega_0\right)}{A/B+2u\left(\omega_0\right)}$$

where we set $u_S = A/B$, the steady state populations become:

$$N_e(\infty) = N\frac{u\left(\omega_0\right)}{u_S+2u\left(\omega_0\right)}$$

and:

$$N_g(\infty) = N - N_e(\infty) = N\frac{u_S+u\left(\omega_0\right)}{u_S+2u\left(\omega_0\right)}$$

- For weak field intensity, $A \gg 2Bu\left(\omega_0\right)$ and:

$$\boxed{N_e(t) \simeq N\frac{B}{A}u\left(\omega_0\right)}$$

  The population of the excited state is proportionnal to the excitation. The system is in the linear regime.

- For intense fields, $A \ll 2Bu\left(\omega_0\right)$ and:

$$\boxed{N_e(t) \simeq \frac{N}{2}}$$

  The population of the excited state tends to the limit value $\frac{N}{2}$, there is a saturation of the excited state population at high intensities. The system is the non-linear regime.

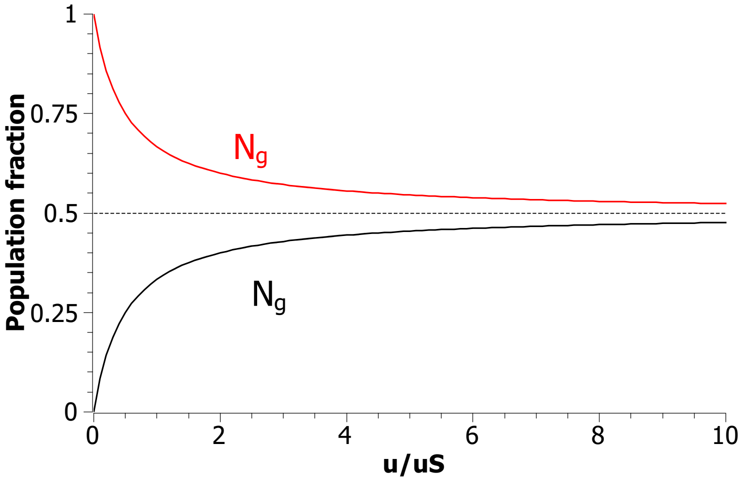


Figure 5: Population of the excited state at long delays as a function of $\dfrac{Bu(\omega_0)}{A}$.

Chapter 2: Single atom in a classical electromagnetic field

October 11, 2022

Contents

1 Introduction

In this chapter, we develop how to model the interaction of a quantized atom with a classic E.M-field. In a first part, we show how to derive the Hamiltonian from the classical one and we discuss the choice of the gauge. Then we calculate the probability by a pertubative treatment. We also present how to take phenomenology into account the finite lifetime of an excited state. Finally, we treat the specific case of the interaction of a two level system that gives rise to Rabi oscillations.

2 Hamiltonian

2.1 Classical Hamiltonian and the Coulomb Gauge

We start from the classical Hamiltonian of a charged particle in an electromagnetic field:

$$H(\mathbf{r},t) = \frac{1}{2m}[\mathbf{p} - q\mathbf{A}(\mathbf{r},t)]^2 + qU(\mathbf{r},t)$$

where $\mathbf{A}$ is the vector potential and U the Coulomb potential. There exists an infinity of potentials $\{\mathbf{A}(\mathbf{r},t), U(\mathbf{r},t)\}$ corresponding to the same values of the E.M-field. We remind that:

$$\begin{cases} \mathbf{E}(\mathbf{r},t) = -\dfrac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} - \boldsymbol{\nabla} U(\mathbf{r},t) \\ \mathbf{B}(\mathbf{r},t) = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r},t) \end{cases}$$

These fields are invariant under the gauge transformation:

$$\begin{cases} U'(\mathbf{r},t) = U(\mathbf{r},t) - \dfrac{\partial}{\partial t}\Phi(\mathbf{r},t) \\ \mathbf{A}'(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \boldsymbol{\nabla}\Phi(\mathbf{r},t) \end{cases}$$

were $\Phi(\mathbf{r},t)$ is an arbitrary scalar function. The Coulomb gauge corresponds to the condition:

$$\boldsymbol{\nabla} \cdot \mathbf{A}(\mathbf{r},t) = 0$$

or, in Fourier space:

$$\mathbf{k} \cdot \boldsymbol{\mathcal{A}}(\mathbf{k},t) = 0$$

The vector potential is purely transverse:

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}_{\perp}(\mathbf{r},t)$$

Consequence for the expression of $\mathbf{E}(\mathbf{r},t)$:

$$\mathbf{E}(\mathbf{r},t) = -\underbrace{\frac{\partial \mathbf{A}_\perp(\mathbf{r},t)}{\partial t}}_{transverse} - \underbrace{\boldsymbol{\nabla} U(\mathbf{r},t)}_{??}$$

The condition for $\mathbf{E}(\mathbf{r},t)$ to be a tranverse field is:

$$\boldsymbol{\nabla} \cdot \mathbf{E}(\mathbf{r},t) = 0$$

Because the curl of a gradient is always zero:

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} U(\mathbf{r},t)) = \mathbf{0}$$

$\boldsymbol{\nabla} U(\mathbf{r},t)$ is necessary longitudinal and:

$$\begin{cases} \mathbf{E}_\perp(\mathbf{r},t) = -\dfrac{\partial \mathbf{A}_\perp(\mathbf{r},t)}{\partial t} \\ \mathbf{E}_\parallel(\mathbf{r},t) = -\boldsymbol{\nabla} U(\mathbf{r},t) \end{cases}$$

The longitudinal component $\mathbf{E}_\parallel(\mathbf{r},t)$ is given by:

$$\mathbf{E}_\parallel(\mathbf{r},t) = \frac{1}{4\pi\varepsilon_0} \int \mathrm{d}^3 r' \, \rho(\mathbf{r}',t) \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}$$

Where $\rho(\mathbf{r}',t)$ is the charge distribution. The charges responsible for the existence of $U(\mathbf{r},t)$), and consequently $\mathbf{E}(\mathbf{r},t)$) are sufficiently far away from the studied system to satisfy:

$$\boldsymbol{\nabla} U(\mathbf{r},t) = 0$$

Since a constant potential has no physical effect, we set $U(\mathbf{r},t) = 0$. $\mathbf{E}_\perp$ can be written in the form of a plane-wave:

$$\mathbf{E}_\perp = E_0 \cos\left(\omega t - k_z \cdot z\right) \boldsymbol{e_x}$$

The magnetic field is calculated using the Maxwell-Faraday equation:

$$\frac{\partial}{\partial t}\mathbf{B} = -\boldsymbol{\nabla} \times \mathbf{E} = k_z \cdot E_0 \cos\left(\omega t - k_z \cdot z\right) \mathbf{e_y}$$

$$\mathbf{B} = -\boldsymbol{\nabla} \times \mathbf{E} = \frac{k_z}{\omega} \cdot E_0 \cos\left(\omega t - k_z \cdot z\right) \mathbf{e}_y$$

and finally, taking into account that:

$$\mathbf{E}(\mathbf{r},t) = -\frac{\partial \mathbf{A}_\perp(\mathbf{r},t)}{\partial t}$$

$$\mathbf{A} = -\frac{E_0}{\omega} \sin\left(\omega t - k_z \cdot z\right) \mathbf{e}_x$$

The Hamiltonian finally is finally written:

$$H(\mathbf{r},t) = \frac{1}{2m}[\mathbf{p} - q\mathbf{A}(\mathbf{r},t)]^2$$

2.2 Quantum Hamiltonian

The Hamiltonian of a single electron bound to an atom in the absence of external fields is given by:

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}}{2m} + V(\hat{\mathbf{r}})$$

where $V(r)$ is the usual Coulomb interaction binding the electron to the nucleus, $r = |\mathbf{r}|$ and $\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$. We assume that energy eigenstate $|n\rangle$ of $\hat{H}_0$, satisfying the time-independent Schrödinger equation:

$$\hat{H}_0 \, |n\rangle = E_n \, |n\rangle$$

are known. In the presence of external field, the Hamiltonian is modified to

$$\hat{H}(\hat{\mathbf{r}}, t) = \frac{1}{2m}[\hat{\mathbf{p}} - q\hat{\mathbf{A}}(\hat{\mathbf{r}}, t)]^2 + V(r)$$

we develop[1]:

$$\hat{H}(\hat{\mathbf{r}}, t) = \frac{\hat{\mathbf{p}}}{2m}^2 + V(r) - \frac{q}{2m}\left(\hat{\mathbf{p}} \cdot \mathbf{A}_\perp(\hat{\mathbf{r}}, t) + \mathbf{A}_\perp(\hat{\mathbf{r}}, t) \cdot \hat{\mathbf{p}}\right) + q^2 \frac{\mathbf{A}_\perp(\hat{\mathbf{r}}, t)}{2m}^2$$

$$\hat{H}(\hat{\mathbf{r}}, t) = \underbrace{\frac{\hat{\mathbf{p}}}{2m}^2 + V(r)}_{\hat{H}_0} - \frac{q}{m}\hat{\mathbf{p}} \cdot \mathbf{A}_\perp(\hat{\mathbf{r}}, t) + q^2 \frac{\mathbf{A}_\perp(\hat{\mathbf{r}}, t)}{2m}^2$$

$\hat{H}_0$ is the usual stationnary Hamiltonian that describes the motion of a charged particle in a static Coulomb potential. The interaction term is

$$\boxed{-\frac{q}{m}\hat{\mathbf{p}} \cdot \mathbf{A}_\perp(\hat{\mathbf{r}}, t) + q^2 \frac{\mathbf{A}_\perp(\hat{\mathbf{r}}, t)}{2m}^2}$$

In the following we will focus on linear optical properties and will make the assumption that the interaction term is small when compared to $\hat{H}_0$. Then, the second term of the interaction Hamiltonian being quadratic with $\mathbf{A}_\perp(\hat{\mathbf{r}}, t)$ will be neglected with regards to the linear term.

In the Coulomb gauge, the applied field is completely characterized by its vector potential $\mathbf{A}_\perp(\hat{\mathbf{r}}, t)$*.*

---

[1] Because $\mathbf{A}_\perp$ is not an oprerator there is no commutation issues.

Long wavelength approximation

In atom-light interactions, the light wavelength λ is usually very large when compared to atomic dimensions. For the hydrogen atom, typical emission and absorption lines have wavelengths in the range of several hundredth of nanometers while the atomic size is $a_0 \simeq 0.053$ nm (Bohr radius of hydrogen atome). The amplitude of the external field is practically constant over the spatial extent of the atom and:

$$\mathbf{A}_\perp(\hat{\mathbf{r}}, t) \simeq \mathbf{A}_\perp(\mathbf{r}_0, t)$$

where $\mathbf{r}_0$ is the position of the nucleus. This is what we call *Long wavelength approximation.*

2.3 Electric dipole Hamiltonian : Göppert-Mayer Gauge

Maria Göppert-Mayer (1906-1972) was a german born american physicist. She was the second woman to get the Nobel prize in physics for proposing the nuclear shell model of the atomic nucleus.

The choice of the present gauge enable to write the interaction Hamiltonian in a form that is similar to the expression of the energy of a classical dipole.

$$W = -\mathbf{d} \cdot \mathbf{E}$$

Starting from the Hamiltonian in the Coulomb Gauge [2]:

$$\hat{H}(\hat{\mathbf{r}}, t) = \frac{1}{2m}[\hat{\mathbf{p}} - q \cdot \mathbf{A}_\perp(\hat{\mathbf{r}}, t)]^2 + V(r)$$

We use the usual gauge transformation:

$$\begin{cases} U'(\hat{\mathbf{r}}, t) = 0 - \dfrac{\partial}{\partial t}\Phi(\hat{\mathbf{r}}, t) \\ \mathbf{A}'_\perp(\hat{\mathbf{r}}, t) = \mathbf{A}_\perp(\hat{\mathbf{r}}, t) + \boldsymbol{\nabla}\Phi(\hat{\mathbf{r}}, t) \end{cases}$$

The Göppert-Mayer gauge consists in choosing:

$$\phi\,(\hat{\mathbf{r}}, t) = -\,(\hat{\mathbf{r}} - \mathbf{r}_0) \cdot \mathbf{A}_\perp(\mathbf{r}_0, t)$$

$$\begin{cases} U'(\hat{\mathbf{r}}, t) = (\hat{\mathbf{r}} - \mathbf{r}_0) \cdot \dfrac{\partial}{\partial t}\mathbf{A}_\perp(\mathbf{r}_0, t) \\ \mathbf{A}'(\hat{\mathbf{r}}, t) = \mathbf{A}_\perp(\hat{\mathbf{r}}, t) - \mathbf{A}_\perp(\mathbf{r}_0, t) \end{cases}$$

---

[2] $\mathbf{A}(\hat{\mathbf{r}}, t) = \mathbf{A}_\perp(\hat{\mathbf{r}}, t)$ and $U(\hat{\mathbf{r}}, t) = 0$

Moreover, we have seen that, in the Coulomb gauge, the electric field associated with the radiation is:

$$\mathbf{E}\left(\hat{\mathbf{r}},t\right)=-\frac{\partial}{\partial t}\mathbf{A}_{\perp}\left(\hat{\mathbf{r}},t\right)$$

the electrostatic energy term becomes:

$$qU'(\hat{\mathbf{r}},t)=-q\left(\hat{\mathbf{r}}-\mathbf{r}_0\right)\cdot\mathbf{E}\left(\hat{\mathbf{r}},t\right)$$

introducing the electric dipole operator:

$$\hat{\mathbf{d}}=q\left(\hat{\mathbf{r}}-\mathbf{r}_0\right)$$

we find:

$$qU'(\hat{\mathbf{r}},t)=-\hat{\mathbf{d}}\cdot\mathbf{E}\left(\hat{\mathbf{r}},t\right)$$

$$\hat{H}(\hat{\mathbf{r}},t)=\frac{1}{2m}[\hat{\mathbf{p}}-q\cdot(\mathbf{A}_{\perp}(\hat{\mathbf{r}},t)-\mathbf{A}_{\perp}(\mathbf{r}_0,t))]^2+V(r)-\hat{\mathbf{d}}\cdot\mathbf{E}\left(\hat{\mathbf{r}},t\right)$$

Long wavelength approximation
Here again we replace the potentials of the applied field by their values evaluated at the atomic nucleus:

$$\mathbf{A}'(\mathbf{r}_0,t)=\mathbf{A}_{\perp}(\mathbf{r}_0,t)-\mathbf{A}_{\perp}(\mathbf{r}_0,t)=0$$

Finally, the Hamiltonian takes the form:

$$\boxed{\hat{H}(\hat{\mathbf{r}},t)=-\frac{\hat{\mathbf{p}}}{2m}^2+V(r)-\hat{\mathbf{d}}\cdot\mathbf{E}\left(\hat{\mathbf{r}},t\right)}$$

The interaction Hamiltonian is the electric dipole operator. It has the same form as the interaction energy of a classical dipole $\mathbf{d}$ located at $\mathbf{r}_0$ in an electric field $\mathbf{E}$.

2.4 Equivalence between $\mathbf{A}\cdot\hat{\mathbf{p}}$ and $\hat{\mathbf{d}}\cdot\boldsymbol{\mathcal{E}}$ Hamiltonians

We want to establish a relation between the matrix elements of $\mathbf{A}\cdot\hat{\mathbf{p}}$ and $\hat{\mathbf{d}}\cdot\boldsymbol{\mathcal{E}}$ Hamiltonians. Let us suppose that $\boldsymbol{\mathcal{E}}$ and $\mathbf{A}$ are polarized alond x. Then, $\mathbf{A}\cdot\hat{\mathbf{p}}$ depends on p_x while $\hat{\mathbf{d}}\cdot\boldsymbol{\mathcal{E}}$ depends on $\hat{x}$ through $\hat{\mathbf{d}}$. We are going to write an equation between the matrix elements of $\hat{x}$ and the matrix elements of $\hat{p}_x$. The evaluation of the commutator:

$$\left[\hat{x},\hat{H}_0\right]=\frac{1}{2m}\left[\hat{x},\hat{p}_x^2\right]$$

will help us in this way. Either if we can find the result by writing

$$\begin{aligned}\left[\hat{x},\hat{p}_x^2\right] &= \left[(\hat{x}\ \hat{p}_x)\ \hat{p}_x - (\hat{p}_x\ \hat{x})\ \hat{p}_x + \hat{p}_x\ (\hat{x}\ \hat{p}_x) - \hat{p}_x\ (\hat{p}_x\ \hat{x})\right] \\ &= \left[\hat{x},\hat{p}_x\right]\ \hat{p}_x - \hat{p}_x\ \left[\hat{x},\hat{p}_x\right]\end{aligned}$$

It is quicker to use:

$$[\hat{x}, F(p_x)] = i\hbar F'(p_x)$$

with $F(\hat{p}_x) = \hat{p}_x^2$. We get directly:

$$\boxed{\left[\hat{x},\hat{H}_0\right] = \frac{i\hbar}{m}\hat{p}_x}$$

We use this relation to calculate the matrix elements:

$$\langle f|[\hat{x},\hat{H}_0]|i\rangle = \frac{i\hbar}{m}\langle f|\hat{p}_x|i\rangle$$

First, we calculate the left-hand side:

$$\begin{aligned}\langle f|[\hat{x},\hat{H}_0]|i\rangle &= \langle f|\hat{x}\ \hat{H}_0|i\rangle - \langle f|\hat{H}_0\ \hat{x}|i\rangle \\ &= E_i\langle f|\hat{x}|i\rangle - E_f\langle f|\hat{x}|i\rangle\end{aligned}$$

$$\langle f|[\hat{x},\hat{H}_0]|i\rangle = (E_i - E_f)\langle f|\hat{x}|i\rangle = \frac{i\hbar}{m}\langle f|\hat{p}_x|i\rangle$$

Finally, we get the expected relation:

$$\boxed{\langle f|\hat{p}_x|i\rangle = i\frac{m}{\hbar}(E_f - E_i)\langle f|\hat{x}|i\rangle}$$

Now, we can compute:

$$-\frac{q}{m}\langle f|\hat{p}_x\ A_x|i\rangle$$

we remind that:

$$A_x(t,0) = -\frac{\mathcal{E}_0}{\omega}\sin(\omega t)$$

So:

$$\begin{aligned}-\frac{q}{m}\langle f|\hat{p}_x\ A_x|i\rangle &= \frac{q}{m}\frac{\mathcal{E}_0}{\omega}\langle f|\hat{p}_x|i\rangle\sin(\omega t) \\ &= \frac{q}{m}\frac{E(t,z)}{\omega}i\frac{m}{\hbar}(E_f - E_i)\langle f|\hat{x}|i\rangle\sin(\omega t) \\ &= \frac{i}{\omega}\frac{E_f - E_i}{\hbar}\langle f|q\hat{x}\mathcal{E}_0|i\rangle\sin(\omega t) \\ &= i\frac{\omega_{fi}}{\omega}\langle f|\hat{\mathbf{d}}\cdot\mathcal{E}_0|i\rangle\sin(\omega t)\end{aligned}$$

Finally:

$$\boxed{\left| -\frac{q}{m} \frac{\langle f|\hat{p}_x \; A_x|i\rangle}{\langle f|\hat{\mathbf{d}} \cdot E(t,z)|i\rangle} \right| = \frac{\omega_{fi}}{\omega}}$$

3 Probability of transition under the influence of a sinusoidal E.M-field

3.1 Perturbative approach

Short reminder: Consider a time independent Hamiltonian operator $\hat{H}_0$ which eigenenergies E_n and eigenstates $|n\rangle$ are known. The most general state of the system is written:

$$|\psi(t)\rangle = \sum_k C_k(t)\,|k\rangle$$

If the system is exposed to a time-dependent external field described by an operator $\hat{W}(t)$, the Hamiltonian becomes:

$$\hat{H}(t) = \hat{H}_0 + \hat{W}(t)$$

If the matrix element $\hat{W}_{fi}(t)$ of $\hat{W}(t)$ between a initial state $|i\rangle$ and a final state $|f\rangle$ is different from zero, a transition occurs. The time dependent perturbation treatment consists in expanding the time-dependent eigenstate on the basis of the stationnary states:

$$|\psi(t)\rangle = \sum_n C_n(t)\,|n\rangle$$

The amplitude of transition between an initial state $|i\rangle$ and a final state $|f\rangle$, under the influence of an operator $\hat{W}(t)$ is given, at the first order, by:

$$S_{if} = \frac{1}{i\hbar}\int_0^t \mathrm{d}t'\,\langle f|\hat{W}(t')|i\rangle\, e^{i[(E_f-E_i)/\hbar]t'}$$

with $E_f - E_i = \hbar\omega_{fi}$. The probability is the square modulus of S_{if}

$$\mathcal{P}_{if} = |S_{if}|^2$$

We are interested in the optical transitions caused by the application of a sinusoidal E.M-field:

$$\boldsymbol{\mathcal{E}}(\mathbf{r}_0,t) = \boldsymbol{\mathcal{E}}(\mathbf{r}_0)\cos(\omega t)$$

The interaction Hamiltonian is the electric-dipole operator in the Göppert-Meyer Gauge with the long-wavelength approximation. The full Hamiltonian (atom+field) is:

$$\hat{H}(\hat{\mathbf{r}},t) = -\frac{\hat{\mathbf{p}}}{2m}^{2} + V(\hat{r}) - \hat{\mathbf{d}} \cdot \boldsymbol{\mathcal{E}}\left(\mathbf{r}_0, t\right)$$

The amplitude of transition between an initial state $|i\rangle$ with energy E_i and a final state $|f\rangle$ with energy E_f is:

$$S_{fi} = -\frac{1}{i\hbar}\int_0^t \mathrm{d}t' \, \langle f|\hat{\mathbf{d}} \cdot \boldsymbol{\mathcal{E}}\left(\mathbf{r}_0, t'\right)|i\rangle \, e^{i(E_f - E_i)t'/\hbar}$$

$$-\langle f|\hat{\mathbf{d}} \cdot \boldsymbol{\mathcal{E}}(\mathbf{r}_0, t)|i\rangle = -\langle f|\hat{d}\cos\theta|i\rangle \cdot \mathcal{E}(\mathbf{r}_0)\cos(\omega t) = -d_{fi} \cdot \mathcal{E}(\mathbf{r}_0)\cos(\omega t)$$

$$S_{fi} = -\frac{d_{fi}}{i\hbar} \cdot \frac{\mathcal{E}(\mathbf{r}_0)}{2}\int_0^t \mathrm{d}t'[e^{i\omega t'} + e^{-i\omega t'}] \cdot e^{i\omega_{fi}t'} = -\frac{d_{fi}}{i\hbar} \cdot \frac{\mathcal{E}(\mathbf{r}_0)}{2}\int_0^t \mathrm{d}t'[e^{i(\omega_{fi}+\omega)t'} + e^{-i(\omega-\omega_{fi})t'}]$$

The integration of this expression gives:

$$S_{fi} = -\frac{d_{fi}}{i\hbar} \cdot \frac{\mathcal{E}(\mathbf{r}_0)}{2}\left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{i(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi}-\omega)}\right]$$

$$S_{fi} = \frac{d_{fi}}{\hbar} \cdot \frac{\mathcal{E}(\mathbf{r}_0)}{2}\left[\frac{1 - e^{i(\omega_{fi}+\omega)t}}{\omega_{fi}+\omega} + \frac{1 - e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}\right]$$

and the probability is:

$$\boxed{\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4}\left|\frac{1 - e^{i(\omega_{fi}+\omega)t}}{\omega_{fi}+\omega} + \frac{1 - e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}\right|^2}$$

3.2 Resonance

The probability is proportionnal to the field intensity and takes significant values when $\omega = \pm\omega_{fi}$. A resonance process occurs when the angular frequency of the perturbation is equal to the Bohr frequency associated with the transition between $|i\rangle$ and $|f\rangle$. We choose the convention of positive frequencies $\omega > 0$.

- $\omega - \omega_{fi} = 0$ means that $\omega_{fi} > 0$ and $E_f - E_i > 0$. The system absorbs the radiation at the frequency ω to go in a higher energy state.

- $\omega + \omega_{fi} = 0$ means that $\omega_{fi} < 0$ and $E_f - E_i < 0$. The system emits a the radiation at the frequency ω to go in a lower energy state.

Absorption and stimulated emission are described by the same probability. For a given time t, the probability $\mathcal{P}_{if}$ depends only on ω.

$$\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left| e^{i(\omega_{fi}+\omega)\frac{t}{2}} \frac{e^{-i(\omega_{fi}+\omega)\frac{t}{2}} - e^{i(\omega_{fi}+\omega)\frac{t}{2}}}{\omega_{fi}+\omega} + e^{i(\omega_{fi}-\omega)\frac{t}{2}} \frac{e^{-i(\omega_{fi}-\omega)\frac{t}{2}} - e^{i(\omega_{fi}-\omega)\frac{t}{2}}}{\omega_{fi}-\omega} \right|^2$$

$$\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left| -ie^{i(\omega_{fi}+\omega)\frac{t}{2}} \frac{\sin{(\omega_{fi}+\omega)\frac{t}{2}}}{(\omega_{fi}+\omega)/2} - ie^{i(\omega_{fi}+\omega)\frac{t}{2}} \frac{\sin{(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)/2} \right|^2$$

$$\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left| A^+ + A^- \right|^2$$

The probability is the sum of two terms: A^+ and A^-. The denominator of A^+ cancels for $\omega = -\omega_{fi}$ while the denominator of A^- cancels for $\omega = \omega_{fi}$. In an emission process, $E_f < E_i$ and $\omega_{fi} < 0$ thus A^- is negligible and is called the antiresonant term when A^+ is the resonant one. On the contrary, in an absorption process $E_f > E_i$ and $\omega_{fi} > 0$ thus A^+ is negligible and is the antiresonant term. In the following, we will neglect the antiresonant terms. This is the so-called **resonant approximation**.

Let's consider absorption, the probability of transition is approximated by:

$$\mathcal{P}_{if} \simeq \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left| -ie^{i(\omega_{fi}+\omega)\frac{t}{2}} \frac{\sin{(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)/2} \right|^2$$

$$\mathcal{P}_{if} \simeq \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left[\frac{\sin{(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)/2} \right]^2$$

The sinc function takes significant values for $-\pi < \delta\omega\frac{t}{2} < \pi$:

$$\omega = \omega_{fi} \pm 2\pi/t$$

The resonance width can be defined as the distance between the first two zeros of $\mathcal{P}_{if}$ about $\omega = \omega_{fi}$. In this interval, the probability takes its largest values:

$$\delta\omega \simeq \frac{4\pi}{t}$$

The larger the time t, the smaller the resonance width. $\delta\omega$ is not related to the intrinsic lineshape of the atomic resonance. It is an uncertainty on the frequency of the applied field due to its finite duration.

We can write the probability in the following way:

$$\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot t^2 \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left[\frac{\sin{(\omega_{fi} - \omega)\frac{t}{2}}}{(\omega_{fi} - \omega)t/2} \right]^2$$

to deal with the well-known sinc function. Then, at the exact resonance, when $\omega = \omega_{fi}$:

$$\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot t^2 \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} = (\frac{\Omega_1}{2} \cdot t)^2$$

where Ω_1 is the **Rabi frequency** of the transition.

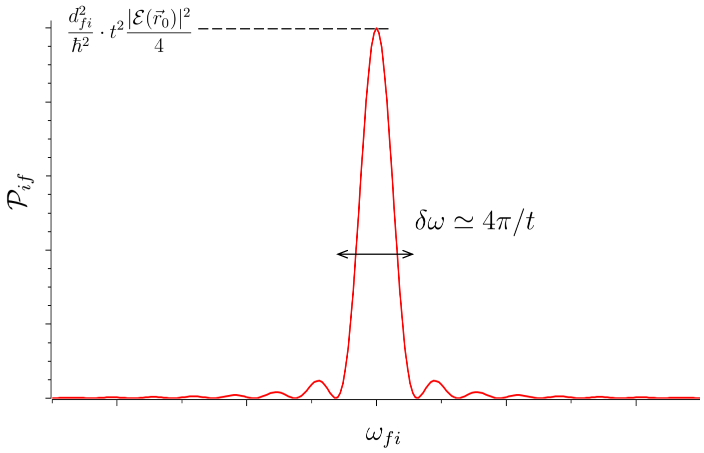


Figure 1: First order probability of transition $\mathcal{P}_{if}$ associated to a sinusoidal perturbation with angular frequency ω.

3.3 Validity of approximations

On one hand, The resonant approximation is valid if:

$$2|\omega_{fi}| \gg \delta\omega$$

with $\delta\omega \simeq 4\pi/t$ *i.e.*:

$$t \gg \frac{2\pi}{|\omega_{fi}|} \simeq \frac{2\pi}{\omega}$$

On the other hand, the perturbation theory is all right if:

$$\mathcal{P}_{if} \ll 1$$

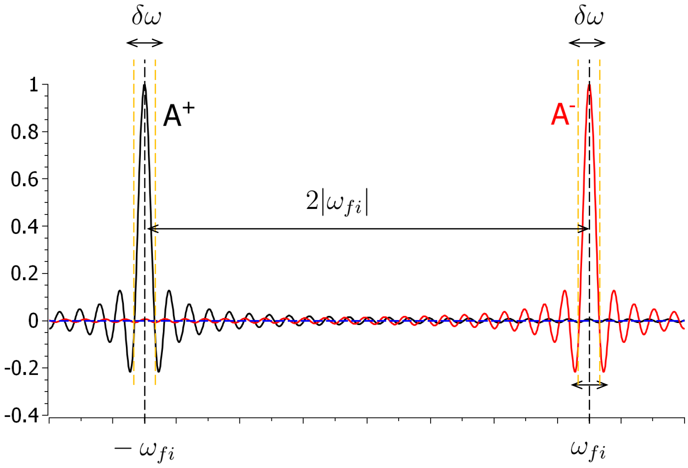


Figure 2: Comparison of $\delta\omega$ and ω_{fi}. The resonant approximation is valid if $\delta\omega \ll \omega_{fi}$.

$$(\frac{\Omega_1}{2} \cdot t)^2 \ll 1$$

$$t \ll \frac{2}{\Omega_1}$$

In conclusion:

$$\boxed{\frac{2\pi}{\omega} \ll t \ll \frac{2}{\Omega_1}}$$

4 Transition rate

In this part, we connect the perturbative approach with the Einstein model, that we have seen in a previous lecture, and that describe the population time-evolution of a two level atom. Its ground and excited levels are noted $|a\rangle$ and $|b\rangle$ respectively. Their populations, N_a and N_b, are in equilibrium with a thermal field and obey the system:

$$\begin{cases} \dfrac{\mathrm{d}N_b}{\mathrm{d}t} = -AN_b - B_{ba}u\left(\omega_0\right)N_b + B_{ab}u\left(\omega_0\right)N_a \\ N_b + N_a = N \end{cases}$$

The density of E.M. energy of the thermal field is:

$$u(\omega) = \frac{1}{2}\varepsilon_0 |\mathcal{E}(\omega, \mathbf{r}_0)|^2$$

Then the density of probability per frequency unit associated to the transition from an the ground state to the excited state is:

$$\mathrm{d}\mathcal{P}_{ab} = \frac{d_{ba}^2}{\hbar^2} \cdot \frac{u(\omega)}{2\varepsilon_0} \left[\frac{\sin{(\omega_0 - \omega)\frac{t}{2}}}{(\omega_0 - \omega)/2} \right]^2 \mathrm{d}\omega$$

The total probability is obtained by integrating on all possible frequencies:

$$\mathcal{P}_{ab} = \frac{d_{ba}^2}{2\varepsilon_0 \hbar^2} \int_0^{+\infty} u(\omega) \left[\frac{\sin{(\omega_0 - \omega)\frac{t}{2}}}{(\omega_0 - \omega)/2} \right]^2 \mathrm{d}\omega$$

When $t \gg \frac{2\pi}{\omega}$, the function $\left[\frac{\sin{(\omega_0 - \omega)t/2}}{(\omega_0 - \omega)/2}\right]^2$ tends to $2\pi t \delta(\omega - \omega_0)$:

$$\mathcal{P}_{ab} = \frac{d_{ba}^2}{2\varepsilon_0 \hbar^2} \cdot 2\pi \int_0^{+\infty} u(\omega)\delta(\omega_0 - \omega)\mathrm{d}\omega$$

By expliciting the matrix element of the dipole operator:

$$d_{ba}^2 = q^2 |\ \langle b|\hat{r}\cos\theta|a\rangle\ |^2 = q^2 r_{ba}^2 \overset{2}{\cos}\theta$$

We find the probability at time t as a function of θ:

$$\mathcal{P}_{ab} = \frac{\pi q^2 r_{fi}^2}{\varepsilon_0 \hbar^2} \cdot \overset{2}{\cos}\theta \cdot u(\omega_0) \cdot t$$

By averaging $\overset{2}{\cos}\theta$ over all the directions[3]:

$$\mathcal{P}_{ab} = \frac{\pi q^2 r_{ba}^2}{3\varepsilon_0 \hbar^2} \cdot u(\omega_0) \cdot t$$

The transition rate per unit time is:

$$\frac{\mathrm{d}\mathcal{P}_{ab}}{\mathrm{d}t} = \frac{\pi q^2 r_{fi}^2}{3\varepsilon_0 \hbar^2} \cdot u(\omega_0)$$

By comparing to the:

$$\frac{\mathrm{d}N_a}{\mathrm{d}t} = N_a \frac{\mathrm{d}\mathcal{P}_{ab}}{\mathrm{d}t} = \frac{\pi q^2 r_{ba}^2}{3\varepsilon_0 \hbar^2} \cdot u(\omega_0) = B_{ab} \cdot u(\omega_0) \cdot N_a$$

$$\boxed{B_{ab} = \frac{\pi q^2 r_{ba}^2}{3\varepsilon_0 \hbar^2}}$$

---

[3] $< \overset{2}{\cos}\theta >= (4\pi)^{-1} \int_0^{2\pi} \int_0^{\pi} \mathrm{d}\theta \overset{2}{\cos}\theta \sin\theta \mathrm{d}\varphi$

The corresponding expression for the stimulated emission is identical except for an interchange of indices a and b since:

$$|\langle a|\hat{r}|b\rangle|^2 = |\langle b|\hat{r}|a\rangle|^2$$

we get $B_{ab} = B_{ba}$. and:

$$A_{ba} = \frac{\hbar\omega_0^3}{\pi^2 c^3} B_{ab} = \frac{\hbar\omega_0^3}{\pi^2 c^3} \frac{\pi q^2 r_{ab}^2}{3\varepsilon_0 \hbar^2}$$

$$\boxed{A_{ba} = \frac{q^2 r_{ab}^2 \omega_0^3}{3\varepsilon_0 \hbar \pi c^3}}$$

We habe obtained the same result as when we use the quantized-field model.

4.1 Finite lifetime and absorption linewidth

$$\mathcal{P}_{12} \simeq \frac{d_{21}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left[\frac{\sin(\delta\omega t/2)}{\delta\omega/2}\right]^2$$

In the absence of the we suppose however that $N_2 \ll N_1$ and $N_1 \simeq N$.

The probability for finding an atom if level $|2\rangle$ is at time t is :

$$N_2(t) = N \cdot \frac{d_{21}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \int_0^t \left[\frac{\sin(\delta\omega t'/2)}{\delta\omega/2}\right]^2 e^{-\Gamma_{21} t'} \mathrm{d}t'$$

$$N_2(t) = N \cdot \frac{d_{21}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \frac{4}{\delta\omega^2} \frac{1}{2} \int_0^t \left[e^{-\Gamma_{21} t'} - \frac{1}{2} e^{i(\delta\omega + i\Gamma_{21})t'} - \frac{1}{2} e^{-i(\delta\omega + i\Gamma_{21})t'}\right] \mathrm{d}t'$$

$$N_2(t) = N \cdot \frac{d_{21}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{2\delta\omega^2} \left[-\frac{1}{\Gamma_{21}} e^{-\Gamma_{21}\tau} - \frac{e^{i(\delta\omega - i\Gamma_{21})t}}{2i(\delta\omega - i\Gamma_{21})} + \frac{e^{-i(\delta\omega + i\Gamma_{21})t}}{2i(\delta\omega + i\Gamma_{21})}\right]_0^t$$

when $t \gg \Gamma_{21}^{-1}$, $e^{i(\delta\omega - i\Gamma_{21})t} \to 1$ and

$$N_2(t) = N \cdot \frac{d_{21}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{2\delta\omega^2} \left[\frac{1}{\Gamma_{21}} + \frac{1}{2i(\delta\omega - i\Gamma_{21})} - \frac{1}{2i(\delta\omega + i\Gamma_{21})}\right]$$

$$\boxed{N_2(t) = \frac{N}{2\Gamma_{21}} \left[\frac{\Omega_1^2}{(\omega^2 - \omega_0)^2 + \Gamma_{21}^2}\right]}$$

The fraction of atoms promoted in the excited state $|2\rangle$ is proportionnal to the intensity of the E.M. wave (Ω_1 term). The process presents a resonant behaviour around the frequency ω_0 that follows a Lorentzian law with a full width at half-maximum $2\Gamma_{21}$. The finite lifetime of the excited state introduces a broadening of the absorption line.

5 Two-level system in intercation with an E.M-field - Rabi oscillations

We consider a two-level atom described by the Hamiltonian:

$$\hat{H}_0 = \frac{\hbar}{2}\begin{pmatrix} +\omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix}$$

with $\omega_0 = (E_b - E_a)/\hbar$. This atom interacts with a classical perdiodic E.M. field:

$$\hat{W}_{ab}(t) = -\left\langle b\right|\hat{\mathbf{d}} \cdot \boldsymbol{\mathcal{E}}(\vec{r}_0)\left|a\right\rangle \cos\omega t = \hbar\ \Omega_1 \cos\omega t$$

The total time-dependent Hamiltonian is:

$$\hat{H}(t) = \hat{H}_0 + \hat{W}_{ab}(t) = \frac{\hbar}{2}\begin{pmatrix} +\omega_0 & 2\Omega_1 \cos\omega t \\ 2\Omega_1 \cos\omega t & -\omega_0 \end{pmatrix}$$

The eigenstates are expanded on the basis of the stationnary states:

$$\left|\psi(t)\right\rangle = C_a(t)e^{i\omega_0 t/2}\left|a\right\rangle + C_b(t)e^{-i\omega_0 t/2}\left|b\right\rangle$$

The time-evolution is given, as always, by the Schrödinger equation:

$$i\hbar\frac{d\left|\psi(t)\right\rangle}{dt} = \hat{H}(t)\left|\psi(t)\right\rangle$$

$$i\hbar\frac{d}{dt}\begin{pmatrix} C_b(t)e^{-i\omega_0 t/2} \\ C_a(t)e^{i\omega_0 t/2} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} -\omega_0 & \Omega_1(e^{i\omega t} - e^{-i\omega t}) \\ \Omega_1(e^{i\omega t} - e^{-i\omega t}) & \omega_0 \end{pmatrix}\begin{pmatrix} C_b(t)e^{-i\omega_0 t/2} \\ C_a(t)e^{i\omega_0 t/2} \end{pmatrix}$$

We apply the rotating-wave approximation:

$$i\begin{pmatrix} \dot{C}_b(t)e^{-i\omega_0 t/2} - i\frac{\omega_0}{2}C_b(t)e^{-i\omega_0 t/2} \\ \dot{C}_a(t)e^{i\omega_0 t/2} + i\frac{\omega_0}{2}C_a(t)e^{i\omega_0 t/2} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} +\omega_0 & \Omega_1 e^{-i\omega t} \\ \Omega_1 e^{+i\omega t} & -\omega_0 \end{pmatrix}\begin{pmatrix} C_b(t)e^{-i\omega_0 t/2} \\ C_a(t)e^{i\omega_0 t/2} \end{pmatrix}$$

The terms ω_0 cancel.

$$\begin{cases} i\dot{C}_a(t)e^{i\omega_0 t/2} & = \dfrac{\Omega_1}{2}C_b(t)e^{-i\omega_0 t/2}e^{i\omega t} \\ i\dot{C}_b(t)e^{-i\omega_0 t/2} & = \dfrac{\Omega_1}{2}C_a(t)e^{i\omega_0 t/2}e^{-i\omega t} \end{cases}$$

Finally:

$$\left|\begin{array}{lll} \dot{C}_a(t) & =\dfrac{\Omega_1}{2i}C_b(t)e^{i(\omega-\omega_0)t} & =\dfrac{\Omega_1}{2i}C_b(t)e^{i\delta\omega t} \\ \\ \dot{C}_b(t) & =\dfrac{\Omega_1}{2i}C_a(t)e^{-i(\omega-\omega_0)t} & =\dfrac{\Omega_1}{2i}C_a(t)e^{-i\delta\omega t} \end{array}\right.$$

In order to remove the time dependency, we set:

$$\left|\begin{array}{lcl} C_a(t) & = & b_a(t)e^{i(\delta\omega/2)t} \\ \\ C_b(t) & = & b_b(t)e^{-i(\delta\omega/2)t} \end{array}\right.$$

It gives:

$$\left|\begin{array}{lcl} \dot{b}_a(t)e^{i(\delta\omega/2)t} + i\dfrac{\delta\omega}{2}b_a(t)e^{i(\delta\omega/2)t} & = & \dfrac{\Omega_1}{2i}b_b(t)e^{i(\delta\omega/2)t} \\ \\ \dot{b}_b(t)e^{-i(\delta\omega/2)t} - i\dfrac{\delta\omega}{2}b_b(t)e^{-i(\delta\omega/2)t} & = & \dfrac{\Omega_1}{2i}b_a(t)e^{-i(\delta\omega/2)t} \end{array}\right.$$

We have to solve a system of coupled differential equations with contant coefficients:

$$\left|\begin{array}{lclcl} \dot{b}_a(t) & = & \dfrac{\delta\omega}{2i}b_a(t) & + & \dfrac{\Omega_1}{2i}b_b(t) \\ \\ \dot{b}_b(t) & = & \dfrac{\Omega_1}{2i}b_a(t) & - & \dfrac{\delta\omega}{2i}b_b(t) \end{array}\right.$$

We can for example transform the system in a second-order equation by substituting $b_b(t)$:

$$\left|\begin{array}{lcl} b_b(t) & = & \dfrac{2i}{\Omega_1}\left[\dot{b}_a(t) - \dfrac{\delta\omega}{2i}b_a(t)\right] \\ \\ \dot{b}_b(t) & = & \dfrac{2i}{\Omega_1}\left[\ddot{b}_a(t) - \dfrac{\delta\omega}{2i}\dot{b}_a(t)\right] \end{array}\right.$$

$$\frac{2i}{\Omega_1}\left[\ddot{b}_a(t) - \frac{\delta\omega}{2i}\dot{b}_a(t)\right] = \frac{\Omega_1}{2i}b_a(t) - \frac{\delta\omega}{2i}\frac{2i}{\Omega_1}\left[\dot{b}_a(t) - \frac{\delta\omega}{2i}b_a(t)\right]$$

The first-order derivatives cancel.

$$\ddot{b}_a(t) + \frac{\dot{b}_a(t)}{4}(\Omega_1^2 + \delta\omega^2) = 0$$

We calculate the discriminant:

$$\Delta = -(\Omega_1^2 + \delta\omega^2)$$

and find the roots:

$$\lambda_{1,2} = \pm\frac{i}{2}\sqrt{\Omega_1^2 + \delta\omega^2} = \pm\frac{i}{2}\Omega$$

$$\left|\begin{array}{ll} b_a(t) & = A\ e^{i(\Omega/2)t} + B\ e^{-i(\Omega/2)t} \\ & \\ b_b(t) & = \dfrac{2i}{\Omega_1}\left[\dot{b}_a(t) - \dfrac{\delta\omega}{2i} b_a(t)\right] \quad = \dfrac{2i}{\Omega_1}\left[(i\dfrac{\Omega}{2}A\ e^{i\Omega t} - i\dfrac{\Omega}{2}B\ e^{-i\Omega t}) - \dfrac{\delta\omega}{2i}(A\ e^{i(\Omega/2)t} + B\ e^{-i(\Omega/2)t})\right] \end{array}\right.$$

$$\left|\begin{array}{ll} b_a(t) & = A\ e^{i\Omega t} + B\ e^{-i\Omega t} \\ & \\ b_b(t) & = \dfrac{2i}{\Omega_1}\left[-A\left(\dfrac{\Omega}{2i} + \dfrac{\delta\omega}{2i}\right) e^{i(\Omega/2)t} + B\left(\dfrac{\Omega}{2i} - \dfrac{\delta\omega}{2i}\right) e^{-i(\Omega/2)t}\right] \end{array}\right.$$

The constants A and B are determined by the intial condition. The system is in the ground-state $|a\rangle$ at $t = 0$.

$$\left|\begin{array}{llll} b_a(0) & = 1 & = & A + B \\ & & & \\ b_b(0) & = 0 & = & \dfrac{1}{\Omega_1}\left[-A\left(\Omega + \delta\omega\right) + B\left(\Omega - \delta\omega\right)\right] \end{array}\right.$$

The solution is:

$$\left|\begin{array}{ll} A & = \dfrac{\Omega - \delta\omega}{2\Omega} \\ & \\ B & = \dfrac{\Omega + \delta\omega}{2\Omega} \end{array}\right.$$

Thus can we write the time-dependency of the coefficients $b_a(t)$ and $b_b(t)$:

$$\left|\begin{array}{ll} b_a(t) & = \dfrac{\Omega - \delta\omega}{2\Omega}\ e^{i\Omega t} + \dfrac{\Omega + \delta\omega}{2\Omega}\ e^{-i\Omega t} \\ & \\ b_b(t) & = \dfrac{1}{\Omega_1}\left[-\dfrac{\Omega - \delta\omega}{2\Omega}\left(\Omega + \delta\omega\right) e^{i(\Omega/2)t} + \dfrac{\Omega + \delta\omega}{2\Omega}\left(\Omega - \delta\omega\right) e^{-i(\Omega/2)t}\right] \end{array}\right.$$

Finally, we get:

$$\boxed{\begin{array}{ll} b_a(t) & = \cos\left(\dfrac{\Omega}{2}t\right) - i\dfrac{\delta\omega}{\Omega}\sin\left(\dfrac{\Omega}{2}t\right) \\ & \\ b_b(t) & = -i\dfrac{\Omega_1}{\Omega}\sin\left(\dfrac{\Omega}{2}t\right) \end{array}}$$

Rabi oscillations

The probability for a transition $|a\rangle$ to $|b\rangle$ to occur, is:

$$\mathcal{P}_{ab}(t) = |C_b(t)|^2 = |b_b(t)|^2 = \frac{\Omega_1^2}{\Omega^2}\sin^2\left(\frac{\Omega}{2}t\right)$$

$$\boxed{\mathcal{P}_{ab}(t) = \frac{\Omega_1^2}{\Omega_1^2 + \delta\omega^2}\sin^2\left(\frac{1}{2}\sqrt{\Omega_1^2 + \delta\omega^2 t}\right)}$$

The probability $\mathcal{P}_{ab}$ oscillates in time at the **generalized Rabi frequency** $\Omega = \sqrt{\Omega_1^2 + \delta\omega^2}$ between 0 and a maximum value:

$$\mathcal{P}_{ab}^{max} = \frac{\Omega_1^2}{\Omega_1^2 + \delta\omega^2} = \frac{\Omega_1^2}{\Omega_1^2 + (\omega - \omega_0)^2}$$

$\mathcal{P}_{ab}^{max}$ presents a resonant behaviour for $\omega = \omega_0$. The lineshape is a Lorentz function the full-width of it is equal to $2\Omega_1$. At very short times we can write:

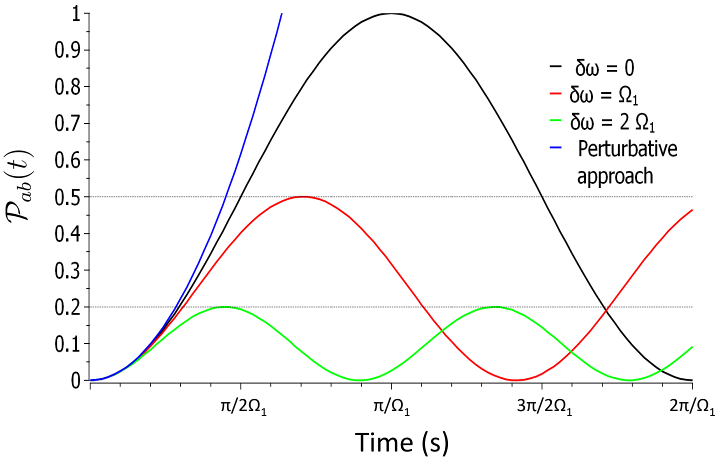


Figure 3: Time evolution of the transition probability $\mathcal{P}_{ab}$ for different values of the detuning $\delta\omega = \omega - \omega_0$. The result of the first order perturbation theory is also displayed.

$$\sin\left(\frac{\Omega}{2}t\right) \simeq \frac{\Omega}{2}t$$

and:

$$\mathcal{P}_{ab}(t) \simeq \frac{\Omega_1^2}{\Omega^2}\left(\frac{\Omega}{2}t\right)^2 = \frac{\Omega_1^2}{4}t^2$$

This the same result that we have obtainde by using the first-order time dependent perturbation theory. As it can be seen in the figure 3, the perurbative approach remains valid while $t \ll \dfrac{2\pi}{\Omega}$.

Coherent transients & $\pi/2$-pulses

A resonant E.M. field ($\delta\omega = 0$) is switched on at $t = 0$ and switched of at $t = \frac{1}{\Omega_1}\frac{\pi}{2}$. The time-evolution of the atomic sate is:

$$|\psi(t)\rangle = b_a(t)e^{i\omega_0 t/2}\,|a\rangle + b_b(t)e^{-i\omega_0 t/2}\,|b\rangle$$

with:

$$\left|\begin{array}{lcl} b_a(t) & = & \cos\left(\dfrac{\Omega}{2}t\right) - i\dfrac{\delta\omega}{\Omega}\sin\left(\dfrac{\Omega}{2}t\right) \\ & & \\ b_b(t) & = & -\,i\dfrac{\Omega_1}{\Omega}\sin\left(\dfrac{\Omega}{2}t\right) \end{array}\right.$$

and $\Omega = \sqrt{\Omega_1^2 + \delta\omega^2}$. If we chose $\delta\omega = 0$, we get:

$$\left|\begin{array}{lcl} b_a(t) & = & \cos\left(\dfrac{\Omega_1}{2}t\right) \\ & & \\ b_b(t) & = & -\,i\sin\left(\dfrac{\Omega_1}{2}t\right) \end{array}\right.$$

Then, in the specific case of a $\frac{\pi}{2}$-pulse, we obtain:

$$\left|\begin{array}{lcccc} b_a(t) & = & \cos\left(\dfrac{\Omega_1}{2}\dfrac{\pi}{2\Omega_1}t\right) & = & \dfrac{1}{\sqrt{2}} \\ & & & & \\ b_b(t) & = & -\,i\sin\left(\dfrac{\Omega_1}{2}\dfrac{\pi}{2\Omega_1}t\right) & = & -\dfrac{1}{\sqrt{2}} \end{array}\right.$$

and, consequently:

$$\boxed{|\psi(t)\rangle = \frac{1}{\sqrt{2}}e^{i\omega_0 t/2}\,|a\rangle - \frac{i}{\sqrt{2}}e^{-i\omega_0 t/2}\,|b\rangle}$$

We notice that:

$$|\,\langle 1|\psi(t)\rangle\,|^2 = |\,\langle 2|\psi(t)\rangle\,|^2 = \frac{1}{2}$$

Thus, the probabilities for the atom to be in either state does not change in time. But, it does not mean that the system does not evolve at all. Let us calculate the expectation value of the electric dipole operator between $|a\rangle$ and $|b\rangle$:

$$\langle\psi(t)|\hat{d}|\psi(t)\rangle = \left[\frac{1}{\sqrt{2}}e^{-i\omega_0 t/2}\langle a| + \frac{i}{\sqrt{2}}e^{i\omega_0 t/2}\langle b|\right]\hat{d}\left[\frac{1}{\sqrt{2}}e^{i\omega_0 t/2}|a\rangle - \frac{i}{\sqrt{2}}e^{-i\omega_0 t/2}|b\rangle\right]$$

Taking into account that $\langle a|\hat{d}|b\rangle = \langle b|\hat{d}|b\rangle = 0$ and $\langle a|\hat{d}|b\rangle = \langle b|\hat{d}|a\rangle = d_{ab}$, we find:

$$\langle\psi(t)|\hat{d}|\psi(t)\rangle = -\frac{i}{2}\langle a|\hat{d}|b\rangle\, e^{-i\omega_0 t} + \frac{i}{2}\langle b|\hat{d}|a\rangle = d_{ab}e^{i\omega_0 t} = -d_{ab}\sin\omega_0 t$$

The dipole-moment oscillates at the Bohr-frequency ω_0. This oscillation goes along with emission of light at the same frequency. Although emitted at the same frequency ω_0 as spontaneous emission between the same two energy levels, this light has different properties related to the coherence of the emission. The phase of the oscillations of the atomic dipole is uniquely determined with respect to that of the incident wave. An assembly of atoms all prepared by the same $\pi/2$-pulse will therefore all emit light with the same phase. This is in contrast to what occurs with spontaneous emission, when individual atoms emit light with a random phase. It is possible to observe the consequences of this coherence in experiments. These include the directionality of the emission, the appearance of phenomena related to the beating of fluorescence light with a beam coherent with the driving light. Such phenomena, known as coherent transients, can be observed only over a timescale which is short compared to the radiative lifetimes of the atomic states involved.

Chapter 3: Density-matrix treatment of a two-level system

December 1, 2022

Contents

1 Introduction

The approaches used in the previous chapter do not allow to take into account the interaction of the atom with its environment (collisions, spontaneous emission). If we are only interested in the way this interaction acts on the dynamics of the system, the density-matrix formalism is very efficient. It enables to combine the advantages of the quantum description and of a phenomenological model. Indeed, the transitions induced by the classical E.M. field are treated in the quantum formalism while the others interactions are introduced in a phenomenological way by use of suitable relaxation terms. In the specific case of a two-level system, the time-evolution of the density-matrix is governed by the optical Bloch equations, the steady-state solutions of which can be exactly determined. The system is equivalent to a one-half spin in a magnetic field and can be represented geometricaly by the Bloch-vector the evolution of which can be sketched in the Bloch-sphere.

2 Essentials of the density-matrix

2.1 Definition

The **density-matrix** is a representation of a linear operator called the density operator. The density operator of a pure state is defined as:

$$\hat{\sigma} = |\psi\rangle \langle\psi|$$

The density-matrix is obtained from the density operator by choice of a basis in the underlying space. If $|\psi\rangle$ is expanded in a basis $|n\rangle$, we get:

$$|\psi\rangle = \sum_n C_n |n\rangle \text{ and } \langle\psi| = \sum_n C_n^* \langle n|$$

Then, the expression of the density-matrix in the $|n\rangle$ basis is:

$$\hat{\sigma} = \sum_{n,m} C_n C_m^* |n\rangle \langle m|$$

In practice, the terms density-matrix and density operator are often used interchangeably.
The density-matrix elements in the $|n\rangle$ basis are:

$$\hat{\sigma}_{ij} = \langle i| \sum_{n,m} C_n C_m^* |n\rangle \langle m|j\rangle = C_n C_m^* \delta_{i,n} \delta_{m,j} = C_i C_j^*$$

The **diagonal terms** $\sigma_{ii} = \langle i|\hat{\sigma}|i\rangle = |C_i|^2$ are is the probability for finding the system in the state vector $|i\rangle$. These terms are the corresponding **populations** of each stationary state $|n\rangle$ constituting the basis. The normalization condition for the state $|\psi\rangle$ leads to:

$$\mathrm{Tr}\,\hat{\sigma} = \sum_n \sigma_{nn} = 1$$

The **off-diagonal terms** $\sigma_{ij} = \langle i|\hat{\sigma}|i\rangle = C_i C_j^*$ are complex numbers that account for interferences between $|i\rangle$ and $|j\rangle$ that can appear when $|\psi\rangle$ is a linear coherent superpositon of these states. For this reason, the off-diagonal elements are named **coherences**.

One of the interests of the density-matrix is the possibility of dealing with mixed states that cannot be described by wavefunctions, like statistical ensembles for exemple. For an ensemble in a mixed state such that each of the pure states $|\psi_k\rangle$ occurs with probability p_k, the density-matrix is defined by:

$$\hat{\sigma} = \sum_k p_k \left|\psi_k\right\rangle \left\langle\psi_k\right| = \sum_k p_k \sigma_k$$

.

2.2 Properties

-The mean value of an observable represented by an operator $\hat{O}$ is:

$$\left\langle \hat{O} \right\rangle = \mathrm{Tr}\left(\hat{\sigma}\hat{O}\right)$$

-The time evolution of the density-operator of an isolated system can be deduced from the Schrödinger equation and is governed by the Liouville-Von Neumann equation:

$$\frac{\mathrm{d}\hat{\sigma}}{\mathrm{d}t} = \frac{1}{i\hbar}\left[\hat{H}, \hat{\sigma}\right]$$

-If the system undergoes interactions at random instants with others systems, their average effect is represented by the addition to the Liouville-Von Neumann equation of a relaxation operator. The relaxation terms of the populations are:

$$\left\{\frac{\mathrm{d}\sigma_{ii}}{\mathrm{d}t}\right\}_{\mathrm{rel}} = -(\sum_{j\neq i} \Gamma_{i\to j})\sigma_{ii} + \sum_{j\neq i} \Gamma_{j\to i}\sigma_{jj}$$

where Γ_{ij} is the transition rate from $|i\rangle$ to $|j\rangle$.

The relaxation terms of the coherences are:

$$\left\{\frac{\mathrm{d}\sigma_{ij}}{\mathrm{d}t}\right\}_{\mathrm{rel}} = -\gamma_{ij}\sigma_{ij}$$

Even if the $\Gamma_{j\to i}$ and γ_{ij} can be evaluated if the interaction Hamiltonian of the system with its environment is known, we will consider them to be introduced phenomenologically.

3 Application to a two-level system - Optical Bloch equations

3.1 Derivation of OBE

As we did in the previous chapter, we consider a two-level atom described by the Hamiltonian:

$$\hat{H}_0 = \frac{\hbar}{2}\begin{pmatrix} +\omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix}$$

with $\omega_0 = (E_b - E_a)/\hbar$. This atom interacts with a classical perdiodic E.M. field:

$$\hat{W}_{ab}(t) = -\left\langle a\right|\hat{\vec{d}}\cdot\vec{\mathcal{E}}(\vec{r}_0)\left|b\right\rangle \cos\omega t = \hbar\ \Omega_1\cos\omega t$$

The total time-dependent Hamiltonian is:

$$\hat{H}(t) = \hat{H}_0 + \hat{W}_{ab}(t) = \frac{\hbar}{2}\begin{pmatrix} +\omega_0 & 2\Omega_1\cos\omega t \\ 2\Omega_1\cos\omega t & -\omega_0 \end{pmatrix}$$

The eigenstates are expanded on the basis of the stationnary states:

$$|\psi(t)\rangle = C_a(t)e^{i\omega_0 t/2}\,|a\rangle + C_b(t)e^{-i\omega_0 t/2}\,|b\rangle$$

As usual, we write the $\cos\omega t$ with complex notation and we remove the non-resonant terms:

$$\hat{H}(t) = \hat{H}_0 + \hat{W}_{ab}(t) = \frac{\hbar}{2}\begin{pmatrix} +\omega_0 & \Omega_1 e^{-i\omega t} \\ \Omega_1 e^{+i\omega t} & -\omega_0 \end{pmatrix}$$

Up to this point, the notations are the ones we previously introduced.

We determine the time-evolution of the density-matrix by use of the Liouville-Von Neumann equation:

$$\frac{\mathrm{d}\hat{\sigma}}{\mathrm{d}t} = \frac{1}{i\hbar}\left[\hat{H},\hat{\sigma}\right]$$

We calculate $\frac{1}{i\hbar}\hat{\sigma}\hat{H}$ and $\frac{1}{i\hbar}\hat{H}\hat{\sigma}$:

$$\begin{aligned}
\frac{1}{i\hbar}\hat{H}\hat{\sigma} = {} & \frac{1}{2}\begin{pmatrix} -i\omega_0 & -i\Omega_1 e^{-i\omega t} \\ -i\Omega_1 e^{+i\omega t} & +i\omega_0 \end{pmatrix} \times \begin{pmatrix} \sigma_{bb} & \sigma_{ba} \\ \sigma_{ab} & \sigma_{aa} \end{pmatrix} \\
= {} & \frac{1}{2}\begin{pmatrix} -i\omega_0\sigma_{bb} - i\Omega_1\sigma_{ab}e^{-i\omega t} & -i\omega_0\sigma_{ba} - i\Omega_1\sigma_{aa}e^{-i\omega t} \\ -i\Omega_1\sigma_{bb}e^{+i\omega t} + i\omega_0\sigma_{ab} & -i\Omega_1\sigma_{ba}e^{+i\omega t} + i\omega_0\sigma_{aa} \end{pmatrix}
\end{aligned}$$

$$\begin{aligned}
\frac{1}{i\hbar}\hat{\sigma}\hat{H} = {} & \begin{pmatrix} \sigma_{bb} & \sigma_{ba} \\ \sigma_{ab} & \sigma_{aa} \end{pmatrix} \times \frac{1}{2}\begin{pmatrix} -i\omega_0 & -i\Omega_1 e^{-i\omega t} \\ -i\Omega_1 e^{+i\omega t} & +i\omega_0 \end{pmatrix} \\
= {} & \frac{1}{2}\begin{pmatrix} -i\omega_0\sigma_{bb} - i\Omega_1\sigma_{ba}e^{+i\omega t} & -i\Omega_1\sigma_{bb}e^{-i\omega t} + i\omega_0\sigma_{ba} \\ -i\omega_0\sigma_{ab} - i\Omega_1\sigma_{aa}e^{+i\omega t} & -i\Omega_1\sigma_{ab}e^{-i\omega t} + i\omega_0\sigma_{aa} \end{pmatrix}
\end{aligned}$$

Finally, we get:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} \sigma_{bb} & \sigma_{ba} \\ \sigma_{ab} & \sigma_{aa} \end{pmatrix} = \begin{pmatrix} i\frac{\Omega_1}{2}(\sigma_{ba}e^{+i\omega t} - \sigma_{ab}e^{-i\omega t}) & i\frac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})e^{-i\omega t} - i\omega_0\sigma_{ba} \\ -i\frac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})e^{+i\omega t} + i\omega_0\sigma_{ab} & -i\frac{\Omega_1}{2}(\sigma_{ba}e^{+i\omega t} - \sigma_{ab}e^{-i\omega t}) \end{pmatrix}$$

The time-evolution of the density-matrix is given by the following set of four coupled differential equations, the **optical Bloch-equations**:

$$\left|\begin{aligned}
\frac{\mathrm{d}\sigma_{aa}}{\mathrm{d}t} &= -i\frac{\Omega_1}{2}(\sigma_{ba}e^{i\omega t} - \sigma_{ab}e^{-i\omega t}) \\
\frac{\mathrm{d}\sigma_{bb}}{\mathrm{d}t} &= i\frac{\Omega_1}{2}(\sigma_{ba}e^{i\omega t} - \sigma_{ab}e^{-i\omega t}) \\
\frac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t} &= -i\frac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})e^{i\omega t} + i\omega_0\sigma_{ab} \\
\frac{\mathrm{d}\sigma_{ba}}{\mathrm{d}t} &= i\frac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})e^{-i\omega t} - i\omega_0\sigma_{ba}
\end{aligned}\right.$$

The relaxation of populations and coherences is taken into account by the addition of the relaxation operator.

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} \sigma_{aa} \\ \sigma_{bb} \\ \sigma_{ab} \\ \sigma_{ba} \end{pmatrix} = \begin{pmatrix} 0 & +\Gamma_{ba} & 0 & 0 \\ 0 & -\Gamma_{ba} & 0 & 0 \\ 0 & 0 & -\gamma_{ab} & 0 \\ 0 & 0 & 0 & -\gamma_{ba} \end{pmatrix} \begin{pmatrix} \sigma_{aa} \\ \sigma_{bb} \\ \sigma_{ab} \\ \sigma_{ba} \end{pmatrix}$$

For convenience, we suppose that $\gamma_{ab} = \gamma_{ba} = \gamma$. The system is closed, the total population is conserved:

$$\frac{\mathrm{d}\sigma_{aa}}{\mathrm{d}t} + \frac{\mathrm{d}\sigma_{bb}}{\mathrm{d}t} = 0$$

Γ_{ba} is the relaxation-rate of the population and γ the relaxation-rate of the dipole. These two quantities have been introduced in the Einstein's and Drude-Lorentz models, respectively. One often writes:

$$\Gamma_{ba} = \frac{1}{T_1},\ \gamma = \frac{1}{T_2}$$

with T_1 the population lifetime, T_2 is the dipole lifetime. We distinguish two opposite situations:

- If the medium is diluted, the only coupling of the atom with its environment is the interaction with the radiation (spontaneous emission). Then, it can be shown that:

  $$\Gamma_{ba} = \Gamma_{sp},\ \gamma = \frac{\Gamma_{sp}}{2}$$

  where Γ_{sp} is the spontaneous relaxation-rate that we have calculated previously.

- If the medium is dense, the relaxation processes can be due to collision between atoms, interaction with phonons, etc. The relaxation is enhanced and:

  $$\gamma \gg \Gamma_{ba}$$

  The relaxation of the dipole is faster than the relaxation of populations. It is easier to blur a phase (leading to a damping of the dipole, or of the coherence) than to modify an energy (needed to damp the population).

The system of equation becomes:

$$\left|\begin{array}{rcl}
\dfrac{\mathrm{d}\sigma_{aa}}{\mathrm{d}t} & = & -i\dfrac{\Omega_1}{2}(\sigma_{ba}e^{i\omega t} - \sigma_{ab}e^{-i\omega t}) + \Gamma_{ba}\ \sigma_{bb} \\
\dfrac{\mathrm{d}\sigma_{bb}}{\mathrm{d}t} & = & i\dfrac{\Omega_1}{2}(\sigma_{ba}e^{i\omega t} - \sigma_{ab}e^{-i\omega t}) - \Gamma_{ba}\ \sigma_{bb} \\
\dfrac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t} & = & -i\dfrac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})e^{i\omega t} + i(\omega_0 + i\gamma)\ \sigma_{ab} \\
\dfrac{\mathrm{d}\sigma_{ba}}{\mathrm{d}t} & = & i\dfrac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})e^{-i\omega t} - i(\omega_0 - i\gamma)\ \sigma_{ba}
\end{array}\right.$$

3.2 Free evolution

In the absence of an external E.M. field, $\Omega_1 = 0$ and the system becomes:

$$\left|\begin{array}{rcl} \dfrac{\mathrm{d}\sigma_{aa}}{\mathrm{d}t} & = & +\,\Gamma_{ba}\;\sigma_{bb} \\ \dfrac{\mathrm{d}\sigma_{bb}}{\mathrm{d}t} & = & -\,\Gamma_{ba}\;\sigma_{bb} \\ \dfrac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t} & = & i(\omega_0 + i\gamma)\;\sigma_{ab} \\ \dfrac{\mathrm{d}\sigma_{ba}}{\mathrm{d}t} & = & -i(\omega_0 - i\gamma)\;\sigma_{ba} \end{array}\right. \text{, the integration of which leads to } \left|\begin{array}{rcl} \sigma_{aa}(t) & = & \sigma_{aa}(0)\;e^{-\Gamma_{ba}t} \\ \sigma_{bb}(t) & = & 1 - \sigma_{aa}(0)\;e^{-\Gamma_{ba}t} \\ \sigma_{ab}(t) & = & \sigma_{ab}(0)\;e^{i\omega_0 t}e^{-\gamma t} \\ \sigma_{ba}(t) & = & \sigma_{ba}(0)\;e^{-i\omega_0 t}e^{-\gamma t} \end{array}\right.$$

If the system is prepared in an intial state with $\sigma_{bb} - \sigma_{aa} \neq 0$, the populations remain constant and the coherences evolve periodically with the angular frequency ω_0.

3.3 Driven system

To solve this system, we remove the rapid time dependence of the σ_{ii} by setting:

$$\begin{array}{rcl} \tilde{\sigma}_{ab} & = & \sigma_{ab}\;e^{-i\omega t} \\ \tilde{\sigma}_{ba} & = & \sigma_{ba}\;e^{+i\omega t} \\ \tilde{\sigma}_{aa} & = & \sigma_{aa} \\ \tilde{\sigma}_{bb} & = & \sigma_{bb} \end{array}$$

It corresponds, as we will see further, to the **rotating-frame transformation**. It consists in writing the coherence terms in the frame that is rotating at the field frequency ω.

$$\begin{array}{rcl} \dfrac{\mathrm{d}\tilde{\sigma}_{aa}}{\mathrm{d}t} & = & -i\dfrac{\Omega_1}{2}(\tilde{\sigma}_{ba} - \tilde{\sigma}_{ab}) + \Gamma_{ba}\;\tilde{\sigma}_{bb} \\ \dfrac{\mathrm{d}\tilde{\sigma}_{bb}}{\mathrm{d}t} & = & i\dfrac{\Omega_1}{2}(\tilde{\sigma}_{ba} - \tilde{\sigma}_{ab}) - \Gamma_{ba}\;\tilde{\sigma}_{bb} \\ \dfrac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t}e^{+i\omega t} + i\omega\;\tilde{\sigma}_{ab}\;e^{+i\omega t} & = & -i\dfrac{\Omega_1}{2}(\tilde{\sigma}_{bb} - \tilde{\sigma}_{aa})\;e^{+i\omega t} + i(\omega_0 + i\gamma)\;\tilde{\sigma}_{ab}\;e^{+i\omega t} \\ \dfrac{\mathrm{d}\tilde{\sigma}_{ba}}{\mathrm{d}t}e^{-i\omega t} - i\omega\;\tilde{\sigma}_{ab}\;e^{-i\omega t} & = & i\dfrac{\Omega_1}{2}(\tilde{\sigma}_{bb} - \tilde{\sigma}_{aa})\;e^{-i\omega t} - (i\omega_0 - i\gamma)\;\tilde{\sigma}_{ba}\;e^{-i\omega t} \end{array}$$

The system becomes a coupled set of differential equations with constant coefficients.

$$\boxed{\begin{aligned}
\frac{\mathrm{d}\tilde{\sigma}_{aa}}{\mathrm{d}t} &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{ba}-\tilde{\sigma}_{ab})+\Gamma_{ba}\ \tilde{\sigma}_{bb}\\
\frac{\mathrm{d}\tilde{\sigma}_{bb}}{\mathrm{d}t} &= i\frac{\Omega_1}{2}(\tilde{\sigma}_{ba}-\tilde{\sigma}_{ab})-\Gamma_{ba}\ \tilde{\sigma}_{bb}\\
\frac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t} &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})+i(\omega_0-\omega+i\gamma)\ \tilde{\sigma}_{ab}\\
\frac{\mathrm{d}\tilde{\sigma}_{ba}}{\mathrm{d}t} &= i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})-i(\omega_0-\omega-i\gamma)\ \tilde{\sigma}_{ba}
\end{aligned}}$$

The system can be solved exactly in some limit cases.

3.4 Stationnary regime

Some analytical solutions can be obtained if we set the time-derivatives equal to zero:

$$\begin{aligned}
0 &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{ba}-\tilde{\sigma}_{ab})+\Gamma_{ba}\ \tilde{\sigma}_{bb}\\
0 &= i\frac{\Omega_1}{2}(\tilde{\sigma}_{ba}-\tilde{\sigma}_{ab})-\Gamma_{ba}\ \tilde{\sigma}_{bb}\\
0 &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})+i(\omega_0-\omega+i\gamma)\ \tilde{\sigma}_{ab}\\
0 &= i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})-i(\omega_0-\omega-i\gamma)\ \tilde{\sigma}_{ba}
\end{aligned}$$

Weak excitation, oscillator strength
if the excitation is weak $\tilde{\sigma}_{bb}\simeq\ 0$ and $\tilde{\sigma}_{aa}\simeq 1$, so $\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa}\simeq\ -1$ and:

$$\frac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t}\ \simeq i\frac{\Omega_1}{2}+i(\omega_0-\omega+i\gamma)\ \tilde{\sigma}_{ab}$$

replacing $\Omega_1=-\frac{1}{\hbar}\vec{d}_{ab}\cdot\vec{\mathcal{E}}$

$$\frac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t}-i(\omega_0-\omega+i\gamma)\ \tilde{\sigma}_{ab}\ =-i\frac{\vec{d}_{ab}\cdot\vec{\mathcal{E}}}{2\hbar}$$

Restoring the antiresonant term that we have neglected before, we find:

$$\begin{aligned}\sigma_{ab} &= \frac{\vec{d}_{ab}\cdot\vec{\mathcal{E}}}{2\hbar}\left[\frac{e^{+i\omega t}}{(\omega_0-\omega+i\gamma)}+\frac{e^{-i\omega t}}{(\omega_0+\omega+i\gamma)}\right]\\ &\qquad\qquad= \frac{\vec{d}_{ab}\cdot\vec{\mathcal{E}}}{2\hbar}\left[\frac{\omega_0-\omega-i\gamma}{(\omega_0-\omega)^2+\gamma^2}e^{+i\omega t}+\frac{\omega_0+\omega-i\gamma}{(\omega_0+\omega)^2+\gamma^2)}e^{-i\omega t}\right]\end{aligned}$$

and

$$\begin{aligned}\sigma_{ba} &= \frac{\vec{d}_{ab}\cdot\vec{\mathcal{E}}}{2\hbar}\left[\frac{e^{-i\omega t}}{(\omega_0-\omega-i\gamma)}+\frac{e^{+i\omega t}}{(\omega_0+\omega-i\gamma)}\right]\\ &\qquad\qquad= \frac{\vec{d}_{ab}\cdot\vec{\mathcal{E}}}{2\hbar}\left[\frac{\omega_0-\omega+i\gamma}{(\omega_0-\omega)^2+\gamma^2}e^{-i\omega t}+\frac{\omega_0+\omega+i\gamma}{(\omega_0+\omega)^2+\gamma^2)}e^{+i\omega t}\right]\end{aligned}$$

The expectation value of the dipole operator is:

$$\left\langle\hat{\vec{d}}\right\rangle = \mathrm{Tr}\left(\hat{\sigma}\hat{\vec{d}}\right) = \vec{d}_{ab}\;\sigma_{ab}+\vec{d}_{ba}\;\sigma_{ba}$$

$$= \frac{|\vec{d}_{ab}|^2\cdot\vec{\mathcal{E}}}{2\hbar}\left[\frac{(\omega_0-\omega)\;e^{+i\omega t}}{(\omega_0-\omega)^2+\gamma^2}+\frac{(\omega_0+\omega)\;e^{-i\omega t}}{(\omega_0+\omega)^2+\gamma^2}-\frac{i\gamma\;e^{+i\omega t}}{(\omega_0-\omega)^2+\gamma^2}-\frac{i\gamma\;e^{-i\omega t}}{(\omega_0+\omega)^2+\gamma^2}+c.c.\right]$$

$$\begin{aligned}\left\langle\hat{\vec{d}}\right\rangle &= \frac{|\vec{d}_{ab}|^2\cdot\vec{\mathcal{E}}}{\hbar}\left[\frac{(\omega_0-\omega)}{(\omega_0-\omega)^2+\gamma^2}+\frac{(\omega_0+\omega)}{(\omega_0+\omega)^2+\gamma^2}\right]\cos(\omega t)\\ &\qquad\qquad+\frac{|\vec{d}_{ab}|^2\cdot\vec{\mathcal{E}}}{\hbar}\left[\frac{\gamma}{(\omega_0-\omega)^2+\gamma^2}-\frac{\gamma}{(\omega_0+\omega)^2+\gamma^2}\right]\sin(\omega t)\end{aligned}$$

far from the resonance, when $\gamma \ll |\omega-\omega_0|$:

$$\left\langle\hat{\vec{d}}\right\rangle \simeq \frac{|\vec{d}_{ab}|^2\cdot\vec{\mathcal{E}}}{\hbar}\left[\frac{1}{\omega_0-\omega}+\frac{1}{\omega_0+\omega}\right]\cos(\omega t) = \frac{|\vec{d}_{ab}|^2\cdot\vec{\mathcal{E}}}{\hbar}\frac{2\omega_0}{\omega_0^2-\omega^2}\cos(\omega t)$$

$$\left\langle\hat{\vec{d}}\right\rangle = q^2\frac{|\vec{r}_{ab}|^2\cdot\vec{\mathcal{E}}}{\hbar}\frac{2\omega_0}{\omega_0^2-\omega^2}\cos(\omega t)$$

Let us compare this expression with the one that we obtained with the **Drude-Lorentz model**:

$$\tilde{p}\,(\omega) = \frac{q^2}{m}\frac{1}{(\omega_0^2-\omega^2-2i\gamma\omega)}\mathcal{E}_0$$

$$p(t) = \frac{1}{2}[\tilde{p}(\omega)\;e^{-i\omega t}+\tilde{p}^*(\omega)\;e^{+i\omega t}] = \frac{q^2\mathcal{E}_0}{2m}\left[\frac{e^{-i\omega t}}{\omega_0^2-\omega^2-2i\gamma\omega}+\frac{e^{+i\omega t}}{\omega_0^2-\omega^2+2i\gamma\omega}\right]$$

Far from the resonance:

$$p(t) \simeq \frac{q^2\mathcal{E}_0}{2m}\left(\frac{e^{-i\omega t}}{\omega_0^2-\omega^2}+\frac{e^{+i\omega t}}{\omega_0^2-\omega^2}\right)=\frac{q^2}{m}\frac{1}{\omega_0^2-\omega^2}\mathcal{E}_0\cos(\omega t)$$

We can rewrite the dipole in the classical form:

$$\left\langle \vec{d}\,\right\rangle = f_{ab}\frac{q^2}{m}\frac{1}{\omega_0^2-\omega^2}\mathcal{E}_0\cos(\omega t)$$

where:

$$f_{ab}=2\frac{m}{\hbar}\omega_0|\vec{r}_{ab}|^2$$

is a dimensionless parameter called the **oscillator strength** of the transition. Then, the macroscopic polarization is:

$$\vec{P}=\frac{N}{V}\frac{q^2}{m}\frac{f_{ab}}{\omega_0^2-\omega^2}\mathcal{E}_0\cos(\omega t)=\varepsilon_0\chi\mathcal{E}_0\cos(\omega t)$$

and:

$$\chi(\omega)=\frac{N}{V}\frac{q^2}{m\varepsilon_0}\frac{f_{ab}}{\omega_0^2-\omega^2}$$

If several transitions contribute to the polarization, then we can generalize the expression of χ

$$\boxed{\chi(\omega)=\frac{N}{V}\frac{q^2}{m\varepsilon_0}\sum_f\frac{f_{af}}{\omega_{fa}^2-\omega^2}}$$

Fast relaxation of coherences, rate equations

In a dense medium $\gamma \gg \Gamma_{ba}$

$$\frac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t}=-i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})+i(\omega_0-\omega+i\gamma)\,\tilde{\sigma}_{ab}$$

The characteristic evolution-time of $\tilde{\sigma}_{ab}$ is γ^{-1}. Similarly σ_{aa} and σ_{bb} evolve on characteristic times $\simeq \Gamma_{ba}^{-1}$. If $\gamma \gg \Gamma_{ba}$, we can make the assumption that $\tilde{\sigma}_{aa}$ and $\tilde{\sigma}_{bb}$ are constant at the scale of γ^{-1}. Thanks to this simplification, we can integrate directly:

$$\frac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t}-i(\omega_0-\omega+i\gamma)\,\tilde{\sigma}_{ab}=-i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})$$

$$\frac{\mathrm{d}\tilde{\sigma}_{ab}}{\mathrm{d}t}e^{-i(\omega_0-\omega+i\gamma)t}-i(\omega_0-\omega+i\gamma)\,\tilde{\sigma}_{ab}\,e^{-i(\omega_0-\omega+i\gamma)t}=-i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})\,e^{-i(\omega_0-\omega+i\gamma)t}$$

$$\begin{aligned}\tilde{\sigma}_{ab}\ e^{-i(\omega_0-\omega+i\gamma)t} &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})\int_0^t\ e^{-i(\omega_0-\omega+i\gamma)t'}dt' \\ \tilde{\sigma}_{ab}\ e^{-i(\omega_0-\omega+i\gamma)t} &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})\frac{e^{-i(\omega_0-\omega+i\gamma)t}-1}{-i(\omega_0-\omega+i\gamma)} \\ \tilde{\sigma}_{ab} &= -i\frac{\Omega_1}{2}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})\frac{1-e^{+i(\omega_0-\omega+i\gamma)t}}{-i(\omega_0-\omega+i\gamma)}\end{aligned}$$

When $t \gg \gamma^{-1}$, we can neglect the damped terms and

$$\boxed{\tilde{\sigma}_{ab} = -i\frac{\Omega_1}{2}\frac{\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa}}{\gamma - i(\omega_0-\omega)} = \frac{\Omega_1}{2}\frac{\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa}}{(\omega_0-\omega)+i\gamma}}$$

we replace with this expression in:

$$\frac{\mathrm{d}\tilde{\sigma}_{bb}}{\mathrm{d}t} = i\frac{\Omega_1}{2}(\tilde{\sigma}_{ba}-\tilde{\sigma}_{ab}) - \Gamma_{ba}\ \tilde{\sigma}_{bb}$$

$$\begin{aligned}\frac{\mathrm{d}\tilde{\sigma}_{bb}}{\mathrm{d}t} &= i\frac{\Omega_1^2}{4}(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})\left[\frac{1}{(\omega_0-\omega)-i\gamma} - \frac{1}{(\omega_0-\omega)+i\gamma}\right] - \Gamma_{ba}\ \tilde{\sigma}_{bb} \\ &= i\frac{\Omega_1^2}{4}(\sigma_{bb}-\sigma_{aa})\left[\frac{i2\gamma}{(\omega_0-\omega)^2+\gamma^2}\right] - \Gamma_{ba}\ \tilde{\sigma}_{bb}\end{aligned}$$

Finally, we get:

$$\boxed{\frac{\mathrm{d}\tilde{\sigma}_{bb}}{\mathrm{d}t} = -(\tilde{\sigma}_{bb}-\tilde{\sigma}_{aa})\frac{\Omega_1^2}{2\gamma}\left[\frac{\gamma^2}{(\omega_0-\omega)^2+\gamma^2}\right] - \Gamma_{ba}\ \tilde{\sigma}_{bb}}$$

If we multiply this equation by the number of atoms per unit-volume N/V, we obtain the rate equation for the excited state population:

$$\begin{aligned}\frac{\mathrm{d}N_b}{\mathrm{d}t} = (N_a-N_b)\frac{\Omega_1^2}{2\gamma}\left[\frac{\gamma^2}{(\omega_0-\omega)^2+\gamma^2}\right] - \Gamma_{ba}\ N_b \\ = \frac{\Omega_1^2}{2\gamma}F(\omega)(N_a-N_b) - \Gamma_{ba}\ N_b\end{aligned}$$

that is similar to the Einstein equation:

$$\frac{\mathrm{d}N_b}{\mathrm{d}t} = Bu\,(\omega_0)\,F(\omega)(N_a-N_b) - AN_b$$

where we have introduced the absorption lineshape $F(\omega)$. We deduce that:

$$Bu(\omega_0) = \frac{\Omega_1^2}{2\gamma}\ ,\ A = \Gamma_{ba} \text{ and } F(\omega) = \frac{\gamma^2}{(\omega_0-\omega)^2+\gamma^2}$$

4 Bloch vector

4.1 The two-level system seen as a spin 1/2

The Hamiltonian of a spin $\frac{1}{2}$ $\mathbf{S}$ in interaction with a magnetic field $\mathbf{B}$ is:

$$\hat{W}_{\mathbf{B}\cdot\mathbf{S}} = -\gamma_B \mathbf{B}\cdot\mathbf{S} = -\gamma_B(B_x S_x + B_y S_y + B_z S_z)$$

with:

$$\mathcal{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \mathcal{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \mathcal{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

$$\hat{W}_{\mathbf{B}\cdot\mathbf{S}} = -\gamma_B \frac{\hbar}{2}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}$$

The Hamiltonian of a two-level system in interaction with an E.M. field is:

$$\hat{H} = \hat{H}_0 + \hat{W} = -\omega_0 \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} + 2\Omega_1 \cos(\omega t) \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix}$$
$$= -\omega_0\ \mathcal{S}_z + 2\Omega_1 \cos(\omega t)\ \mathcal{S}_x$$

Remark: The minus sign before $\hat{H}_0$ comes from the fact that in a classical representation of a real spin 1/2, the spin tends to be parallel to the static magnetic field $\mathbf{B_0}$. It results that, in the Bloch sphere representation, the $|+\rangle$ state is at the top of the sphere. In the case of the two-level system, it is the opposite: the effective magnetic field brings the system into the ground state $|a\rangle$ that corresponds to the top of the Bloch sphere.

It is equivalent to the Hamiltonian of a spin 1/2 in a magnetic field

$$\mathbf{B} = -2(\Omega_1/\gamma_B)\cos(\omega t)\ \mathbf{e}_x + (\omega_0/\gamma_B)\ \mathbf{e}_z = 2B_1\cos(\omega t)\ \vec{e}_x - B_0\ \vec{e}_z$$

Hamiltonians $\hat{H}_0$ and $\hat{W}$ can therefore be considered like Hamiltonians describing the interaction of a fictitious spin with magnetic fields B_0 and $2B_1\cos(\omega t)$, respectively parallel to Oz and Ox, and of amplitudes such as the Larmor precession-frequencies of the spin around these two fields are ω_0 and $2\Omega_1\cos(\omega t)$. The time evolution of a spin $\mathbf{S}$ in a magnetic field is given by:

$$\frac{\mathrm{d}\mathbf{S}}{\mathrm{d}t} = \gamma_B\ \mathbf{S}\times\mathbf{B}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\mathcal{S}_x\\ \mathcal{S}_y\\ \mathcal{S}_z\end{pmatrix} = \gamma_B \begin{pmatrix}\mathcal{S}_x\\ \mathcal{S}_y\\ \mathcal{S}_z\end{pmatrix} \times \begin{pmatrix}2B_1\cos(\omega t)\\ 0\\ -B_0\end{pmatrix}$$

$$= \gamma_B \begin{pmatrix}-B_0\mathcal{S}_y\\ 2B_1\cos(\omega t)\mathcal{S}_z + B_0\mathcal{S}_x\\ -2B_1\cos(\omega t)\mathcal{S}_y\end{pmatrix} = \begin{pmatrix}+\omega_0\mathcal{S}_y\\ -2\Omega_1\cos(\omega t)\mathcal{S}_z - \omega_0\mathcal{S}_x\\ +2\Omega_1\cos(\omega t)\mathcal{S}_y\end{pmatrix}$$

4.2 Definition of the Bloch vector

The Bloch vector is defined as the expectation value of a dimensionless spin-vector:

$$\mathbf{U} = (u, v, w) = \left\langle \hat{\mathbf{S}} \right\rangle$$

The three components of $\hat{\mathbf{S}}$ are the Pauli matrices

$$\mathcal{S}_x = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\ ,\ \mathcal{S}_y = \frac{1}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\ ,\ \mathcal{S}_z = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

Using the properties of the density-matrix, we find

$$u = \mathrm{Tr}(\hat{\sigma}\cdot\mathcal{S}_x) = \frac{1}{2}(\sigma_{ab} + \sigma_{ba})$$

$$v = \mathrm{Tr}(\hat{\sigma}\cdot\mathcal{S}_y) = \frac{1}{2i}(\sigma_{ba} - \sigma_{ab})$$

$$w = \mathrm{Tr}(\hat{\sigma}\cdot\mathcal{S}_z) = \frac{1}{2}(\sigma_{aa} - \sigma_{bb})$$

and:

$$u + iv = \sigma_{ba}$$

$$u - iv = \sigma_{ab}$$

By use of the OBE:

$$\left|\begin{aligned}
\frac{\mathrm{d}\sigma_{aa}}{\mathrm{d}t} &= -i\frac{\Omega_1}{2}(\sigma_{ba} - \sigma_{ab})\ \cos(\omega t) + \Gamma_{ba}\ (1 - \sigma_{aa})\\
\frac{\mathrm{d}\sigma_{bb}}{\mathrm{d}t} &= i\frac{\Omega_1}{2}(\sigma_{ba} - \sigma_{ab})\ \cos(\omega t) - \Gamma_{ba}\ \sigma_{bb}\\
\frac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t} &= -i\frac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})\ \cos(\omega t) + i(\omega_0 + i\gamma)\ \sigma_{ab}\\
\frac{\mathrm{d}\sigma_{ba}}{\mathrm{d}t} &= i\frac{\Omega_1}{2}(\sigma_{bb} - \sigma_{aa})\ \cos(\omega t) - i(\omega_0 - i\gamma)\ \sigma_{ba}
\end{aligned}\right.$$

we calculate the time-derivative of **U**:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}u\\ v\\ w\end{pmatrix}=\begin{pmatrix}+\omega_0 v\\ -2w\Omega_1\cos(\omega t)-\omega_0 u\\ +2v\Omega_1\cos(\omega t)\end{pmatrix}$$

The time-evolution of the Bloch-vector is equivalent to the motion of a dimensionless spin interacting with an effective magnetic field. If we include the relaxation terms:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}u\\ v\\ w\end{pmatrix}=\begin{pmatrix}+\omega_0 v-\gamma\ u\\ -2w\Omega_1\cos(\omega t)-\omega_0 u-\gamma\ v\\ +2v\Omega_1\cos(\omega t)-\Gamma_{ba}(w-\frac{1}{2})\end{pmatrix}$$

4.3 Geometrical representation

A general state of a two-level system can be written:

$$|\psi\rangle=\cos\frac{\theta}{2}\ e^{-i\phi/2}\,|a\rangle+\sin\frac{\theta}{2}\ e^{+i\phi/2}\,|b\rangle$$

The corresponding density-matrix is:

$$\hat{\sigma}=\begin{pmatrix}|C_a|^2 & C_aC_b^*\\ C_bC_a^* & |C_b|^2\end{pmatrix}=\begin{pmatrix}\cos^2\frac{\theta}{2} & \sin\frac{\theta}{2}\cos\frac{\theta}{2}e^{-i\phi}\\ \sin\frac{\theta}{2}\cos\frac{\theta}{2}e^{+i\phi} & \sin^2\frac{\theta}{2}\end{pmatrix}=\begin{pmatrix}\cos^2\frac{\theta}{2} & \frac{1}{2}\sin\theta\ e^{-i\phi}\\ \frac{1}{2}\sin\theta\ e^{+i\phi} & \sin^2\frac{\theta}{2}\end{pmatrix}$$

$$\begin{aligned}u&=\frac{1}{2}(\sigma_{ab}+\sigma_{ba})=\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left(\frac{e^{+i\phi}+e^{-i\phi}}{2}\right)=\frac{1}{2}\sin\theta\cos\phi\\ v&=\frac{1}{2i}(\sigma_{ba}-\sigma_{ab})=\sin\frac{\theta}{2}\cos\frac{\theta}{2}\left(\frac{e^{+i\phi}-e^{-i\phi}}{2i}\right)=\frac{1}{2}\sin\theta\sin\phi\\ w&=\frac{1}{2}(\sigma_{aa}-\sigma_{bb})=\frac{1}{2}\left(\cos^2\frac{\theta}{2}-\sin^2\frac{\theta}{2}\right)=\frac{1}{2}\cos\theta\end{aligned}$$

$$|\boldsymbol{U}|=\sqrt{u^2+v^2+w^2}=\sqrt{\frac{1}{4}\sin^2\theta\left(\cos^2\phi+\sin^2\phi\right)+\frac{1}{4}\cos^2\theta}=\frac{1}{2}$$

The tip of the Bloch vector spans the surface of a sphere the radius of which is $\frac{1}{2}$. The angles θ and ϕ are the polar coordinates of **U**. The projection of **U** on the vertical axis gives the population difference while the projection in the transverse plane gives the complex representation of the coherence. The stationnary states $|a\rangle$ and $|b\rangle$ correspond to the sphere poles A and B, respectively.

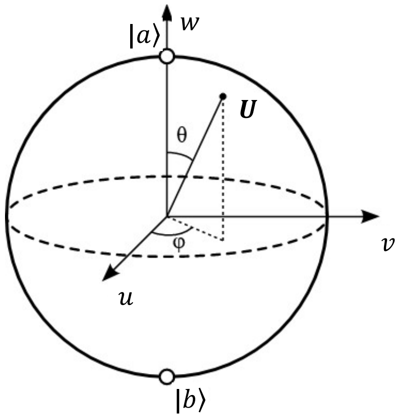


Figure 1: Sketch of the Bloch vector $\mathbf{U}$ describing a pure state of a two-level system.

5 Applications

5.1 Free evolution (No applied E.M. field)

Without relaxations

$$\left|\begin{array}{lcl} \dot{u} & = & +\omega_0 v \\ \dot{v} & = & -\omega_0 u \\ \dot{w} & = & 0 \end{array}\right.$$

We solve the system by substituting $\dot{v} = +\ddot{u}/\omega_0$:

$$\begin{aligned} \ddot{u} + \omega_0^2 u = & \quad 0 \\ \ddot{v} + \omega_0^2 v = & \quad 0 \\ w = & \quad w(0) \end{aligned}$$

The solutions are:

$$\left|\begin{array}{rl} u(t) = & u(0)\cos(\omega_0 t + \alpha_0) \\ v(t) = & -u(0)\sin(\omega_0 t + \alpha_0) \\ w(t) = & w(0) \end{array}\right.$$

At $t = 0$, the projection of $\mathbf{U}$ in the Bloch-sphere are:

$$u = \frac{1}{2}\sin\theta_0\cos\phi_0$$
$$v = \frac{1}{2}\sin\theta_0\sin\phi_0$$
$$w = \frac{1}{2}\cos\theta_0$$

We deduce that:

$$\left|\begin{array}{rl} u(t) = & \frac{1}{2}\sin\theta_0\cos(\omega_0 t+\phi_0) \\ v(t) = & \frac{1}{2}\sin\theta_0\sin(\omega_0 t+\phi_0-\pi) \\ w(t) = & \frac{1}{2}\cos\theta_0 \end{array}\right.$$

$$\sigma_{ab}(t) = u(t) - iv(t) = \frac{1}{2}\sin\theta_0\left[\cos(\omega_0 t+\phi_0) + i\sin(\omega_0 t+\phi_0)\right] = \sigma_{ab}(0)e^{i(\omega_0 t+\phi_0)} = \sigma_{ba}^*(t)$$

The population of $|a\rangle$ and $|b\rangle$ remains constant but the coherences are rotating around Oz at the frequency ω_0

With relaxations

$$\left|\begin{array}{rl} \dot{u} = & +\omega_0 v - \gamma\ u \\ \dot{v} = & -\omega_0 u - \gamma\ v \\ \dot{w} = & -\Gamma_{ba}(w - \frac{1}{2}) \end{array}\right.$$

It can be shown that:

$$\left|\begin{array}{rl} u(t) = & \frac{1}{2}\sin\theta_0\cos(\omega_0 t+\phi_0)e^{-\gamma t} \\ v(t) = & \frac{1}{2}\sin\theta_0\sin(\omega_0 t+\phi_0-\pi)e^{-\gamma t} \\ w(t) = & \frac{1}{2}+\frac{1}{2}(\cos\theta_0 - 1)e^{-\Gamma_{ba}t} \end{array}\right.$$

The General solution of $\dot{w} + \Gamma_{ba} w = 0$ is $w(t) = Ae^{-\Gamma_{ba}t}$. A particular solution when $\dot{w} = 0$ is $w = 1/2$. The constant A is determined by using the initial condition $w(0) = 1/2\ \cos\theta_0$.

$$\lim_{t\to+\infty} w(t) = \lim_{t\to+\infty}\frac{1}{2}(\sigma_{aa}-\sigma_{bb}) = \frac{1}{2}$$

5.2 Two-level system driven by the E.M. field

Rotating frame transformation

$\mathbf{U}$ obeys the equation:

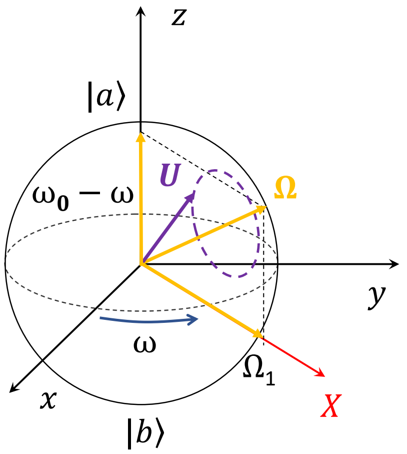


Figure 2: Precession of the Bloch vector $\mathbf{U}$ around the effective magentic field $\boldsymbol{\Omega}$. $\boldsymbol{\Omega}$ is constant in the rotating frame.

$$\frac{\mathrm{d}\mathbf{U}}{\mathrm{d}t} = \gamma_B \mathbf{U} \times \mathbf{B} = \mathbf{U} \times [+\omega_0 \mathbf{e}_z - 2\Omega_1 \cos(\omega t)\mathbf{e}_x]$$

Let be $\mathcal{R}'$ the frame rotating around the z axis with the frequency ω. Then, we can write:

$$\left(\frac{\mathrm{d}\mathbf{U}}{\mathrm{d}t}\right)_{\mathcal{R}} = \left(\frac{\mathrm{d}\mathbf{U}}{\mathrm{d}t}\right)_{\mathcal{R}'} + \omega \mathbf{e}_z \times \mathbf{U}$$

The field $2B_1 \cos(\omega t)$, parallel to Ox, can be split into two fields, of the same amplitude B_1 rotating in the xOy plane at the frequency ω in the forward and in the reverse directions. If $\omega \simeq \omega_0$, the component rotating in the direct direction accompanies the spin in its Larmor precession around B_0 and can therefore efficiently act on it, while the other component spins a too fast compared to the spin (at the frequency - 2ω) to have a substantial effect. In the frame $OXYZ$, in rotation around Oz at the frequency ω, the rotating component that we conserve becomes a constant component $B_1 \mathbf{e}_X$.

$$\left(\frac{\mathrm{d}\mathbf{U}}{\mathrm{d}t}\right)_{\mathcal{R}'} = \left(\frac{\mathrm{d}\mathbf{U}}{\mathrm{d}t}\right)_{\mathcal{R}} - \omega\ \mathbf{e}_z \times \mathbf{U} = \mathbf{U} \times [(\omega_0 - \omega)\mathbf{e}_z - \Omega_1 \mathbf{e}_X]$$

The components $(\tilde{u}, \tilde{v}, \tilde{w})$ of $\mathbf{U}$ in the rotating frame $\mathcal{R}'$ obey the system of equations:

$$\left|\begin{array}{rl}\dot{\tilde{u}} = & (\omega_0 - \omega)\ \tilde{v} - \gamma\ \tilde{u} \\ \dot{\tilde{v}} = & -\Omega_1\ \tilde{w} - (\omega_0 - \omega)\ \tilde{u} - \gamma\ \tilde{v} \\ \dot{\tilde{w}} = & \Omega_1\ \tilde{v} - \Gamma_{ba}\ (\tilde{w} - \frac{1}{2})\end{array}\right.$$

The same set of equations can be obtained from:

$$\tilde{u} = \frac{1}{2}\ (\tilde{\sigma}_{ab} + \tilde{\sigma}_{ba})$$
$$\tilde{v} = \frac{1}{2i}\ (\tilde{\sigma}_{ba} - \tilde{\sigma}_{ab})$$
$$\tilde{w} = \frac{1}{2}\ (\tilde{\sigma}_{aa} - \tilde{\sigma}_{bb})$$

By analogy with a classical field, we can write:

$$\frac{\mathrm{d}\tilde{\mathbf{U}}}{\mathrm{d}t} = \mathbf{\Omega} \times \tilde{\mathbf{U}} = \begin{pmatrix}\Omega_x \\ \Omega_y \\ \Omega_z\end{pmatrix} \times \begin{pmatrix}\tilde{u} \\ \tilde{v} \\ \tilde{w}\end{pmatrix} = \begin{pmatrix}\Omega_y\tilde{w} - \Omega_z\tilde{v} \\ \Omega_z\tilde{u} - \Omega_x\tilde{w} \\ \Omega_x\tilde{v} - \Omega_y\tilde{u}\end{pmatrix}$$

we deduce that

$$\mathbf{\Omega} = \begin{pmatrix}\Omega_1 \\ 0 \\ \omega_0 - \omega\end{pmatrix}$$

The Bloch vector $\mathbf{U}$ is precessing around the effective magnetic field Ω_1 with the frequency $\Omega = \sqrt{\Omega_1^2 + (\omega_0 - \omega)^2}$. $\mathbf{\Omega}$ is in the (X, Z) plane of the rotating frame and α is the angle between $\mathbf{\Omega}$ and Oz with

$$\sin\alpha = \frac{\Omega_1}{\Omega} \text{ and } \cos\alpha = \frac{OH}{1/2}$$

During the precession, the projection of $\mathbf{U}$ oscillates around $\tilde{w}_0$ between $\tilde{w}_0 - \delta\tilde{w}$ and $\tilde{w}_0 + \delta\tilde{w}$ at the frequency Ω.

$$\tilde{w}(t) = w_0 + \delta\tilde{w}\ \cos(\Omega t)$$

This expression is compatible with an initial condition for which the system is in its ground state and

$$\tilde{w}(0) = \frac{1}{2} = w_0 + \delta\tilde{w}$$

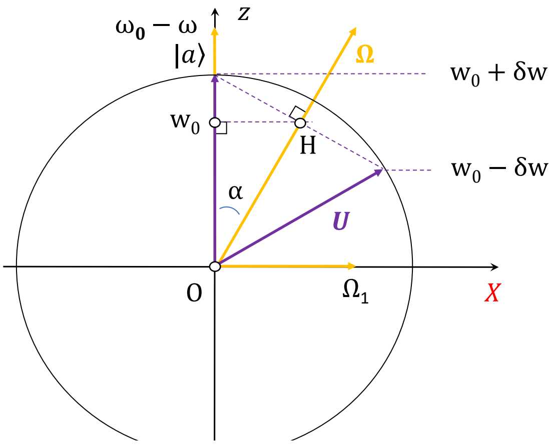


Figure 3: Geometrical determination of $\tilde{w}(t)$.

w_0 is the projection of OH on Oz so, consequently:

$$w_0 = \frac{1}{2}\cos^2\alpha$$

and

$$\delta\tilde{w} = \frac{1}{2} - \frac{1}{2}\cos^2\alpha = \frac{1}{2}\sin^2\alpha$$

Finally, we can write the time-evolution of $\tilde{w}$:

$$\tilde{w}(t) = \frac{1}{2}\left(\cos^2\alpha + \sin^2\alpha\cos(\Omega t)\right) = \frac{1}{2}(\tilde{\sigma}_{aa} - \tilde{\sigma}_{bb}) = \frac{1}{2}(1 - 2\tilde{\sigma}_{bb})$$

$$\tilde{\sigma}_{bb} = \frac{1}{2}\left(1 - \cos^2\alpha - \sin^2\alpha\ \cos(\Omega t)\right) = \frac{1}{2}\sin^2\alpha\left(1 - \cos(\Omega t)\right)$$

$$\tilde{\sigma}_{bb} = \left(\frac{\Omega_1}{\Omega}\right)^2 \sin^2\left(\frac{\Omega}{2}t\right) = \frac{\Omega_1^2}{\Omega_1^2 + (\omega_0 - \omega)^2}\sin^2\left(\sqrt{\Omega_1^2 + (\omega_0 - \omega)^2}\frac{t}{2}\right)$$

Resonance

When $\omega = \omega_0$, the E.M. field is resonant with the atomic transition and

$$\mathbf{\Omega} = \begin{pmatrix} \Omega_1 \\ 0 \\ 0 \end{pmatrix}$$

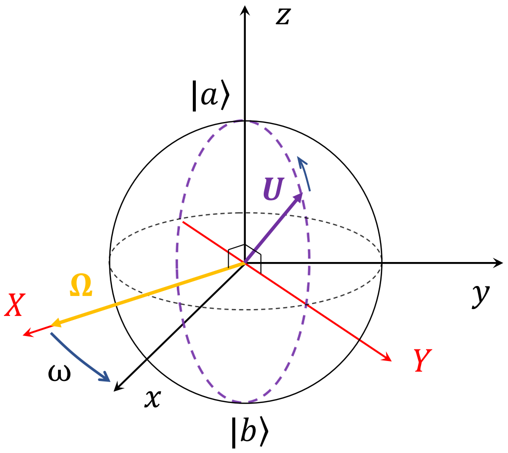


Figure 4: When the two-level system is driven by a resonant E.M. field, the Bloch vector $\mathbf{U}$ performs a precession in the vertical plane (Y, Z) of the rotating frame.

The time-evolution of $\mathbf{U}$ is given by

$$\left| \begin{array}{rl} \dot{\tilde{u}} = & 0 \\ \dot{\tilde{v}} = & -\Omega_1 \ \tilde{w} \\ \dot{\tilde{w}} = & \Omega_1 \ \tilde{v} \end{array} \right.$$

It is easy to find that

$$\left| \begin{array}{rl} \tilde{u} = & 0 \\ \tilde{v} = & -\dfrac{1}{2}\sin\Omega_1 t \\ \tilde{w} = & \dfrac{1}{2}\cos\Omega_1 t \end{array} \right.$$

$\mathbf{\Omega}$ is along the OX axis of the rotating frame and $\mathbf{U}$ precesses around $\mathbf{\Omega}$, in the (Y, Z) plane, at the Rabi-frequency Ω_1. The population of the excited state is

$$\tilde{\sigma}_{bb} = \sin^2\left(\frac{\Omega_1}{2} t\right)$$

Chapter 4: Optical transition in atoms: the case of hydrogen

December 1, 2022

Contents

1 Introduction

In previous chapters, we have seen that the interaction between an atom and an E.M. field is described, in the semi-classical model, by the electric-dipole operator:

$$\hat{W}_{DE} = -\hat{\mathbf{d}} \cdot \boldsymbol{\mathcal{E}}_0 \cos \omega t$$

According to the time-dependent perturbation theory, the probability to perform an optical transition from an initial state $|i\rangle$ to the final state $|f\rangle$, under the influence of this operator, is:

$$\mathcal{P}_{if} = \frac{d_{fi}^2}{\hbar^2} \cdot \frac{|\mathcal{E}(\mathbf{r}_0)|^2}{4} \left| \frac{1 - e^{i(\omega_{fi}+\omega)t}}{\omega_{fi}+\omega} + \frac{1 - e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega} \right|^2$$

The ω-dependent term has been studied in previous chapters. It takes substancial values when the frequency of the field is close to the Bohr-frequency of the atomic transition. The transition probability is large when:

$$\omega = \pm \omega_{fi}$$

However, this condition is necessary but not sufficient.To occur, a transition between $|i\rangle$ and $|f\rangle$ must satisfy:

$$d_{fi} = q \langle f|r|i\rangle \neq 0$$

It is the role of the selection rules for electric– dipole transitions to specify the transitions that may occur between the states of interest. They are based on an examination of the transition dipole moment. If the latter is different fom zero, the transition is said to be **allowed**. In the opposite situation, it is **forbidden**.

The value of $\langle f|r|i\rangle$ depends on the symetries of the wavefunctions associated with $|i\rangle$ and $|f\rangle$. A general case of forbidden transition is when the wavefunctions $\psi_i(\mathbf{r})$ and $\psi_f(\mathbf{r})$, associated with $|i\rangle$ and $|f\rangle$, have same parity. It involves that their product is even and:

$$\langle f|r|i\rangle = \int \psi_f(\mathbf{r})^* \psi_i(\mathbf{r}) d^3\mathbf{r} = 0$$

A transition can only occur between states with different parities and must conserve some physical quantities that characterize $|i\rangle$ and $|f\rangle$(such as energy, orbital momentum, spin...) to insure the matrix element of $\hat{r}$ to be non-zero.. The **optical selection rules** express these conservation laws in the form of mathematical relations between the values of the quantum numbers characterizing the initial state and the values of the equivalent quantum numbers associated with the final state,

2 Eigenstates and eigenfunctions

The eigenstates of the hydrogen atom are characterized by three quantum numbers (the electron-spin will be considered later): n, ℓ and m.

- n is the principal quantum number. It is an integer different from 0 and is associated with the energy eigenvalues:

$$E_n = -\frac{E_1}{n^2} \text{ with } E_1 = 13,6 \text{ eV}$$

- ℓ is the azimuthal quantum number. It is the angular momentum in unit of $\hbar$.
- m is the magnetic quantum number. It is the projection, in unit of $\hbar$, of ℓ on an axis of quantization.

The wavefunction is the product of a radial part by an angular part:

$$\psi_{n,\ell,m} = R_{n,\ell}\; Y_\ell^m(\theta,\varphi)$$

$Y_\ell^m(\theta,\varphi)$ is a spherical harmonic and is eigenstate of the anfugular momentum operator:

$$\hat{L}^2 Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2\; Y_\ell^m(\theta,\varphi)$$

and of its projection along a quantization axis:

$$\hat{L}_z Y_\ell^m(\theta,\varphi) = m\hbar\; Y_\ell^m(\theta,\varphi)$$

The first spherical harmonics are

$$\boxed{\begin{aligned} Y_0^0 &= \frac{1}{\sqrt{4\pi}} \\ Y_1^0 &= \sqrt{\frac{3}{4\pi}}\cos\theta \\ Y_1^{\pm 1} &= \mp\sqrt{\frac{3}{8\pi}}\sin\theta\; e^{\pm i\varphi} \end{aligned}}$$

These expression are useful to express $\cos\theta$ and $\sin\theta\; e^{i\varphi}$ as a function of Y_ℓ^m.

3 Optical Transitions

3.1 Linearly polarized light

We consider a hydrogen atom located at $r = 0$ submitted to a light linearly-polarized along the z axis:

$$\mathcal{E}(0,t) = \mathcal{E}_0 \cos \omega t \ \mathbf{e}_z$$

The interaction with the E.M.field is described by the electric-dipole operator:

$$\hat{W}_{DE} = -q\hat{z}\mathcal{E}_0 \cos \omega t = \hat{W}_{DE} = -q\hat{z}\mathcal{E}_0 \frac{e^{i\omega t} + e^{-i\omega t}}{2}$$

$|i\rangle = |n_i, \ell_i, m_i\rangle$ and $|f\rangle = |n_f, \ell_f, m_f\rangle$ being the initial and final states, respectively, the matrix element associated with the corresponding transition is:

$$\langle f|\hat{W}_{DE}|i\rangle = -q\frac{\mathcal{E}_0}{2} \langle n_f, \ell_f, m_f|\hat{z}|n_i, \ell_i, m_i\rangle \, e^{i\omega t}$$

$$- q\frac{\mathcal{E}_0}{2} \langle n_f, \ell_f, m_f|\hat{z}|n_i, \ell_i, m_i\rangle \, e^{-i\omega t}$$

If we agree to choose $\omega \geq 0$, the first term in the right-hand side is resonant for $\omega_{fi} < 0$ (stimulated emission) while the second term is resonant for $\omega_{fi} > 0$ (absorption).

$$\langle f|\hat{W}_{DE}|i\rangle \propto -q\mathcal{E}_0 \int r^2 \sin\theta \mathrm{d}r \ \mathrm{d}\theta \ \mathrm{d}\varphi z R^*_{n_f,\ell_f}(r) R_{n_i,\ell_i}(r) Y^{n_f*}_{\ell_f}(\theta,\varphi) Y^{n_i}_{\ell_i}(\theta,\varphi)$$

In spherical coordinates, the expression of z is:

$$z = r\cos\theta$$

and $\cos\theta$ can be written as a function of the spherical harmonics:

$$z = r\cos\theta = r\sqrt{\frac{4\pi}{3}} Y^0_1(\theta,\varphi)$$

$$\langle f|\hat{W}_{DE}|i\rangle \propto -q\mathcal{E}_0 \sqrt{\frac{4\pi}{3}} \int R^*_{n_f,\ell_f}(r) \, R_{n_i,\ell_i}(r) \, r^3 \mathrm{d}r \times$$

$$\int \sin\theta \mathrm{d}\theta \mathrm{d}\varphi \ Y^{m_f*}_{\ell_f}(\theta,\varphi) \, Y^0_1(\theta,\varphi) \, Y^{m_i}_{\ell_i}(\theta,\varphi)$$

It can be shown that the integral is non-zero when:

$$\begin{cases} \ell_f = & \ell_i \pm 1 \\ m_f = & m_i \end{cases}$$

Example
The initial state is $|n = 2, \ell = 1, m\rangle$

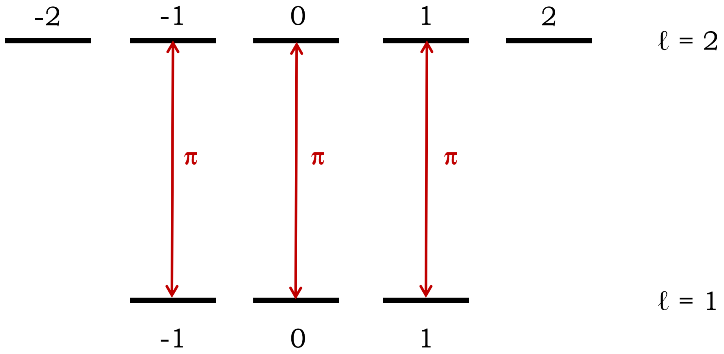


Figure 1: Optical selection rules between the states $|2, 1, m\rangle$ and $|2, 2, m\rangle$ of the hydrogen atom for a linearly-polarized light.

3.2 Circularly polarized light

We consider a light the electric field of which is:

$$\mathcal{E}(0,t) = \frac{\mathcal{E}_0}{\sqrt{2}} \left[\cos\omega t \ \mathbf{e}_x + \sin\omega t \ \mathbf{e}_y\right]$$

This field is rotating at the angular frequency ω in the anticlockwise direction around the z axis. The electric dipole operator of a σ^+- polarized light is

$$\begin{aligned}\hat{W}_{DE} &= q\frac{\mathcal{E}_0}{\sqrt{2}} \left[\hat{x}\cos\omega t + \hat{y}\sin\omega t\right] = q\frac{\mathcal{E}_0}{\sqrt{2}} \left[\hat{x}\ \frac{e^{i\omega t} + e^{-i\omega t}}{2} + \hat{y}\ \frac{e^{i\omega t} - e^{-i\omega t}}{2i}\right] \\ &= q\frac{\mathcal{E}_0}{\sqrt{2}} \left[(\hat{x} - i\hat{y})\,\frac{e^{\,i\omega t}}{2} + (\hat{x} + i\hat{y})\,\frac{e^{\,-i\omega t}}{2}\right] = \hat{W}^+\ e^{i\omega t} + \hat{W}^-\ e^{-i\omega t}\end{aligned}$$

If we agree to choose $\omega \geq 0$, the first term in the bracket is resonant for $\omega_{fi} < 0$ (stimulated emission) while the second term is resonant for $\omega_{fi} > 0$

(absorption).

$$\langle f|\hat{W}^{+}|i\rangle \propto -q\frac{E_0}{\sqrt{2}}\langle n_f,\ell_f,m_f|\hat{x}+i\hat{y}|n_i,\ell_i,m_i\rangle$$

$$= \int r^2\sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi R^{*}_{n_f,\ell_f}(r)\,Y_{\ell_f}^{m_f *}(\theta,\varphi)\,(\hat{x}+i\hat{y})\,R_{n_i,\ell_i}(r)\,Y_{\ell_i}^{m_i}(\theta,\varphi)$$

In spherical coordinates:

$$\hat{x}+i\hat{y} = \hat{r}\sin\theta\cos\varphi + i\hat{r}\sin\theta\sin\varphi = \hat{r}\sin\theta\ e^{i\varphi}$$

By use of:

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\ e^{\pm i\varphi}$$

we express the operator as:

$$\hat{x}+i\hat{y} = -\hat{r}\sqrt{\frac{8\pi}{3}}Y_1^1(\theta,\varphi)$$

and

$$\langle f|\hat{W}^{+}|i\rangle = \int R^{*}_{n_f,\ell_f}(r)\,R_{n_i,\ell_i}\ r^3\mathrm{d}r$$

$$\times\int Y_{\ell_f}^{m_f *}(\theta,\varphi)\,Y_1^1(r)\,Y_{\ell_i}^{m_i}(\theta,\varphi)\ \ \sin\theta\mathrm{d}\theta\mathrm{d}\varphi$$

It can be shown that the integral is non-zero when:

$$\begin{cases} \ell_f = & \ell_i \pm 1 \\ m_f = & m_i + 1 \end{cases}$$

For a σ^- polarized light:

$$\begin{cases} \ell_f = & \ell_i \pm 1 \\ m_f = & m_i - 1 \end{cases}$$

Normal Zeeman effet

The application of an external static magnetic field $\mathbf{B}_0$ along the quantization axis is described by the Zeeman Hamiltonian:

$$\hat{H}_Z = -\gamma_e \ell_z B_0$$

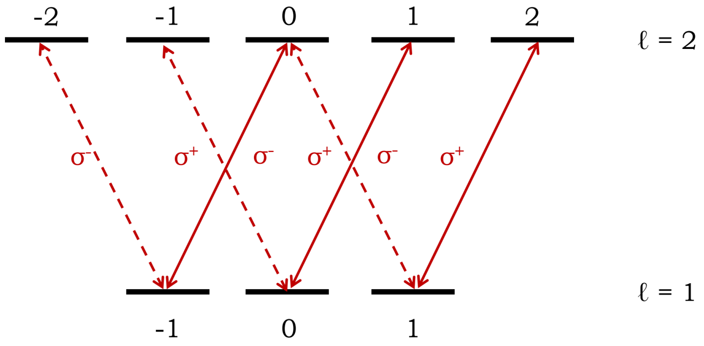


Figure 2: Optical selection rules between the states $|2,1,m\rangle$ and $|2,2,m\rangle$ of the hydrogen atom for a circularly-polarized light.

The first-order correction to the energy of the m_ℓ state of the $\ell = 1$ level is therefore:

$$\langle \ell, m_\ell | \hat{H}_Z | \ell, m_\ell \rangle = -\gamma_e m_l \hbar B_0 = \mu_B m_\ell B_0$$

where μ_B is the Bohr magneton[1].

We have already seen that transitions with different values of Δm_ℓ correspond to different polarization of electromagnetic radiation. In the present case, an observer perpendicular to the magnetic field sees that the outer lines of the trio (those corresponding to $\Delta m_\ell = \pm 1$ are circularly polarized in opposite senses. These lines are called the $\sigma-$lines. The central line (which is due to $\Delta m_\ell = 0$) is linearly polarized parallel to the applied field. It is called the $\pi-$line.

4 Fine structure

4.1 Spin-orbit coupling

The electron moves at a velocity $\mathbf{v}$ in the electrostatic field $\mathbf{E}$ of the proton. Special relativity indicates that the electron undergoes a magnetic field in its

---

[1] For the electron $\gamma_e = q/2m < 0$ and μ_B>0

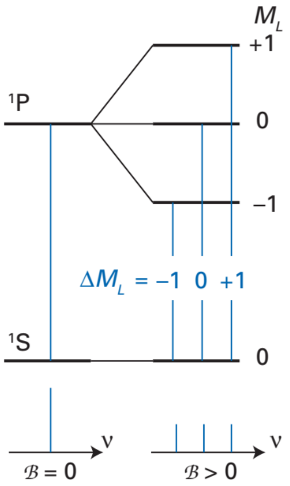


Figure 3: The splitting of energy levels of an atom in the normal Zeeman effect, and the splitting of the transitions into three groups of coincident lines.

rest frame:

$$\mathbf{B} = -\frac{1}{c^2}\mathbf{v} \times \mathbf{E} \propto \mathbf{p} \times \mathbf{r} = \mathbf{L}$$

The electron possesses an intrinsic magnetic moment $\mathbf{M}_s = q\frac{\mathbf{S}}{m_e}$ that interacts with the field $\mathbf{B}$.

The corresponding interaction energy is written

$$\hat{W} = -\mathbf{M}_s \cdot \mathbf{B} \propto \mathbf{L} \cdot \mathbf{S}$$

It can be shown that the spin-orbit operator takes the form:

$$\hat{H}_{so} = \xi(r)\mathbf{L} \cdot \mathbf{S}$$

The spin orbit interaction modifies the previous energy spectrum by lifting some of the degeneracy of the states relatively to the orbital momentum. The wavefunctions that diagonalize $\hat{H}_0 + \hat{H}_{so}$ are the eigenstate of the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The eigenvalues j of $\hat{\mathbf{J}}$ are integer numbers ranging from $|\ell - s|$ to $\ell + s$. The projection of $\hat{\mathbf{J}}$ along the quantization axis is called m_j. For each eigenvalue j of $\hat{\mathbf{j}}$, m_j is an integer such as $-j \leq m_j \leq j$.

$$\begin{aligned} |\ell - s| \leq \quad j \quad &\leq \quad \ell + s \\ -j \leq \quad m_j \quad &\leq \quad j \end{aligned}$$

Each level is characterized by a **spectroscopic term**:$^{2s+1}\{l\}_j$ where l is a letter corresponding to the value of ℓ (s,p,d...) and $2s+1$ is the multiplicity. For example, the four-fold degenerate $|\ell = 1, s = 1/2\rangle$ state of the hydrogen atom is split into $^2p_{3/2}$ and $^2p_{1/2}$.

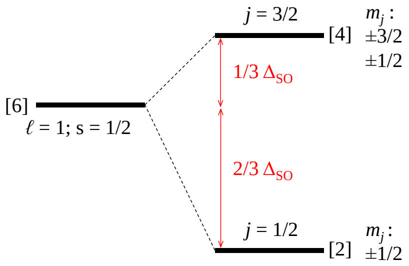


Figure 4: The splitting of the states of a p-electron by spin–orbit coupling.

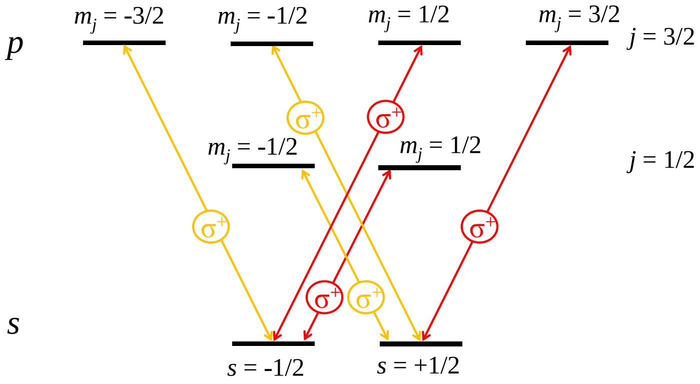


Figure 5: Optical selection rules for a circularly-polarized light.

Regarding the order of magnitude of Δ_{SO}, for a hydrogen 2p-electron the splitting is $\Delta_{SO} \simeq 45.10^{-6}$ eV. In condensed matter, the splitting due to the spin-orbit interaction can reach several hundreds of meV.

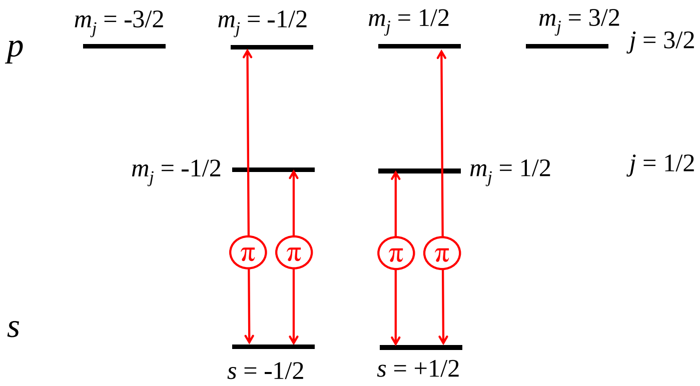


Figure 6: Optical selection rules for a linearly-polarized light.

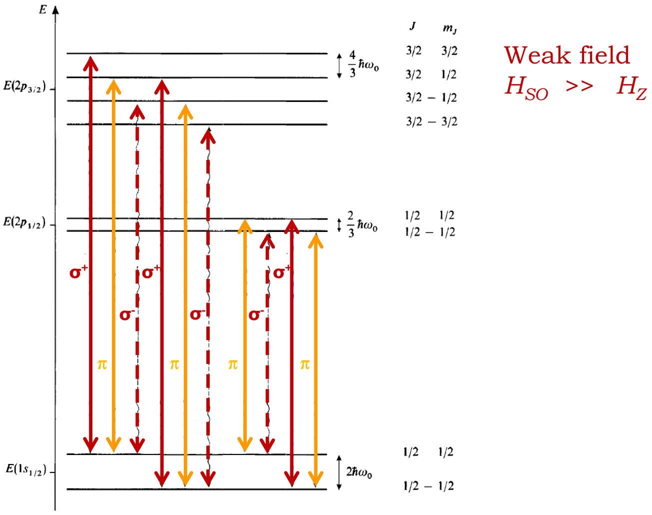
4.2 Anomalous Zeeman effect

A magnetic field $\mathbf{B}_0$ along the quantization axis Oz lifts the state degeneracy according to the eigenvelues of the total angular momentum. The corresponding Zeeman Hamiltonian is written:

$$\hat{H}_z = \omega_0(\hat{L}_z + 2\hat{S}_z)$$

where ω_0 is the Larmor frequency $\omega_0 = -q/mB_0$. The Zeeman Hamiltonian does not mix states with different angular momentum j, it lifts the energy degeneracy between the different values of m_j within a subspace with a given j.

Remark
Note that, because the perturbing Hamiltonian does not contain any spin operators, the spin quantum number m_s cannot change during a transition. Hence, we have the additional selection rule that



C. Cohen-Tannoudji, B. Diu, F. Laloë, “Quantum mechanics”

Figure 7: Zeeman effect on the levels $n = 1$ and n fine structure of the hydrogen atom Optical selection rules between the states $|2, 1, m\rangle$ and $|2, 2, m\rangle$ of the hydrogen atom for a circularly-polarized light.

Chapter 5: Optical transition in diatomic molecules

December 1, 2022

Contents

We consider the case of the simplest molecule ever, the H_2^+ molecule. It is constituted of one electron and two protons.

1 Eigenstates

1.1 Hamiltonian

The full Hamiltonian is

$$\hat{H}_0 = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_e^2}_{\text{electron kinetic energy}} \underbrace{-\frac{\hbar^2}{2M_1}\nabla_1^2 - \frac{\hbar^2}{2M_2}\nabla_2^2}_{\text{Nuclei kinetic energy}} + \underbrace{V(r, R_1, R_2)}_{\text{Coulomb potentiel}}$$

with

$$\begin{aligned} V(r, R_1, R_2) &= -\frac{q}{4\pi\varepsilon_0}\left[\frac{1}{(r-R_1)} + \frac{1}{(r-R_2)} + \frac{1}{(R_2-R_1)}\right] \\ &= -\frac{q}{4\pi\varepsilon_0}\left[\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{R}\right] \end{aligned}$$

We do the Born-Oppenheimer approximation: because of the large mass difference between the electron and the proton, the timescale associated with the electron motion is much smaller than the one related to the motion of protons. The electronic wavefunction is able to "follow" continuously the nuclear motion and changes in the internuclear distance do not cause electronic transitions. The nuclear position act only as a parameter that slightly modifies the electronic wavefuntion.

The electronic and nuclear motions are decoupled by writing

$$\psi(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2) = \phi(\mathbf{r}, \mathbf{R}_1, \mathbf{R}_2)\xi(\mathbf{R}_1, \mathbf{R}_2)$$

and we neglect the derivatives of ϕ relatively to R_1 and R_2:

$$-\frac{\hbar^2}{2M_j}\nabla_j^2\phi\xi = -\frac{\hbar^2}{2M_j}\left[\phi\nabla_j^2\xi + \xi\nabla_j^2\phi + 2\nabla_j\phi\nabla_j\xi\right] \simeq -\frac{\hbar^2}{2M_j}\phi\nabla_j^2\xi$$

We subsitute ψ in the Schrödinger equation:

$$\hat{H}_0\phi\xi = E\phi\xi$$

$$E\phi\xi = \left[-\frac{\hbar^2}{2m_e}\nabla_e^2\phi + V(r, R_1, R_2)\phi\right]\xi - \phi\sum_j \frac{\hbar^2}{2M_j}\nabla_j^2\xi$$

$$= E_e(R)\phi\xi - \phi\sum_j \frac{\hbar^2}{2M_j}\nabla_j^2\xi$$

ξ is solution of:

$$\left[-\sum_j \frac{\hbar^2}{2M_j}\nabla_j^2 + U(R)\right]\xi = E\xi$$

where $R = |R_2 - R_1|$ and $U(R) = E_e(R)$ is the solution of the electronic equation and plays the role of a potential energy that depends only of the internuclear distance.

1.2 Nuclear motion

The Hamiltonian of the nuclear motion is

$$\hat{H}_N = -\frac{\hbar^2}{2M_1}\nabla_1^2 - \frac{\hbar^2}{2M_2}\nabla_2^2 + U(R)$$

We express this operator in the frame of the center of mass G by setting:

$$\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$$

$$\mathbf{R}_G = (M_1\mathbf{R}_1 + M_2\mathbf{R}_2)/(M_1 + M_2)$$

$$\mathbf{R}_j = \mathbf{R}_G + \mathbf{R}\ M_j/(M_1 + M_2)$$

$\hat{H}_N$ becomes

$$\hat{H}_N = -\frac{\hbar^2}{2M}\nabla_{R_G}^2 - \frac{\hbar^2}{2\mu}\nabla_R^2 + U(R)$$

The problem is turned into the study of a fictitious particle of reduced mass $\mu = M_1^{-1} + M_2^{-1}$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + U(R)\right]\xi = E\xi$$

In the vicinity of its minimum, $U(R)$ can be expanded using a Taylor series:

$$U(R) = U(R_0) + \frac{1}{2}\left(\frac{\mathrm{d}^2U}{\mathrm{d}R^2}\right)_{R_0}(R - R_0)^2$$

Finally, we have to solve the Schrödinger equation of a a particle in a quadratic potential :

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + \frac{1}{2}\mu\omega_0^2(R - R_0)^2 - |U(R_0)|\right]\xi = E\xi$$

For the sake of convenience, we set $U(R_0) = 0$. The Laplacian is:

$$-\frac{\hbar^2}{2\mu}\nabla_R = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2}$$

The Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2} + \frac{1}{2}\mu\omega_0^2(R-R_0)^2$$

We look form the wavefunction in the form:

$$\xi_{\nu,\ell,m_\ell}(R,\theta,\varphi) = \frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

we substitute in the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R + V(R)\right]\xi_{\nu,\ell,m_\ell}(R,\theta,\varphi) = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

$$+\left[\frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + V(R)\right]\frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi) = E\frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

where we used

$$\hat{L}^2 Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2\ Y_\ell^m(\theta,\varphi)$$

By dividing both sides by $\frac{1}{R}Y_\ell^{m_\ell}$, we get

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + V(R)\right]\chi_{\nu,\ell}(R) = E_{\nu,\ell}\ \chi_\nu(R), \text{ with } V(R) = \frac{1}{2}\mu\omega_0^2(R-R_0)^2 - |U(R_0)|$$

For the sake of convenience, we set $U(R_0) = 0$.

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + \frac{1}{2}\mu\omega_0^2(R-R_0)^2\right]\chi_\nu(R) = E_{\nu,\ell}\ \chi_\nu(R)$$

Assuming

$$\frac{\hbar^2\ell(\ell+1)}{2\mu R^2} \simeq \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}$$

we get

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{1}{2}\mu\omega_0^2(R-R_0)^2\right]\chi_\nu(R) = \left[E_{\nu,\ell} - \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}\right]\ \chi_\nu(R)$$

$$\hbar\omega_0(\nu+1/2) = E_{\nu,\ell} - \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}$$

$$\boxed{E_{\nu,\ell} = \hbar\omega_0(\nu + 1/2) + \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}}$$

$\chi_\nu(R)$ is solution of the one-dimensional harmonic oscillator:

$$\chi_\nu(R) = N_\nu H_\nu(u) e^{-u^2/2}$$

where H is a Hermite polynomial, $u = (R - R_0)/\alpha$ and $\alpha = (\hbar/\mu\omega_0)^{1/2}$.

Properties of the Hermite polynomials

1. $H_\nu(u)$ is solution of $H_\nu'' - 2uH_\nu' + 2\nu H_\nu$
2. $H_{\nu+1} = 2uH_\nu - 2\nu H_{\nu-1}$ (recursivity).
3. $\int_{-\infty}^{+\infty} H_\nu H_{\nu'} e^{-u^2} \mathrm{d}u = \delta_{\nu,\nu'}$ (orthogonality).
4. $\int_{-\infty}^{+\infty} H_\nu^2 e^{-u^2} \mathrm{d}u = 2^\nu \sqrt{\pi}\nu!$

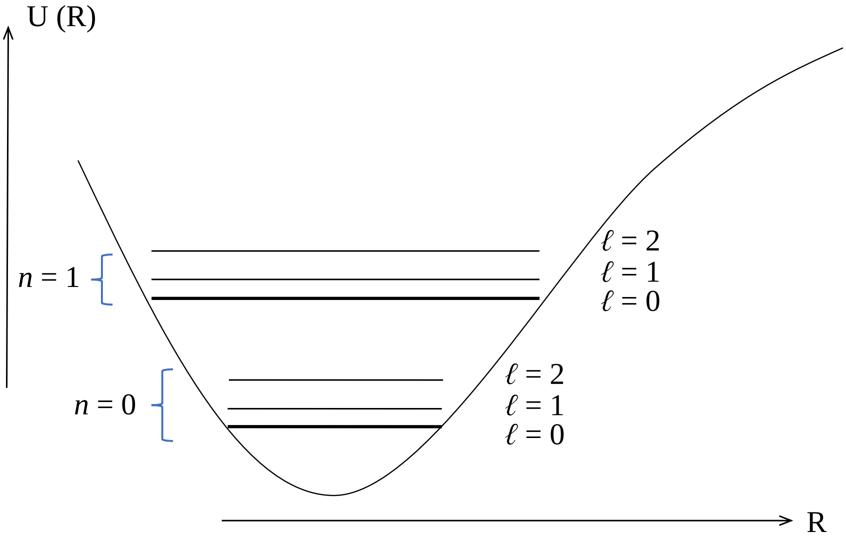


Figure 1: Eigenstate of a diatomic molecule in the electronic groundstate.

2 Selection rules

2.1 Optical transitions

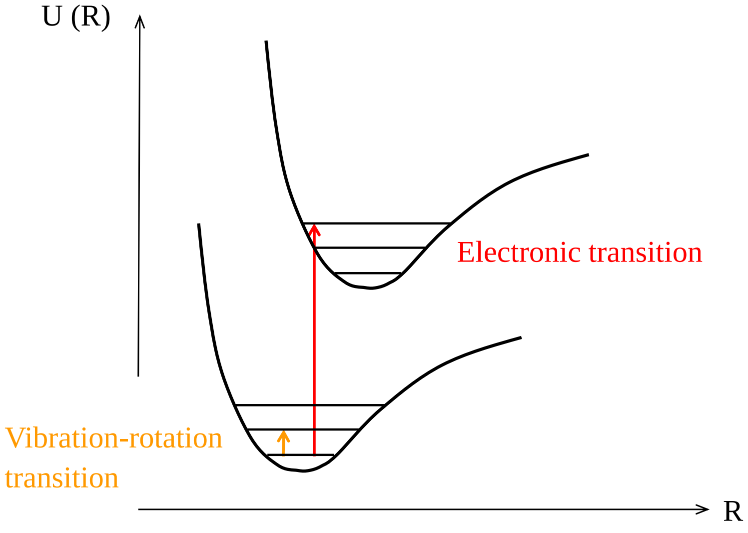


Figure 2: Possible optical transitions from the groundstate of a diatomic molecule.

2.2 Vibration-rotation transitions

The dipole moment is directed along the straight line joining the two nuclei. It can be written as an expansion in powers of R

$$d(R) = d_0 + d_1(R - R_0)$$

For a homonuclear molecule $d(R) = 0$.

Considering that:

$$\xi_{\nu,\ell,m_\ell}(R,\theta,\varphi) = \frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

and

$$\cos\theta = \sqrt{\frac{4\pi}{3}}Y_1^0$$

We can evaluate the matrix element of the dipole-moment operator

$$\langle \nu_f, \ell_f, m_{\ell,f} | d(R)\ \cos\theta | \nu_i, \ell_i, m_{\ell,i} \rangle = \sqrt{\frac{4\pi}{3}} \int_0^{+\infty} \chi^*_{\nu_f}(R) d(R) \chi_{\nu_i}(R) \mathrm{d}R$$

$$\times \int Y^{m_f *}_{\ell_f}(\theta,\varphi)\, Y^0_1(r)\, Y^{m_i}_{\ell_i}(\theta,\varphi)\ \sin\theta \mathrm{d}\theta \mathrm{d}\varphi$$

The angular part is different from zero when $\ell_f = \ell_i \pm 1$. Concerning the radial part

$$I_{\nu_i,\nu_f} = \int_0^{+\infty} \chi^*_{\nu_f}(R) d(R) \chi_{\nu_i}(R) = \int_{-\infty}^{+\infty} \chi^*_{\nu_f}(R) d(R) \mathrm{d}R \chi_{\nu_i}(R)$$

because $\chi_{\nu_i}(R) = 0$ when $R < 0$.

$$I_{\nu_i,\nu_f} = d_0 \int_{-\infty}^{+\infty} \chi^*_{\nu_f}(R) \chi_{\nu_i}(R) \mathrm{d}R \ +\ d_1 \int_{-\infty}^{+\infty} \chi^*_{\nu_f}(R)\ (R - R_0)\ \chi_{\nu_i}(R) \mathrm{d}R$$

$$= \alpha d_0 N_{\nu_f} N_{\nu_i} \int_{-\infty}^{+\infty} H^*_{\nu_f}(u) H_{\nu_i}(u) e^{-u^2} \mathrm{d}u + \alpha^2 d_1 N_{\nu_f} N_{\nu_i} \int_{-\infty}^{+\infty} H^*_{\nu_f}(u) H_{\nu_i}(u) u e^{-u^2} \mathrm{d}u$$

$$= \alpha d_0 N_{\nu_f} N_{\nu_i} \delta_{\nu_f,\nu_i} + \alpha^2 d_1 N_{\nu_f} N_{\nu_i} \int_{-\infty}^{+\infty} H^*_{\nu_f}(u) H_{\nu_i}(u) u e^{-u^2} \mathrm{d}u$$

Using the recursion relation $H_{\nu+1} = 2uH_\nu - 2\nu H_{\nu-1}$, we express:

$$\int_{-\infty}^{+\infty} H^*_{\nu_f}(u) H_{\nu_i}(u) u\ e^{-u^2} \mathrm{d}u = \int_{-\infty}^{+\infty} H^*_{\nu_f}(u) H_{\nu_i+1}(u) e^{-u^2} \mathrm{d}u$$

$$+ \nu_i \int_{-\infty}^{+\infty} H^*_{\nu_f}(u) H_{\nu_i-1}(u) e^{-u^2} \mathrm{d}u = \delta_{\nu_f,\nu_i+1} + \nu_i \delta_{\nu_f,\nu_i-1}$$

Finally

$$\boxed{I_{\nu_i,\nu_f} = \alpha d_0 N_{\nu_f} N_{\nu_i} \delta_{\nu_f,\nu_i} + \alpha^2 d_1 N_{\nu_f} N_{\nu_i} \left[\frac{1}{2}\delta_{\nu_f,\nu_i+1} + \nu \delta_{\nu_f,\nu_i-1}\right]}$$

$\langle \nu_f, \ell_f, m_{\ell,f} | d(R)\ \cos\theta | \nu_i, \ell_i, m_{\ell,i} \rangle \neq 0$ if

$$\begin{cases} \ell_f = & \ell_i \pm 1 \\ \nu_f = & \nu_i - 1,\ \nu_i + 1 \end{cases}$$

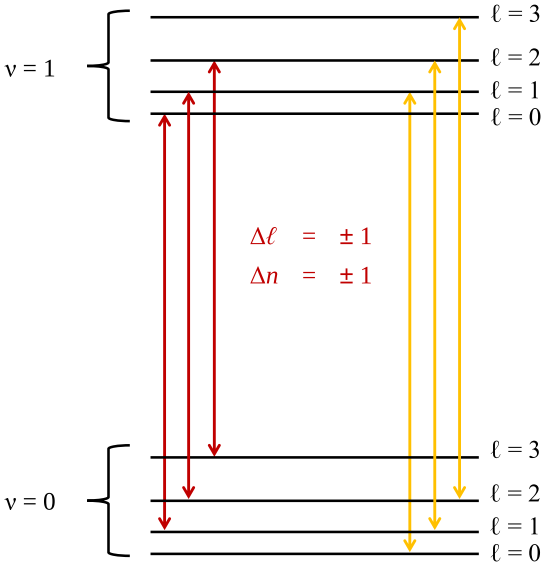


Figure 3: Sketch of the optical selection rules for vibration-rotation transition a diatomic molecule.

Form of the spectrum

Let us consider the possible transitions between an initial state

$$E_{0,\ell_i} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar^2}{2\mu R_0^2}\ell_i(\ell_i+1)$$

and a final state

$$E_{1,\ell_f} = \frac{3}{2}\hbar\omega_0 + \frac{\hbar^2}{2\mu R_0^2}\ell_f(\ell_f+1)$$

with $\Delta\ell = \pm 1$.

First case $\ell_f = \ell_i + 1$

$$E_{1,\ell_f} = \frac{3}{2}\hbar\omega_0 + \frac{\hbar^2}{2\mu R_0^2}(\ell_i+1)(\ell_i+2)$$

and

$$E_{1,\ell_f} - E_{0,\ell_i} = \hbar\omega_0 + \frac{\hbar^2}{\mu R_0^2}(\ell_i+1)$$

This condition gives rise to series of regularly spaced absorption lines, which energies are larger than $\hbar\omega_0$, and that consitute the **”R-Branch”**.

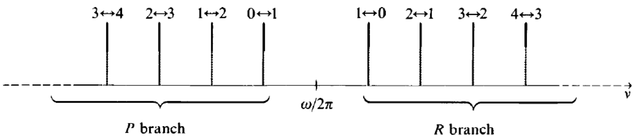
Second case $\ell_i = \ell_f + 1$

$$E_{1,\ell_f} = \frac{3}{2}\hbar\omega_0 + \frac{\hbar^2}{2\mu R_0^2}(\ell_f+1)(\ell_f+2)$$

and

$$E_{1,\ell_f} - E_{0,\ell_i} = \hbar\omega_0 - \frac{\hbar^2}{\mu R_0^2}(\ell_i+1)$$

This condition gives rise to series of regularly spaced absorption lines, which energies are smaller than $\hbar\omega_0$, and that consitute the **"Q-Branch"**.



C. Cohen-Tannoudji, B. Diu, F. Laloë, "Quantum mechanics"

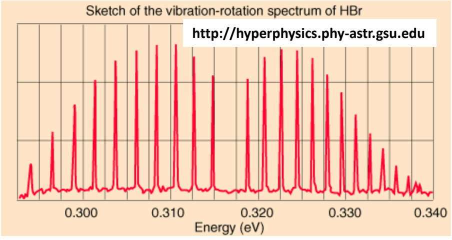
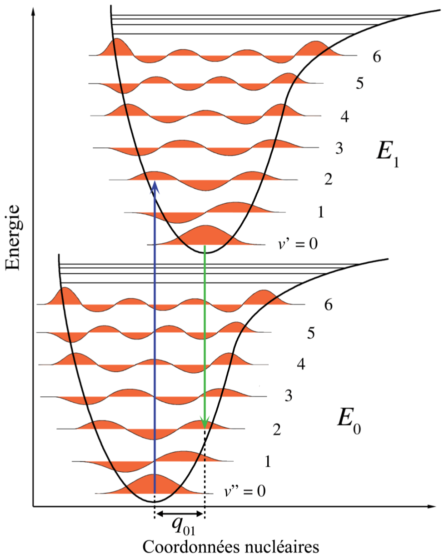


Figure 4: Theoretical and experimental absorption spectra of vibration-rotation transition. The experimantal spectrum is related to the HBr molecule.

2.3 Electronic transitions

Because nuclear masses are so much larger than the mass of an electron, an electronic transition occurs within a stationary nuclear framework and the nuclear wavefunction remains unchanged during an electronic transition. Classically, the transition occurs when the internuclear separation is equal to the equilibrium bond length R_0 of the lower electronic state, when the nuclei are stationary, and that internuclear separation and state of motion are preserved during the transition. As a result, the transition terminates where a vertical line cuts through the upper molecular potential energy curve. Then, the molecule relaxes to its new equilibrium position that correspond to the nuclear groundstate $\nu = 0$ of the excited electronic-state. This relaxation occurs by emitting phonons.



https://fr.wikipedia.org/wiki/Principe_Franck-Condon

Figure 5: Franck–Condon principle energy diagram. Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The potential wells are shown favoring transitions between $\nu = 0$ and $\nu = 2$.

In a molecule, the electric dipole moment operator depends on the locations and charges of the electrons r_i, and q, and the locations and charges of the nuclei, which we denote R_I and $Z_I q$, respectively:

$$\hat{d} = -q \sum_i \mathbf{r}_i + q \sum_I Z_I \mathbf{R}_I = \hat{d}_e(r) + \hat{d}_N(R)$$

If we assume the electric-field to be $z-$polarized, the projection of $\hat{d}$ on Oz is

$$\hat{d} \cos\theta = \sqrt{\frac{4\pi}{3}} Y_1^0(\theta, \varphi)$$

The matrix element of $\hat{d}$ between initial and final states is:

$$\langle E_f, \ell_f, \nu_f | \hat{d} | E_i, \ell_f, \nu_i \rangle =$$

$$\int \overset{*}{Y}{}_{\ell_f}^{m_f}(\theta,\varphi)\, Y_1^0(\theta,\varphi)\, Y_{\ell_i}^{m_i}(\theta,\varphi) \mathrm{d}\Omega \int \chi_{\nu_f}^*(R) \Big[\int \phi_{E_f}^*(\mathbf{r}, R) \hat{d}_e(r) \phi_{E_i}(\mathbf{r}, R) \mathrm{d}^3\mathbf{r} \Big] \chi_{\nu_i}(R) \mathrm{d}R$$

$$+ \int \overset{*}{Y}{}_{\ell_f}^{m_f}(\theta,\varphi)\, Y_1^0(\theta,\varphi)\, Y_{\ell_i}^{m_i}(\theta,\varphi) \mathrm{d}\Omega \int \chi_{\nu_f}^*(R) \hat{d}_N(R) \chi_{\nu_i}(R) \Big[\int \underbrace{\phi_{E_f}^*(\mathbf{r}, R) \phi_{E_i}(\mathbf{r}, R) \mathrm{d}^3\mathbf{r}}_{=0} \Big] \mathrm{d}R$$

$$= \delta_{\ell_f, \ell_i \pm 1}\, \delta_{m_f, m_i} \int \chi_{\nu_f}^*(R) d_{E_i, E_f}(R) \chi_{\nu_i}(R) \mathrm{d}R \simeq \delta_{\ell_f - 1, 0} d_{E_i, E_f} \int \chi_{\nu_f}^*(R) \chi_{\nu_i}(R) \mathrm{d}R$$

The integral $\langle \phi_{E_f} | \phi_{E_i} \rangle$ over the electron coordinates is zero because the electronic states are orthogonal to one another for each selected value of R. Therefore, if we assume the dipole moment to be independent of the nuclear position, the overall electric dipole transition moment is

$$\langle E_f, \ell_f, \nu_f | \hat{d} | E_i, \ell_f, \nu_i \rangle = \delta_{\ell_f, \ell_i \pm 1}\, \delta_{m_f, m_i}\, d_{E_i, E_f} \int \chi_{\nu_f}^*(R) \chi_{\nu_i}(R) \mathrm{d}R$$

The probabilitity transition from $|E_i, \ell_f, \nu_i\rangle$ to $|E_i, \ell_f, \nu_i\rangle$ is proportionnal to

$$\boxed{\Big| \langle E_f, \ell_f, \nu_f | \hat{d} | E_i, \ell_f, \nu_i \rangle \Big|^2 = \delta_{\ell_f, \ell_i \pm 1}\, \delta_{m_f, m_i}\, \left| d_{E_i, E_f} \right|^2\, \left| I(\nu_i, \nu_f) \right|^2}$$

where

$$I(\nu_i, \nu_f) = \int \chi_{\nu_f}^*(R) \chi_{\nu_i}(R) \mathrm{d}R$$

is the **Franck–Condon factor**.

Overlap integral between vibronic-states

It can be shown that, if only the state $\nu_i = 0$ is populated, then

$$\left| \int \chi_{\nu_f}^*(R) \chi_0(R) \mathrm{d}R \right|^2 = e^{-S} \frac{S^\nu}{\nu!} \equiv F_0^\nu$$

S is the **Huang-Rhys factor**: it represents the strength of coupling to the nuclear degrees of freedom. The Huang-Rhys factor is related to the equilibrium position offset ΔR_0 by

$$S = \mu \frac{\omega_0}{\hbar} \Delta R_0^2$$

Hence, if $\Delta R_0 = 0$, $I(\nu_i, \nu_f) = \delta_{\nu_f, \nu_i}$: the $|\chi_\nu\rangle$ in the ground and excited states are identical and, because of their orthogonality, $\langle \chi_{\nu_f} | \chi_{\nu_i} \rangle = 0$ when $\nu_f \neq \nu_i$.

When $\Delta R_0 \neq 0$, transitions between states with different values of ν_i and ν_f become allowed. Significant values of the overlap integral $I(\nu_i, \nu_f)$ are found for a progression of vibrational states ν_f, so transitions occur with varying probabilities to all of them. Thus, a progression of transitions, a series of vibrational transitions, is observed in the electronic spectrum (see figure 6). The larger ΔR_0, the larger the number of allowed transitions. The relative intensities of the corresponding spectral lines are proportional to the square of the electric dipole transition moments and hence to the Franck–Condon factors, $|I(\nu_i, \nu_f)|^2$. Increasing ΔR_0 also implies that $|I(\nu_i, \nu_f)|^2$ takes it highest value for larger ν_f.

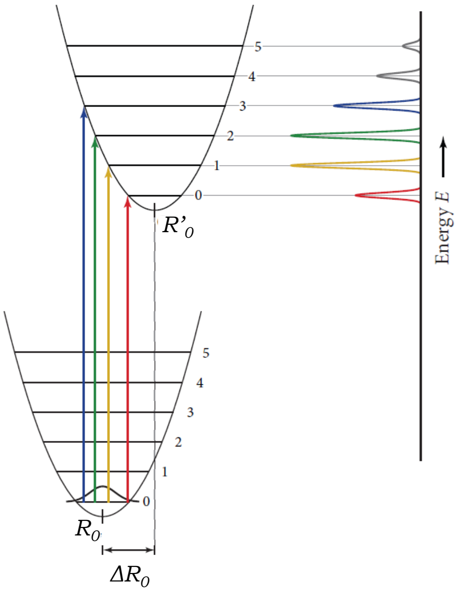


Figure 6: Absorption between vibronic states. The expected absorption and emission spectra are a series of lines regularly spaced at separation $\hbar\omega_0$ with relative intensities according to F_ν^0.

Relaxation to the ground state - Stokes shift

During the absorption process, the internuclear equilibrium distance is preserved. However, after the photon absorption, the molecule relaxes non-radiatively to the state $\nu' = 0$ in the excited electronic state with the new equilibrium distance R_0'. The excess energy is lost by emetting one or several vibration quanta $\hbar\omega_0$.The radiative sponaneous emission occurs from $\nu' = 0$

and the selection rules for emission are the same as for absorption. Thus, the nature of vibronic states implies a systematic energy shift called Stokes shift between emission and absorption (7).

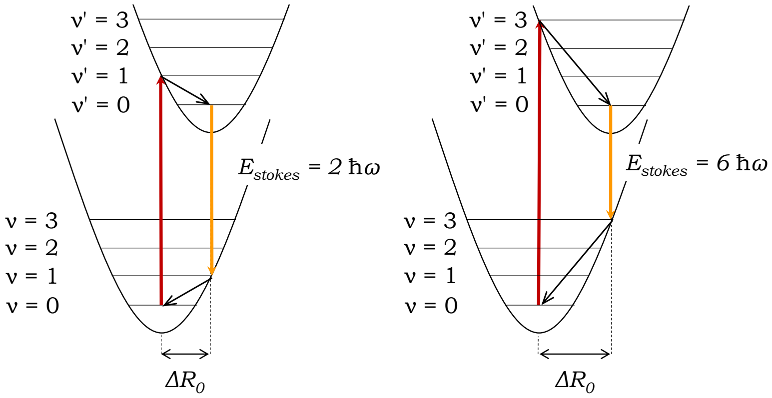


Figure 7: Increase of the Stokes shift E_{Stokes} with Δ_{R_0}.

The larger the Huang-Rhys factor, the larger the Stokes-shift.

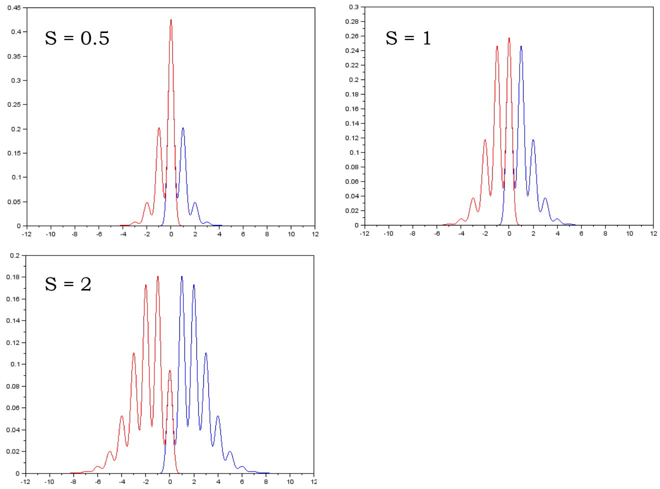


Figure 8: Calculated absorption(blue) and emission(red) spectra of a diatomic molecule for different values of its Huang-Rhys factor S.

Appendix

We look form the wavefunction in the form:

$$\xi_{\nu,\ell,m_\ell}(R,\theta,\varphi) = \frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

by using

$$\hat{L}^2 Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2\ Y_\ell^m(\theta,\varphi)$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R + V(R)\right]\xi_{\nu,\ell,m_\ell}(R,\theta,\varphi) = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

$$+\left[\frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + V(R)\right]\frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi) = E\frac{1}{R}\chi_\nu(R)\ Y_\ell^{m_\ell}(\theta,\varphi)$$

by dividing both sides by $\frac{1}{R}Y_\ell^{m_\ell}$, we get

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + V(R)\right]\chi_{\nu,\ell}(R) = E_{\nu,\ell}\ \chi_\nu(R)$$

with

$$V(R) = \frac{1}{2}\mu\omega_0^2(R-R_0)^2 - |U(R_0)|$$

For the sake of convenience, we set $U(R_0) = 0$.

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + \frac{1}{2}\mu\omega_0^2 R^2\right]\chi_\nu(R) = E_{\nu,\ell}\ \chi_\nu(R)$$

we assume that $\frac{\hbar^2\ell(\ell+1)}{2\mu R^2} \simeq \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}$

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{1}{2}\mu\omega_0^2 R^2\right]\chi_\nu(R) = \left[E_{\nu,\ell} - \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}\right]\ \chi_\nu(R)$$

$$\hbar\omega_0(\nu+1/2) = E_{\nu,\ell} - \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}$$

$$\boxed{E_{\nu,\ell} = \hbar\omega_0(\nu+1/2) + \frac{\hbar^2\ell(\ell+1)}{2\mu R_0^2}}$$

$\chi_\nu(R)$ is solution of the one-dimensional harmonic oscillator:

$$\chi_\nu(R) = N_\nu H_\nu(u) e^{-u^2/2}$$

where H is a Hermite polynomial, $u = (R-R_0)/\alpha$ and $\alpha = (\hbar/\mu\omega_0)^{1/2}$.

Chapter 6: Optical transition in semiconductors

January 3, 2023

Contents

1 Electronic states and band structure

1.1 Crystal structure

Condensed matter consists in the agregation of atoms with a density of a few 10^{22} cm^{-3}. Crystalline materials, as semiconductor compounds are, see their atoms (or molecules) periodically arranged in a higly ordered microscopic stucture. A crystal is built up by repetitive translation of its unit cell along its principal axes. It is characterized by the symetry-operations through which it remains identical. The number of crystalline structure in nature is so large that it consitute the topic of crystallography. However, the most studied semiconductors present simple arrangement such as diamond, zinc-blend (cubic) or wurtzite (hexagonal) structures.

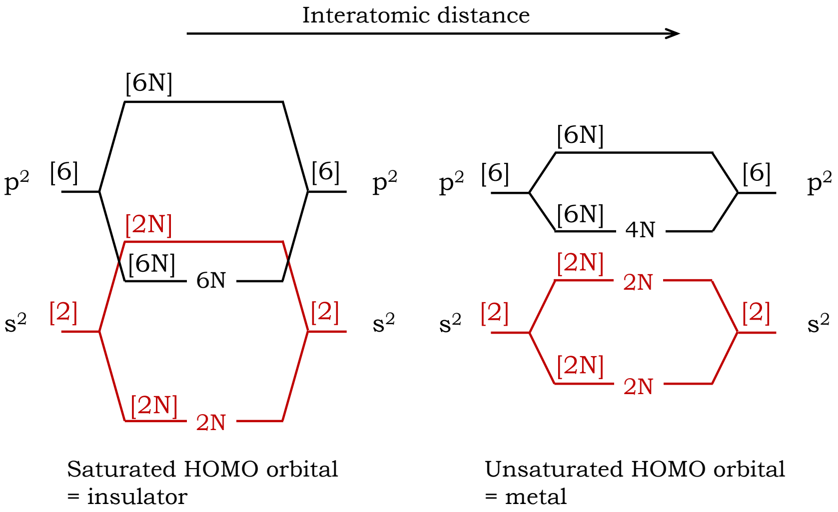


Figure 1: Construction of the crystal orbitals starting from the s and p orbitals of an atom with s^2p^2 electronic configuration.

1.2 Electronic states

The electronic structure of solids can be regarded as an extension of molecular orbital theory to aggregates consisting of a virtually infinite number of atoms.

The simplest example of the use of LCAO is illustrated by the calculation of the electronic states of a homonuclear diatomic molecule. Its wavefunction is written as a linear combination of atomic 1-s orbitals. One has to solve the secular determinant is equal to:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

the eigenvalues of which are:

$$E^{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$$

The corresponding wavefunctions are:

$$\phi^{\pm}(r) = \frac{1}{\sqrt{2(1 \pm S)}} \left[\phi_{1s}(r - R_1) \pm \phi_{1s}(r - R_2)\right]$$

or, with a more general notation:

$$\phi(r) = \sum_{n=1}^{2} C_n \phi_{1s}(r - R_n)$$

The coupling lifts the degeneracy between the electronic states with the same symetry leading to the existence of bonding and antibonding orbitals. Both of them are two-fold degenerate.

We can apply the same technique to semiconductors compounds. Their possess 8 valence electrons.

Examples

- Si: [Ne] $3s^2 3p^2$
- GaN Ga: [Ar]$3d^{10}4s^2 4p^1$ & N:[He]$2s^2 2p^3$
- CdTe Cd: [Kr]$4d^{10}5s^2$ & Te: [Kr]$4d^{10}5s^2 5p^4$

Let us consider a chain of N identical atoms with s^2p^2 configuration (this is the case for Si for example). The electronic states of the crystal arise from the coupling between atomic orbital having the same symetry that lifts the degeneracy between them.The electronic states of the crystal can be obtained by generalizing the concept of LCAO to a chain of N atoms, each of which having one valence $s-$orbital that can only overlap with its two immediate neighbours. the solution of which results in the existence of s and p, bonding and antibonding orbitals that are $N-$fold degenerate. The way these orbitals are ordered and occupied by the $8N$ valence electrons determine the insulating or metallic character of the compound. The coupling depends on the interatomic distance (figure 1). Depending on the relative energies of the bonding p-orbital and the antibonding s-orbital, the highest occupied molecular orbital (HOMO) can be saturated or unsaturated. Semiconductors correspond to the case where the HOMO-orbital is saturated.

1.3 Fine structure

In most of the semiconductors, the top valence band is a six-fold degenerate $\ell = 1$ state while the conduction band is a two-fold degenerate s-state. If we take into account the electron spin, the states at $k = 0$ are eigenstates of the total angular momentum operator $\hat{J}$ that can take the values $j = 1/2$ and $j = 3/2$. The six bands are labelled $|j, m_j\rangle$ where m_j is the projection of j on the quantization axis. The spin-orbit interaction lifts the degeneracy between $j = 3/2$ and $j = 1/2$ at $k = 0$.

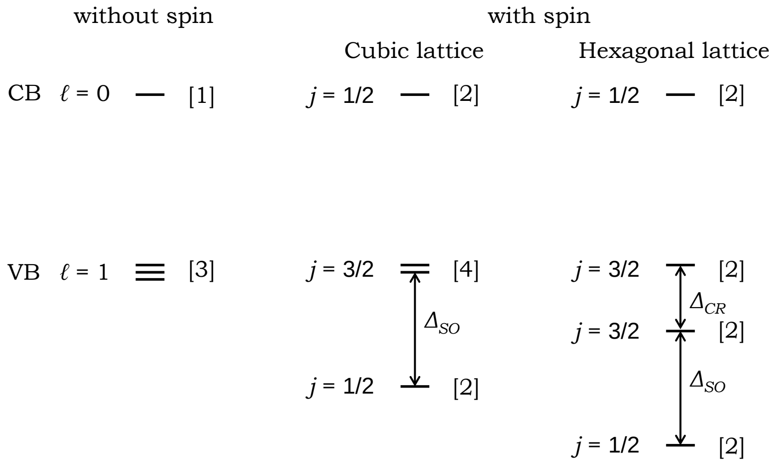


Figure 2: Fine structure at $k = 0$.

1.4 Bloch theorem, dispersion

Up to now, we did not consider the translationnal invariance of the Coulomb potential due to the periodic arrangement of atoms. If we consider a one-dimensionnal infinite chain of atoms with a characteristic lattice vector **a**. Because the arrangement is invariant through a translation of vector **a**, the electronic density of probability must satisfy:

$$|\psi(x+ma)|^2 = |\psi(x)|^2$$

that is to say

$$\psi(x+ma) = e^{ikma}\psi(x)$$

This condition is fullfilled if $\psi(x)$ has the form:

$$\psi(x) = e^{-ikx}u(x) \text{ where } u(x+na) = u(x)$$

where $0 < |\mathbf{k}| < \pi/a$. This is the **Bloch-theorem**.

$\psi(x)$ satisfies the Bloch-theorem on the condition that:

$$\psi(x) = N\sum_n e^{-ik\cdot na}\phi(x-na) \text{ where } N \text{ is a normalization factor.}$$

k lifts the degeneracy between the crystal states that are spread and constitutes quasi-continuous energy bands: there is energy dispersion as a function of **k** in the reciprocal space(see figure 3). The highest occupied band is the **valence band** while the lowest unoccupied band is the **conduction band**. They are separated by the energy bandgap $\mathbf{E}_g$. If the valence band maximum and the conduction band minimum correspond to the same value of k, the compound is said to be a direct bandgap semiconductor. If it is not the case, it is said to be and indirect bandgap semiconductor. The band structure is periodic in reciprocal space and is usually represented in the first Brillouin zone with k ranging from 0 to π/a. In the following, we focus on the region around $k=0$ which is the one that is probed with optics.

1.5 Fine structure and effective mass

At $k \neq 0$, the dispersion lift the degeneracy between bands of different j. Near the band extrema, the Taylor expansions of the different energies are quadratic:

$$E_n(k) = E_n(k_0) + (k-k_0)\frac{\partial E_n}{\partial k} + \frac{1}{2}(k-k_0)^2\frac{\partial^2 E_n}{\partial k^2} + \dots$$

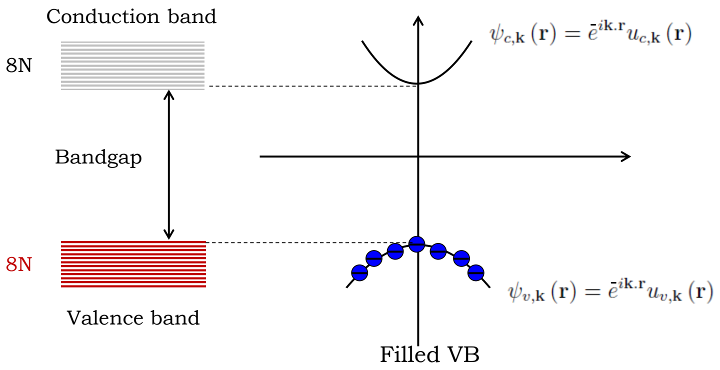


Figure 3: Dispersion of the valence and conduction bands in reciprocal space.

By setting

$$m^* = \hbar^2 \left(\frac{\partial^2 E_n}{\partial k^2} \right)^{-1}$$

The energy dependence with k becomes similar to the dispersion of a free electron with an effective mass m^*.

2 Optical transitions

2.1 Caculation of the dipole moment matrix element

The probability of transition between an initial state $|v, \mathbf{k}_v\rangle$ and a final state $|c, \mathbf{k}_c\rangle$ is:

$$|W_{fi}| = -q\mathcal{E}_0 \langle c, \mathbf{k}_c | \hat{\mathbf{r}} \; e^{-i\mathbf{k}\cdot\mathbf{r}} | v, \mathbf{k}_v \rangle$$

$$\langle c, \mathbf{k}_c | \hat{\mathbf{r}} \; e^{-i\mathbf{k}\cdot\mathbf{r}} | v, \mathbf{k}_v \rangle = \frac{1}{V} \int_{\text{crystal}} u^*_{c,\mathbf{k}_c}(\mathbf{r}) \; u_{v,\mathbf{k}_v}(\mathbf{r}) e^{i(\mathbf{k}_c - \mathbf{k}_v - \mathbf{k}_0)} \; \mathbf{r} \mathrm{d}^3\mathbf{r}$$

The crystal being periodic, we can express $\mathbf{r}$ as:

$$\mathbf{r} = \mathbf{r}_j + \mathbf{R}$$

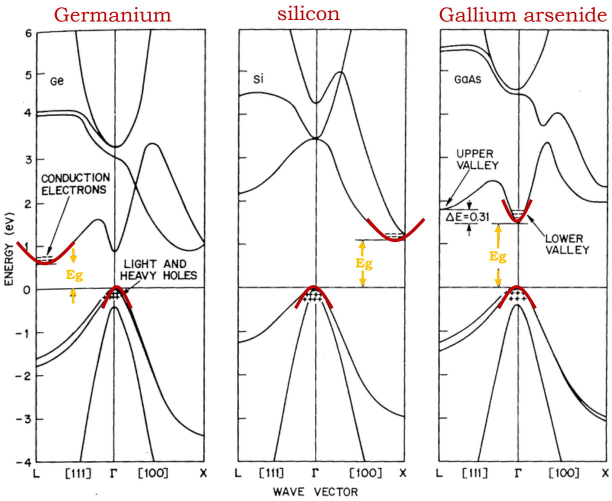


Figure 4: Examples of band stuctures: germanium and silicon are indirect bandgap semiconductor. Gallium arsenide is a direct one.

where $\mathbf{r}_j$ denotes the location of the j^{th}unit cell and $\mathbf{R}$ the position within this unit cell. The exponential functions are slowly varying in space as compared to u_c and u_v. The integral over the whole crystal is broken up into a sum of integrals over all the primitive cells

$$|W_{fi}| = -q\frac{\mathcal{E}_0}{V}\sum_j \int_{\text{unit cell}} u^*_{c,\mathbf{k}_c}(\mathbf{r}_j+\mathbf{R})\; u_{v,\mathbf{k}_v}(\mathbf{r}_j+\mathbf{R})\; e^{i(\mathbf{k}_c-\mathbf{k}_v-\mathbf{k}_0)\cdot(\mathbf{r}_j+\mathbf{R})}(\mathbf{r}_j+\mathbf{R})\mathrm{d}^3\mathbf{R}$$

The exponential functions are replaced by their average values in each primitive cell and pulled out of the integral.

$$|W_{fi}| = -q\frac{\mathcal{E}_0}{V}\sum_j e^{i(\mathbf{k}_c-\mathbf{k}_v-\mathbf{k}_0)\cdot\mathbf{r}_j} \int_{\text{unit cell}} u^*_{c,\mathbf{k}_c}(\mathbf{r}_j+\mathbf{R})\; u_{v,\mathbf{k}_v}(\mathbf{r}_j+\mathbf{R})\; (\mathbf{r}_j+\mathbf{R})\mathrm{d}^3\mathbf{R}$$

We use the periodicity of u_v and u_c

$$|W_{fi}| = -q\frac{\mathcal{E}_0}{V}\sum_j e^{i(\mathbf{k}_c-\mathbf{k}_v-\mathbf{k}_0)\cdot\mathbf{r}_j} \int_{\text{unit cell}} u^*_{c,\mathbf{k}_c}(\mathbf{R})\; u_{v,\mathbf{k}_v}(\mathbf{R})\; (\mathbf{r}_j+\mathbf{R})\mathrm{d}^3\mathbf{R}$$

$$\begin{aligned}|W_{fi}| = -q\frac{\mathcal{E}_0}{V}\sum_j e^{i(\mathbf{k}_c-\mathbf{k}_v-\mathbf{k}_0)\cdot\mathbf{r}_j}\Bigg[&\int_{\text{unit cell}} u^*_{c,\mathbf{k}_c}(\mathbf{R})\; u_{v,\mathbf{k}_v}(\mathbf{R})\;\mathbf{R}\;\mathrm{d}^3\mathbf{R}\\ &+\underbrace{\mathbf{r}_j\int_{\text{unit cell}} u^*_{c,\mathbf{k}_c}\; u_{v,\mathbf{k}_v}(\mathbf{R})\;\mathrm{d}^3\mathbf{R}}_{=0}\Bigg]\end{aligned}$$

The second integral in the brackets is equal to zero because the periodic part the Bloch waves are orthogonals for different $\mathbf{k}$. $\sum_j e^{i(\mathbf{k}_c-\mathbf{k}_v-\mathbf{k}_0)}$ is a sum of oscillating terms, it is equal to zero except for $\mathbf{k}_c-\mathbf{k}_v-\mathbf{k}_0=0$. Finally, we find:

$$\boxed{|W_{fi}| = -q\frac{\mathcal{E}_0}{V}\delta_{\mathbf{k}_c-\mathbf{k}_v,\mathbf{k}_0}\int_{\text{unit cell}} u^*_{c,\mathbf{k}_c}(\mathbf{R})\; u_{v,\mathbf{k}_v}(\mathbf{R})\;\mathbf{R}\;\mathrm{d}^3\mathbf{R}}$$

2.2 Selection rules

In reciprocal space The optical transition is allowed if

$$\mathbf{k}_c-\mathbf{k}_v=\mathbf{k}_0$$

with $k_0=\frac{2\pi}{\lambda_0}$. In the visible range, $\lambda_0\simeq 500$ nm. The extension of the first Brillouin zone is $\frac{2\pi}{a}$ with $a\simeq 0.5$ nm. So, at the scale of the first Brillouin zone, the transitions are vertical in the reciprocal space:

$$\mathbf{k}_c\simeq\mathbf{k}_v$$

and:

$$|W_{fi}|\simeq -q\frac{\mathcal{E}_0}{V}\int_{\text{unit cell}} u^*_{c,0}(\mathbf{R})\; u_{v,0}(\mathbf{R})\;\mathbf{R}\;\mathrm{d}^3\mathbf{R}$$

Angular momentum conservation At the Γ point $u_{c,\mathbf{k}}$ and $u_{v,\mathbf{k}}$ are eigenstate of the angular momentum operator:

$$u_{c,\mathbf{0}}=|s,s_z\rangle$$

$$u_{v,\mathbf{0}}=|j,j_z\rangle$$

When a circularly polarized photon is absorbed, this angular momentum is distributed between the photo-excited electron and hole according to the selection rules determined by the band structure of the semiconductor.

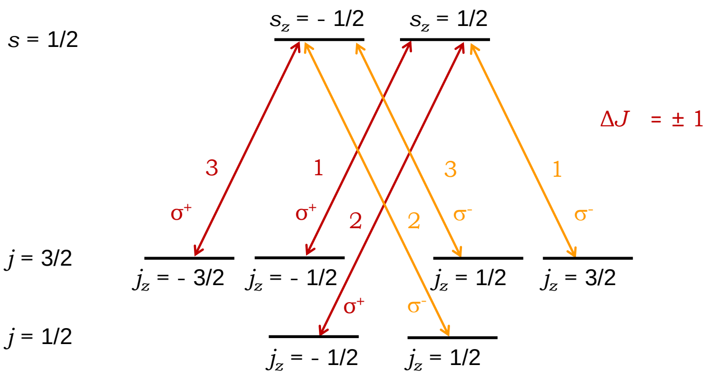


Figure 5: SC Optical Selection Rules.

2.3 Electrons and holes

An amount of energy can promote an electron from the valence to the conduction band excitation, $n-1$ electrons remaining in the valence band. This equivalent to creation of one electron-hole pair.

2.4 Absorption and spontaneous emission

The transition rate per unit time between a discrete state and a continuum is given by the Fermi's golden rule.

$$\Gamma = \frac{2\pi}{\hbar}|W_{fi}|\rho(E_f - E_i) = \frac{\mathrm{d}P_{if}}{\mathrm{d}t}$$

where $\rho(E_f - E_i)$ is the density of states associated with the final state. For a transition occuring between the VB and the CB, both the initial and final states belong to a continuum.

2.5 Direct and indirect bandgaps

v In a direct bandgap semiconductor, the maximum of the valence band and the minimum of the conduction band correspond to the same value of $\mathbf{k}$ in

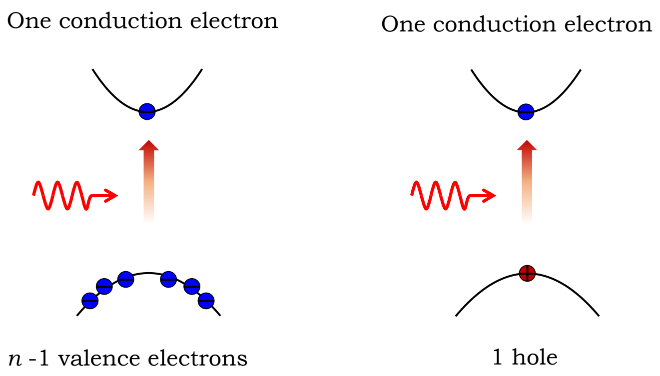


Figure 6: $n-1$ negatively charged electrons in the valence band are equivalent to one positively charged hole.

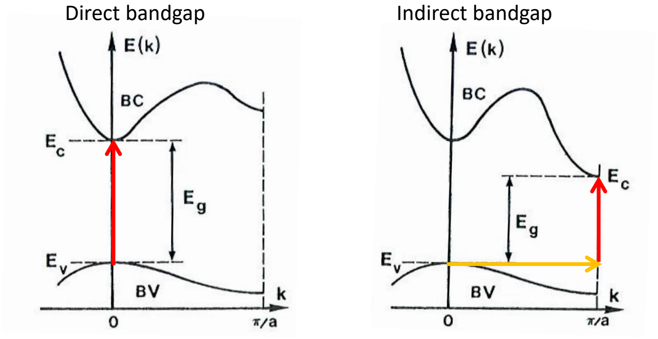
reciprocal space. On the contrary, in an indirect bandgap semiconductor, these two extrema are located at different values of $\mathbf{k}$. As a consequence, in indirect bandgap semiconductors, the $\mathbf{k}$ conservation rule cannot be satisfied for a transition between the top of the valence band and the bottom of the conduction band. This is not a problem for light absorption process because it can occur between the maximum of the valence band However, the interaction with a phonon can conserve the momentum. One consequence of this, is that indirect bandgap semiconductors are poor light-emitters.

3 Excitons

4 Nanostructures

$$\left.\begin{array}{l} \boldsymbol{k_0} \sim 2\pi \,/\, \lambda \text{ with } \lambda \sim 500 \text{ nm} \\ \boldsymbol{k_c}\,,\ \boldsymbol{k_v} \sim 2\pi \,/\, a \text{ with } a \sim 0.5 \text{ nm} \end{array}\right\} \quad \boldsymbol{k_0} << \boldsymbol{k_c}\,,\ \boldsymbol{k_v}$$

Transitions are vertical in reciprocal space


Direct bandgap

Indirect bandgap

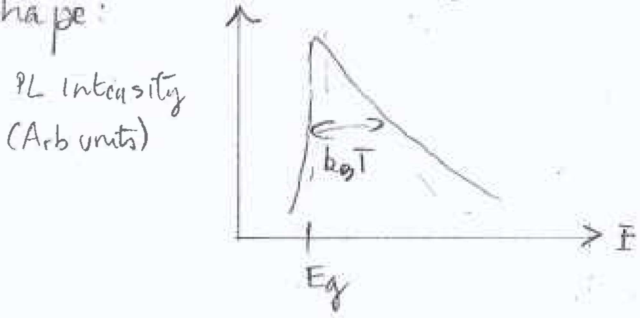
Figure 7: Direct and Indirect Transitions.

Experimentally, we observe the recombination of a thermalized population.

→ quasi-thermal equilibrium

$$n_e(E) \propto (E-E_c)^{1/2} \exp\left\{-\frac{(E-E_c)}{k_BT}\right\} \; ; \; n_h(E) \propto (E-E_v)^{1/2} \exp\left\{-\frac{(E-E_v)}{k_BT}\right\}$$

Lineshape:



Sharp rise at $E = E_g$ and exponential decay at high energy with a decay constant of k_BT

Linewidth $\simeq k_BT$.

IV. Excitons:

ground state of the crystal:

N electrons in the valence band

First excited state:

N-1 electrons in the valence band + one electron in the conduction band.

The electron in the CB and the hole in the VB are bound by the Coulomb interaction. This bound state is the first excited state of the the crystal and is called exciton

Wannier-Mott exciton: Radius ≫ lattice parameter a
(semiconductors)
Binding energy ≃ 0,01 eV

Frenkel exciton - Radius ≃ a
Binding energy 0,1 - 1 eV

in Both cases: state delocalized over the whole crystal

The exciton is described by a two particle Hamiltonian similar to the one of the hydrogen atom

$$H = -\underbrace{\frac{\hbar^2}{2m_e^*}\vec{\nabla}_e^2}_{\text{electron kinetic energy}} - \underbrace{\frac{\hbar^2}{2m_h^*}\vec{\nabla}_h^2}_{\text{hole kinetic energy}} - \underbrace{\frac{e^2}{4\pi\varepsilon|\vec{r}_e-\vec{r}_h|}}_{\text{Coulomb potential}}$$

In the same way the motion of the center of mass is separated from the relative motion by introducing:

$$\begin{cases} \vec{r} = \vec{r}_e - \vec{r}_h \\ \mu = \dfrac{m_e^* m_h^*}{m_e^* + m_h^*} \end{cases} \qquad \begin{cases} \vec{R} = \dfrac{m_e^* \vec{r}_e + m_h^* \vec{r}_h}{m_e^* + m_h^*} \\ M = m_e^* + m_h^* \end{cases}$$

The wavefunction is factorized = $\Psi_{ex}(\vec{r},\vec{R}) = F(\vec{r})\, f(\vec{R})$

Motion of the center of mass

The motion of the mass is the propagation of a free particle of mass M and wavevector $\vec{K}$:

$$f(\vec{R}) = e^{i\vec{K}.\vec{R}} \qquad E_{CM} = \frac{\hbar^2\vec{K}^2}{2M}$$

$$M = m_e^* + m_h^* \qquad \vec{K} = \vec{k}_e + \vec{k}_h \qquad \frac{\vec{k}}{\mu} = \frac{\vec{k}_e}{m_e} - \frac{\vec{k}_h}{m_h}$$

$$\vec{k}_e = \frac{m_e}{M}\vec{K} + \vec{k}, \quad \vec{k}_h = \frac{m_h}{M}\vec{K} + \vec{k}$$

Relative motion

The wavefunction of the relative motion is the same as the one of the hydrogen atom:

$$F(r) = F_{n,l,m}(\vec{r}) = R_{n,l}(r)\, Y_l^m(\theta,\varphi)$$

The total wavefunction is a linear combination of

$$e^{-i\vec{k}_e\vec{r}_e}\, u_{c,\vec{k}_e}(\vec{r}_e)\; e^{-\vec{k}_h\,\vec{r}_h}\, u_{v,\vec{k}_h}(\vec{r}_h)$$

$$\Psi_{ex}(\vec{r_e},\vec{r_h}) = \frac{1}{V^{1/2}}\sum_k F_{n,\ell,m}(\vec{k})\, e^{-i\vec{k}\vec{r}}\, e^{-i\vec{K}.\vec{R}}\, u_{c,\vec{k_e}}(\vec{r_e})\, u_{v,\vec{k_h}}(\vec{r_h}).$$

Neglecting the dependance of u_c and u_v with $\vec{k}$

$$\Psi_{ex}(\vec{r_e},\vec{r_h}) = \frac{1}{V^{\frac{1}{2}}}\, F_{n,\ell,m}(\vec{r})\, e^{-i\vec{K}.\vec{R}}\, u_c(\vec{r_e})\, u_v(\vec{r_h})$$

in the lowest energy state the wavefunction is the 1s hydrogenic wavefunction :

$$F_{1,0,0}(r) = \frac{1}{\sqrt{\pi a_B^3}}\, e^{-r/a_B}$$

a_B is the effective Bohr radius $a_B = \frac{m_0 \varepsilon_0}{\mu\, \varepsilon} \times 0{,}053\ \text{nm}$

It's Fourier transform is : $F_{1,0,0}(\vec{k}) = \frac{8\pi^{1/2}}{V^{1/2} a_B^{5/2}} \frac{1}{\left[k^2 + a_B^{-2}\right]^2}$

The distribution in reciprocal space has a full width at half maximum equal to $\frac{2}{a_B}$

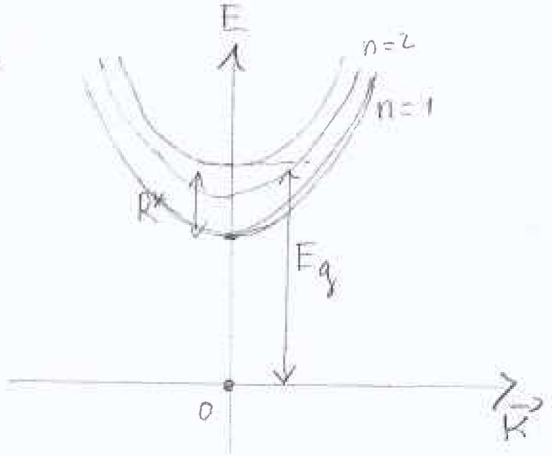
hydrogenic series

Eigen energies : Bound states $E < E_g$ $E_n(\vec{K}) = E_g - \frac{R_y^*}{n^2} + \frac{\hbar^2 \vec{K}^2}{2M}$

Unbound states : $E > E_g$: $E_k(\vec{K}) = E_g + \frac{\hbar^2\vec{k}^2}{2\mu} + \frac{\hbar^2\vec{K}^2}{2M}$

$$= E_g + \frac{\hbar^2 \vec{k_e}^2}{2m_e^*} + \frac{\hbar^2\vec{k_h}^2}{2m_h^*}$$

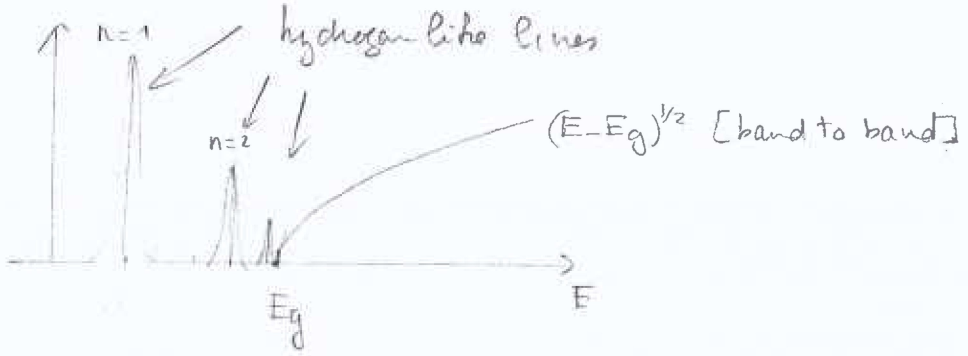
R_y^* is the effective Rydberg. $R_y^* = \frac{\mu}{m_0}\frac{\varepsilon_0^2}{\varepsilon^2} \times 13{,}6\ \text{eV}$



Crystal	E_g (eV)	R_y^* (meV)	a_B (nm)
GaAs	1,5	4,2	13
CdTe	1,6	12	6,7
GaN	3,5	23	3,1
ZnO			

Optical transitions:

The transition has to satisfy the conservation of the wavevector: $\vec{k_e} = -\vec{k_h}$ and $\vec{K} = \vec{0}$

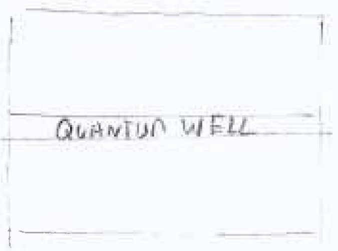


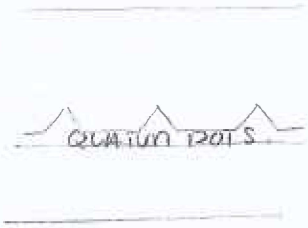
Excitonic structures are observable in good quality crystals. The excitonic signature disapears for $kT > R_y^*$

V_ Nanostructures:

1_ Introduction

Growth techniques such as molecular beam epitaxy allows to synthetise quantum wells and quantum dots





The electronic wavefunction is confined in one or several directions.

2. Quantum wells

a). Electronic states:

Bulk material: carriers free to propagate in 3 dimension. the motion is characterized by a wave vector $\vec{k}(k_x, k_y, k_z)$

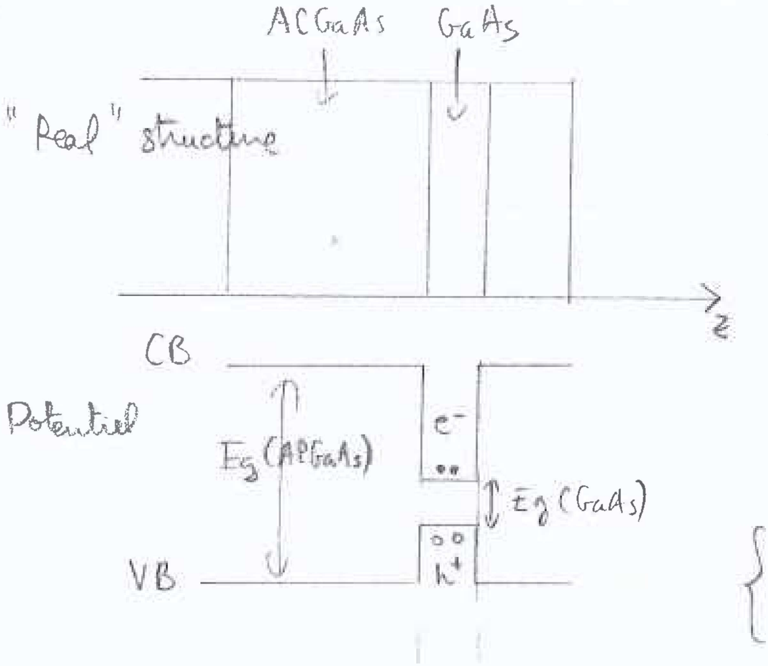
The eigenstates are Bloch-states:

$$\psi_{n,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \underbrace{e^{-i\vec{k}.\vec{r}}}_{\substack{\text{enveloppe}\\ = \text{plane wave}}} \underbrace{u_{n,\vec{k}}(\vec{r})}_{\substack{\text{periodic}\\ \text{part}}}$$

Nanostructures: The confinement potential breaks the translation symmetry in one or several direction.

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{k}} A_n(\vec{k}) e^{-i\vec{k}.\vec{r}} u_{n,\vec{k}}(\vec{r}) \simeq F(\vec{r}) u_n(\vec{r})$$

Example: Quantum well



z and (x,y) motions are decoupled

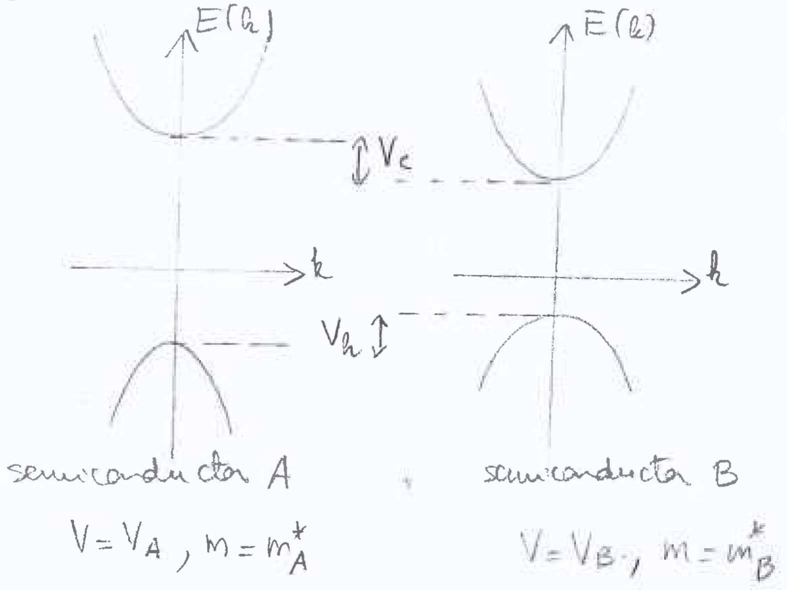
$$F(\vec{r}) = f_n(z) \cdot e^{-i(k_x x + k_y y)}$$

when $f_n(z)$ is solution of:

$$\left\{ \frac{\hbar^2 k_z^2}{2m^*} + V(z) \right\} f_n(z) = E_n f_n(z)$$

V(z) is the confinement potential caused by the band discontinuity.

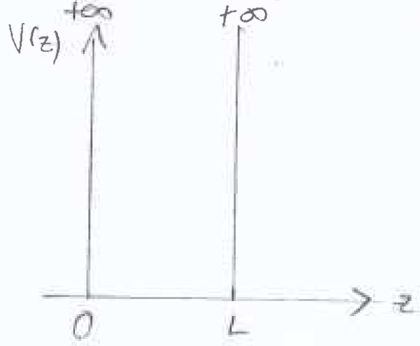
Origin of the confinement potential



semiconductor A — $V = V_A$, $m = m_A^*$

semiconductor B — $V = V_B$, $m = m_B^*$

Simple model with an analytic solution = QW with infinite barrier height



Enveloppe function equation:

$$\left\{ \frac{\hbar^2 k_z^2}{2m^*} - E_n \right\} f_n(z) = 0$$

Boundary condition:

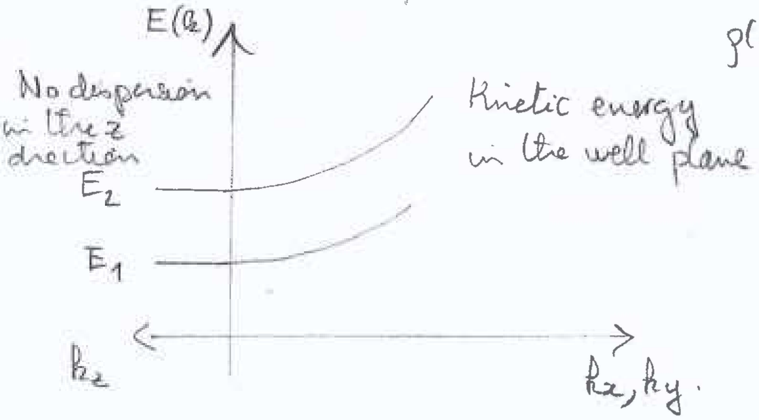
$$f_n(0) = f_n(L) = 0 \Rightarrow k_n = n\frac{\pi}{L}$$

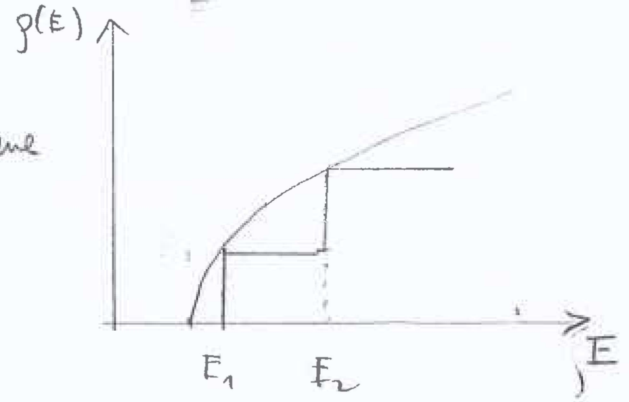
Solutions: $f_n(z) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi}{L}z\right)$ $\quad E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{\hbar^2}{2m^*}\left(\frac{n\pi}{L}\right)^2$

Consequence of the confinement: discretization of allowed values of k_z and of energy states.

→

In plane dispersion and density of states



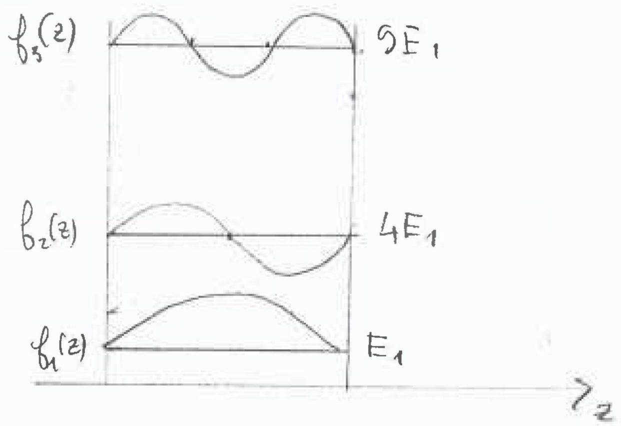


$$E_n(k_x, k_y) = \frac{\hbar^2}{2m^*}\left\{\left(\frac{n\pi}{L}\right)^2 + k_x^2 + k_y^2\right\}$$

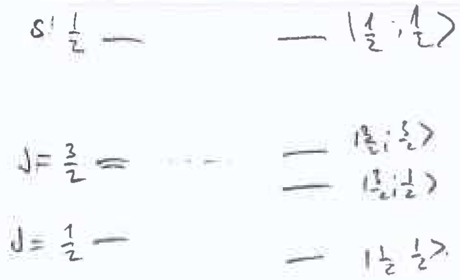
Each sub-band exhibits a constant density of electronic states

Envelope functions:

$$\rho(\hbar\omega) = \frac{m^*}{\pi\hbar^2}\sum_n \theta(\hbar\omega - E_n)$$



the confinement lifts the degeneracy between the valence subbands.



b. Band to band optical transitions

a.1 selection rules :

$$|W_{fi}| = -qE \langle \psi_{ck_c} | \hat{r}\, e^{-i\vec{k}_0 \vec{r}} | \psi_{v,k_v} \rangle$$

$$\psi_{q\vec{k}}(\vec{r}) = N \cdot e^{-i(k_x x + k_y y)} f_{0n}(z) \cdot u_{c,\vec{k}}(\vec{r})$$

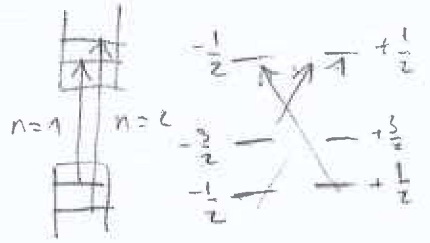
Performing the same calculation as for the bulk material.

$$|W_{fi}| = -\frac{qE}{V} \cdot \underbrace{\delta(\vec{k}_c^{\,\prime\prime} - \vec{k}_v^{\,\prime\prime} - \vec{k}_0)}_{\substack{\text{vertical} \\ \text{transition.}}} \cdot \int f_{0n}(z_e) f_{0n}(z_h)\, dz \int_{\substack{\text{unit}\\ \text{cell}}} u^*_{c,k_c}(\vec{R})\, \vec{R}\, u_{v,k_v}(\vec{R})\, d^3\vec{R}$$

in the case of a QW with infinite barriers :

$$\int f_{0n}(z_e) f_{0m}(z_h)\, dz = \frac{2}{L} \int_0^L \sin(k_n z_e) \sin(k_m z_h)\, dz = \delta_{n,m}$$

$$\left\{ \begin{array}{ll} \vec{k}_c^{\,\prime\prime} - \vec{k}_v^{\,\prime\prime} = 0 & \text{vertical transitions} \\ \Delta j_z = \pm 1 & \text{nature of the subband} \\ \Delta n = 0 & \text{symmetry of the envelopps along } z \end{array} \right.$$

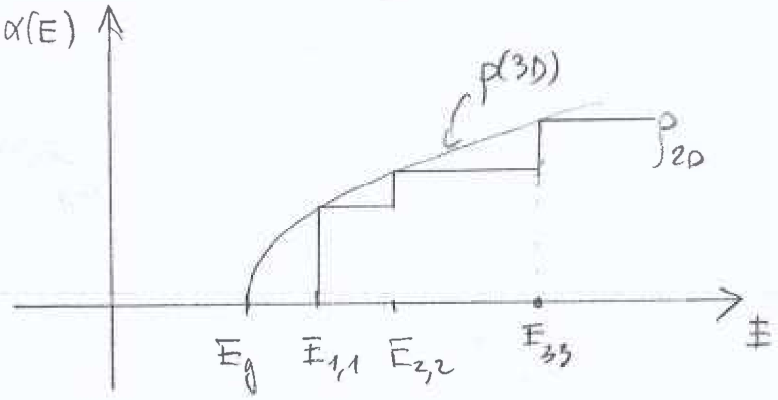


- Transition Energies → appendix
- transition rate.

$$\Gamma = \frac{2\pi}{\hbar} |W_{fi}|^2 \rho\left[E - (E_n^e - E_n^h)\right]$$

$$\rho\left[E - (E_n^e - E_n^h)\right] = \frac{m_R}{\pi\hbar^2}\, \theta\left[E - (E_n^e - E_n^h)\right]$$

$$\alpha(E) \propto \sum_n |R_{cv}|^2 I_{n,n} \frac{m_r^*}{\pi\hbar^2} \Theta\left[E - (E_n^e - E_n^h)\right] f(E_n^h)\left[1 - f(E_n^e)\right]$$



4. Excitons in quantum wells.

Excitons are described by a 2D. hydrogenoid function:

$$\psi(z_e, z_h, r) = N f(z_e) f(z_h) \exp\left\{-\frac{r}{a_B}\right\}$$

The quantum confinement enhances the exciton binding energy.

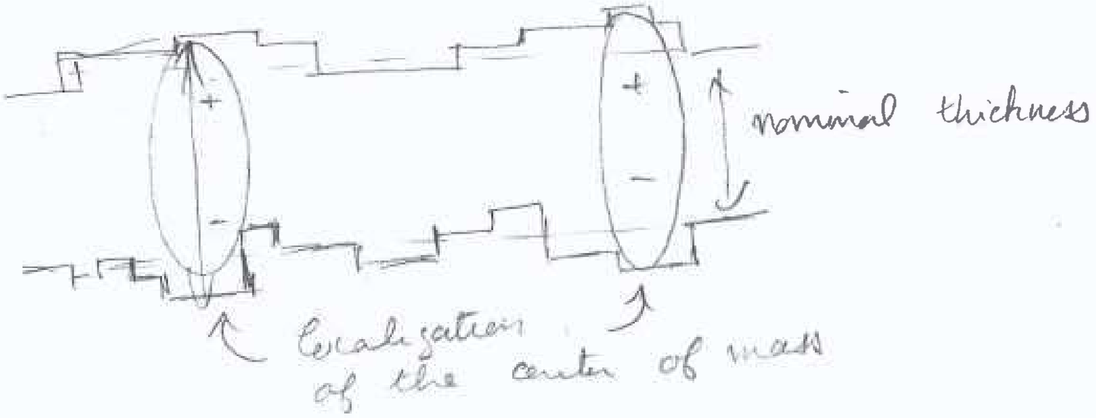
Energy spectrum of bound excitonic states:

$$E_n = -\frac{R_y^*}{(n - \frac{1}{2})^2}$$

For $n = 1$ $\qquad E_n = 4R_y^*$

5. Inhomogeneous broadening

Real QWs exhibit, at both interfaces fluctuations of at least one monolayer height as shown schematically below



Master MCN

Light-matter interactions – Exercise classes

Session No. 1, Oct 4th, 2022
S. Haacke & M. Gallart

Light-induced population inversion in 2- and 3-level systems

A) The 2-level system

We consider a two-level system as depicted in figure 1, where the populations N_1 and N_2 of the ground and excited state, respectively, are subject to spontaneous emission (A), absorption (B_{12}) and stimulated emission (B_{21}). The latter two processes are induced by an external EM field with energy field $<W(\omega)>$.

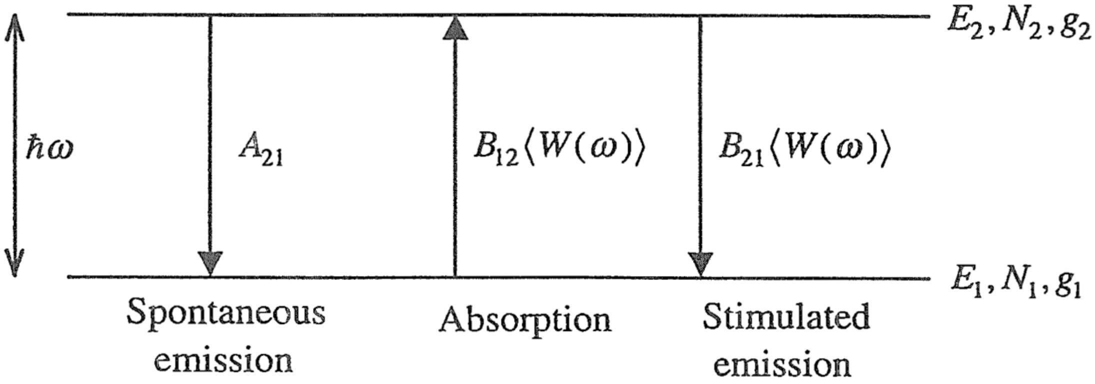


Figure 1: Two-level system with transitions as defined by the Einstein coefficients. The EM field at frequency ω is resonant with the energy difference of the two states.

Recall on the lecture

1. When the energy density is increased, the rate of absorption increases, as much as the rate of stimulated emission. Justify the behaviour described in figure 2, the dependence of the populations N_1 and N_2 as a function of the energy density $<W(\omega)>$.
2. What defines the saturation density W_s ?

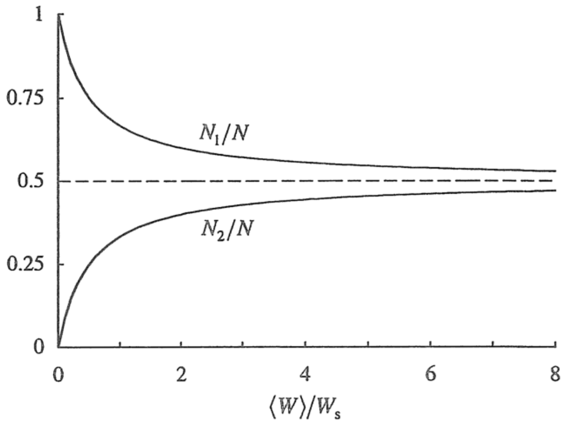


Figure 2: Steady-state atomic population as a function of the radiative energy density

3. In the limit of <W> → infinity, what would be the effective temperature T of the atoms, assuming $g_1 = g_2$? Use the Boltzmann form
$$N_2 = N_1 e^{-\frac{E_2 - E_1}{k_B T}}$$, where k_B is the Boltzmann constant

4. In the case of a hypothetical ***population inversion***, i.e. $N_2 > N_1$, how would this temperature change ? Conclusion ?

B) Population inversion in a 3-level system, optical gain, amplification

We now consider the 3-level system depicted in figure 3. The atomic system is excited by an EM radiation resonant with the 0-2 transition and under a rate R. A second EM wave, resonant with the 1-2 transition allows for absorption and stimulated emission between the levels 1 and 2. Spontaneous emission is allowed between all levels (coeff. A).

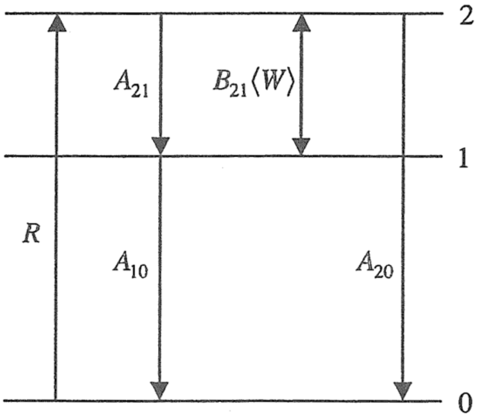


*Figure 3: A three-level system "pumped" by R into level 2. What is the attenuation or amplification of the EM wave W(ω) resonant with the 1-2 transition ? Is it possible to have a **population inversion between 2 and 1** in this configuration ?*

We assume the refractive index to be 1 in this dilute gas.

1. Derive the rate equations for the change of populations per time $\frac{\partial N_0}{\partial t}, \frac{\partial N_1}{\partial t}, \frac{\partial N_2}{\partial t}$, and show that – under steady state conditions, i.e. $\frac{\partial}{\partial t} = 0$, the following relations hold:
$$N_2(A_{21} + B_{21}\langle W\rangle) = N_1(A_{10} + B_{21}\langle W\rangle) \qquad (1)$$
$$A_{10}N_1 + A_{20}N_2 = N_0 R \qquad (2)$$

   Use the fact that the sum of populations is a constant: $N_0 + N_1 + N_2 = N$

2. In order to observe **population inversion**, N2 > N1, what does eq. (1) imply for the coefficient A_{21} with respect to A_{10} ? Give a physical interpretation of this relation in terms of the corresponding spontaneous emission rates.
3. Combine eqs. (1) and (2) to obtain the following
$$N_2 - N_1 = \frac{N_0 R(A_{10} - A_{21})}{A_{10}(A_{20} + A_{21}) + (A_{10} + A_{20})B_{21}\langle W\rangle} \qquad (3)$$

   We assume now that the depletion of N_0 is small, meaning $N_0 \approx N$. Assuming $A_{10} > A_{21}$, make a schematic drawing of $(N_2 - N_1)/N$ as a function of the energy density <W>. How does this compare to Figure 2 ?

Calculation of the gain coefficient

We now want to derive how the energy density <W> evolves, as it propagates through the volume of gas. In the case of population inversion, the rate of stimulated emission is higher than the one of absorption between levels 1 and 2. Hence, one can expect that more EM energy comes out than what is put in, since stim. emission produces two outgoing photons for one incoming photon. This is called **optical gain.**

For the temporal change of the energy density <W>, the following equation derived in the lecture still holds

$$\frac{\partial\langle W\rangle}{\partial t} = (N_2 - N_1)F(\omega)B_{12}\langle W\rangle\hbar\omega. \tag{4}$$

$F(\omega)$ is the normalised line shape function (a Lorentzian or a Gaussian) expressing the fact that the atomic transition resonances have a finite broadening.

4. Under population inversion, how does <W> evolve in time ?
5. We will now establish the spatial dependence of the light intensity $I(z)$ along the propagation direction z. To this end, justify the following two relations given in the lecture: $I = c < W >$, with c the velocity of light, and $\frac{\partial I}{\partial z} = \frac{\partial <W>}{\partial t}$.
6. Combine eq. (3) and (4) to establish the following differential equation

$$\frac{1}{I(z)}\left(1 + \frac{I(z)}{I_S}\right)\frac{\partial I(z)}{\partial z} = \frac{R(A_{10}-A_{21})}{A_{10}(A_{20}+A_{21})}NF(\omega)B_{12}\,\hbar\omega/c = G(\omega) \tag{5}$$

where $G(w)$ is the "gain coefficient", as will become clear in the following, and the saturation intensity is

$$I_S = \frac{cA_{10}(A_{20}+A_{21})}{(A_{10}+A_{20})B} \tag{6}$$

7. Show that the general solution of eq. (5) is

$$ln\left(\frac{I(z)}{I(z=0)}\right) + \frac{I(z)-I(z=0)}{I_S} = G(\omega)z \tag{7}$$

8. Consider the behaviour for two limiting cases: a) I(z) is much smaller than the saturation value I_s, and b) the opposite. Draw the curve $I(z)/I(0)$ as a function of $G(w)z$, for two different values of the saturation intensity, and for two different values of R. Comment the qualitative changes.
9. What are the parameters, which lead to a small saturation intensity I_S ?

Practical use in lasers

Population inversion between to quantum levels **1** and **2** → optical gain or amplification of radiation that is resonant with the transition energy $h\nu = E_2 - E_1$. This is used in the **gain medium** of a laser. Population inversion can either be induced through optical pumping, as in the example given here (the quantity R), or by injection of carriers through electric current like in a semiconductor diode laser. Besides the gain medium, what are the additional components to make a laser ?

Master MCN

Light-matter interactions – Exercise classes

Session No. 2, Oct 18, 2022
S. Haacke & M. Gallart

Time-dependent perturbation theory

A) Lecture revision and interpretation.

Within time-dependent perturbation theory exposed in the lecture, the transition probability between two state i and k is given by

$$P_{ik} = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt' W(t') \exp\left(\frac{i\left(E_k - E_i\right)t'}{\hbar}\right)\right|^2$$

1. For the case of a two-level system, revisit the lecture material and justify the expression for the transition probability, between the two discrete states i and f, under the action of a sinusoidal perturbation:

$$P_{if} = \frac{\left|W_{fi}\right|^2}{4\hbar^2} t^2 \left(\frac{\sin\left[\left(\omega_{fi} - \omega\right)t/2\right]}{\left(\omega_{fi} - \omega\right)t/2}\right)^2$$, with $\omega_{fi} = \left(E_f - E_i\right)/\hbar$.

   Plot the result as a function of ω, and discuss the time range of validity, keeping in mind that $P_{ik} \leq 1$.

2. For a constant perturbation, derive the result found in the lecture:

$$P_{if} = \frac{\left|W_{fi}\right|^2}{\hbar^2} t^2 \left(\frac{\sin\left(\omega_{fi}t/2\right)}{\left(\omega_{fi}t/2\right)}\right)^2$$

3. Trace this probability for different values of t, and give an intuitive description of the time-dependent transition probability.

B) Two-level system with a constant non-resonant perturbation, full treatment: Rabi oscillations

We explore here an alternative, more general treatment of perturbations, which, in the case of a two-level system, is simpler in formalism and can be used without limitations to the strength/amplitude of the perturbation interaction W. In this context, we'll introduce the two limits of "strong" and "weak" coupling, which are frequently used concepts for the description of light-matter interactions of QM systems (e.g. atoms/molecules in an EM cavity).

1. We study a two-level system, defined by the orthogonal eigenstates of an unpertubed Hamiltonian H_0.

$$H_0\left|\varphi_1\right\rangle = E_1\left|\varphi_1\right\rangle$$
$$H_0\left|\varphi_2\right\rangle = E_2\left|\varphi_2\right\rangle \qquad \left\langle\varphi_i\middle|\varphi_j\right\rangle = \delta_{ij}$$

Under the effect of a perturbation W, the full Hamiltonian is $H = H_0 + W$. In the unperturbed basis W is a Hermitian matrix: $W = \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}$, with $W_{21} = W_{12}^*$.

The system is described by new eigenstates and eigenenergies E_+ and E_-:

$$H|\varphi_+\rangle = E_+|\varphi_+\rangle$$
$$H|\varphi_-\rangle = E_-|\varphi_-\rangle$$

Show that the new eigenenergies are given by

$$E_\pm = \frac{1}{2}(E_1 + W_{11} + E_2 + W_{22}) \pm \frac{1}{2}\sqrt{(E_1 + W_{11} - E_2 - W_{22})^2 + 4|W_{12}|^2}$$

It can be shown (cf. Cohen-Tannoudji, vol. 1, supplement B$_{\text{IV}}$) that the eigenstates are given by

$$\boxed{\begin{aligned} |\psi_+\rangle &= cos\frac{\theta}{2}e^{-i\varphi/2}|\varphi_1\rangle + sin\frac{\theta}{2}e^{+i\varphi/2}|\varphi_2\rangle \\ |\psi_-\rangle &= -sin\frac{\theta}{2}e^{-i\varphi/2}|\varphi_1\rangle + cos\frac{\theta}{2}e^{+i\varphi/2}|\varphi_2\rangle \end{aligned}}$$

, with $tan\theta = \frac{2|W_{12}|}{E_1 + W_{11} - E_2 - W_{22}}$; $W_{21} = |W_{12}|e^{i\varphi}$

2. A graphical representation of the eigenenergies

The perturbation mixes states 1 and 2 due to the non-diagonal matrix elements W_{12}. We will only retain these in the following and assume $W_{11}=W_{22}=0$.

Introduce the quantities $E_m = \frac{1}{2}(E_1 + E_2)$, and $\Delta = \frac{1}{2}(E_1 - E_2)$, and draw the two branches of $E_\pm$, as a function of Δ. When the energy axis of Δ crosses the energy axis in the ordinate E_m, the curves for $E_\pm$, are two hyperbolas which are symmetric to the coordinate axes. E_1 and E_2 can be represented as straight lines with slope +1 and -1, respectively.

- Describe how the effect of the perturbation $E_+ - E_1$ $(\Delta > 0)$ or $E_+ - E_2$ $(\Delta < 0)$ changes as a function of $|\Delta|$.
- What is the value of the "resonance splitting" for $\Delta = 0$?
- Give examples of quantum mechanical systems, which show modified eigenenergies due to such non-diagonal interaction terms (W_{12}).

3. The dynamic evolution

The state of the whole system is in a superposition of the eigenstates

$$|\Psi(t)\rangle = \lambda e^{-iE_+t/\hbar}|\psi_+\rangle + \mu e^{-iE_-t/\hbar}|\psi_-\rangle$$

In order to obtain the time-dependent evolution in the states ϕ_1 and ϕ_2, we'll assume that the system is initially in $|\Psi(t=0)\rangle = |\varphi_1\rangle$ and project its evolution on the basis ϕ_1 and ϕ_2.

a) Express $|\Psi(t=0)\rangle = |\varphi_1\rangle$ in the basis $|\psi_+\rangle$ and $|\psi_-\rangle$.

b) Write the time-dependence of $\Psi(t)\rangle$ in this basis.

c) Show that the time-dependent probability for transition into $\varphi_2\rangle$ is given by

$$\boxed{P_{12}(t) = \frac{4|W_{12}|^2}{4|W_{12}|^2 + (E_1 - E_2)^2} sin^2\left(\sqrt{4|W_{12}|^2 + (E_1 - E_2)^2}\,\frac{t}{2\hbar}\right)}$$

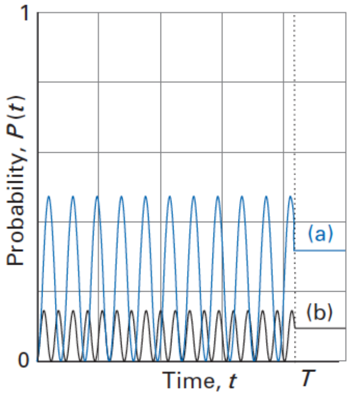
This is called the "Rabi transition probability".

4. Discussion – Evolution as a function of the perturbation

a) Show that P_{12} oscillates with the Rabi frequency $\omega_{+/-} = (E_+ - E_-)/2\hbar$, and with maximum amplitude $sin^2\theta$. Draw the time evolution.

b) Give an interpretation of this result, and discuss the two limiting cases $E_1 = E_2$ and "weak coupling" $(E_1 - E_2) \gg |W_{12}|$.

c) Which case is represented by the two curves (a) and (b) on the right. How does the coupling or the energy difference E_1-E_2 change between (a) and (b) ?



Master MCN

Light-matter interactions – Exercise classes

Session No. 3, Oct 25, 2022
S. Haacke & M. Gallart

Bloch vector representation of a two-level system

1. The most general form of a two-level system eigenstate is:

$$|\psi\rangle = cos\left(\frac{\vartheta}{2}\right)e^{+i\frac{\Phi}{2}}|a\rangle + sin\left(\frac{\vartheta}{2}\right)e^{-i\frac{\Phi}{2}}|b\rangle.$$

We note $\hat{\sigma}$ the corresponding density matrix operator.

Let us consider the so-called *Bloch vector* $\vec{\boldsymbol{U}} = \begin{pmatrix} u \\ v \\ w \end{pmatrix}$, the coordinates of which are defined as

$$\begin{cases} u = \frac{1}{2}(\sigma_{ab} + \sigma_{ba}) \\ v = \frac{1}{2i}(\sigma_{ab} - \sigma_{ba}) \\ w = \frac{1}{2}(\sigma_{aa} - \sigma_{bb}) \end{cases}$$

By using the general expression of $|\psi\rangle$, compute the expression of u, v and w as a function of θ and ϕ. Show that the extremity of $\vec{U}$ spans the surface of a sphere with radius ½. Draw a sketch displaying the angles θ and ϕ.

2. Now, we assume that $|\psi\rangle$ describes the eigenstate of a two-level system interacting with a sinusoidal electromagnetic field with angular frequency ω. The optical Bloch equations, in the absence of relaxations, are:

$$\begin{aligned} \dot{\sigma}_{aa} &= -i\frac{\Omega_1}{2}\left(\sigma_{ba}e^{+i\omega t} - \sigma_{ab}e^{-i\omega t}\right) \\ \dot{\sigma}_{bb} &= +i\frac{\Omega_1}{2}\left(\sigma_{ba}e^{+i\omega t} - \sigma_{ab}e^{-i\omega t}\right) \\ \dot{\sigma}_{ab} &= +i\omega_0\sigma_{ab} - i\frac{\Omega_1}{2}e^{+i\omega t}(\sigma_{bb} - \sigma_{aa}) \\ \dot{\sigma}_{ba} &= -i\omega_0\sigma_{ba} + i\frac{\Omega_1}{2}e^{-i\omega t}(\sigma_{bb} - \sigma_{aa}) \end{aligned}$$

where Ω_1 is the Rabi frequency and ω_0 is the Bohr frequency of the transition. Use the rotating frame transformation to eliminate the rapid time-dependence in the previous equation set. What is the physical meaning of this transformation?

3. By use of the results obtained in question 2, write the differential equations that are obeyed by $\tilde{u}$, $\tilde{v}$ and $\tilde{w}$, the three components of $\tilde{\boldsymbol{U}}$ in the rotating frame. Show that $\tilde{\boldsymbol{U}}$ undergoes a precession around a vector $\boldsymbol{\Omega}$ whose coordinates will be given. What is the frequency of this precession?

4. We focus on the case where the electric field frequency is resonant with the Bohr frequency of the transition, with the system initially in the ground state

$|a\rangle$. Give the equation of motion of $\tilde{\boldsymbol{U}}$. How is the precession modified as compared to the case treated in question 3? What is its new frequency? What is the time evolution of the excited state population?

Master MCN

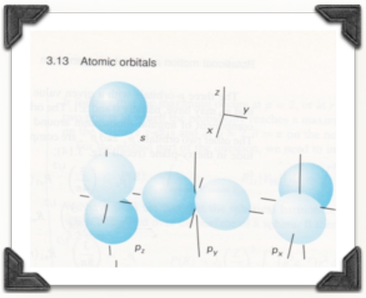
Electromagnetism – Exercise classes

November 15, 2022

S. Haacke & M. Gallart

The transition dipole moment – transition rates – selection rules – how to measure the TDM

1) Transition dipole moments of the 3p$_z$ – 2s transition in H atom



In the Sun's atmosphere, the H$_\alpha$ emission occurs due to emission of a gaz of hot H atoms. The transition is the longest wavelength emission in the Balmer series: **3p$_z$ –> 2s**.

a) Determine the transition frequency, and the wavelength of emission.

b) Show that the z-component of transition dipole moment is

$$\mu_z = -e\iiint \psi^*_{3p_z}\, z\, \psi_{2s}\, r^2 \sin\theta\, d\varphi d\theta\, dr = -Ca_0$$

and determine C (e: elementary charge, a$_0$: Bohr radius). To this end use the hydrogenoid wavefunctions provided in the appendix

c) Show that the TDM of the **3s** –> **2s** is zero. Try to predict a general rule for the occurrence of TDM = 0, in terms of the inversion symmetry of the wavefunctions of the initial and final states.
These rules are termed "<u>selection rules</u>" since they select the quantum mechanically allowed transitions among all those, which are energetically possible.

d) Is the emission due to stimulated or spontaneous emission ?

- Evaluate the transition rate given by $T_{i\rightarrow f} = B_{3p\rightarrow 2s}\, \rho_{rad}(\nu)$. Here, the Einstein coefficient $B_{3p\text{-}2s}$ is related to the total TDM by $B_{i\rightarrow f} = \dfrac{\left|\langle i|\vec{\mu}|f\rangle\right|^2}{6\varepsilon_0\hbar^2}$, and the spectral power density of the sun, approximated by a black body is $\rho_{\mathrm{rad}} = \dfrac{8\pi \mathrm{h}\nu^3/\mathrm{c}^3}{\exp\left(\dfrac{\mathrm{h}\nu}{\mathrm{kT}}\right)-1}$. Use 5400 K for the T of the sun's photosphere.
- Compare this rate to the one of spontaneous emission given by $A_{3p\rightarrow 2s} = B_{3p\rightarrow 2s}\dfrac{8\pi h\nu^3}{c^3}$

2) How can we measure the TDM ?

We'll show in this exercise that the extinction coefficient or absorption cross section of any material allows to determine the TDM, or equivalently, the oscillator strength of the measured transition.

a) Consider a two-level system with an initial low energy state $|i>$ and a high-energy final state $|f>$. Write down the <u>rates of change of population</u> in the inital and final states $T_{i\rightarrow f}$ and

$T_{f\rightarrow i}$, due to absorption and stimulated emission of light with the frequency $\nu = (E_f - E_i)/h$. To this end, use the standard description with Einstein coeffients $B_{i\text{-}f} = B_{f\text{-}i}$, and the spectral energy density $\rho_{rad}(\nu)$.

b) **Relate the Einstein coefficient to the transition dipole moment.** To this end, we recall Fermi's golden rule for the transition rate (unit 1/s) between initial an final state due to a perturbation W:

$$T_{i\rightarrow f} = \frac{2\pi}{\hbar}\left|\langle i|W|f\rangle\right|^2 \rho\left(E_{fi}\right)$$

. Here, $\rho(E_{fi})$ is the density of excited states, reached by absorption of photons with $\nu = (E_f - E_i)/h$.

Develop the expression for the transition rate using the electric dipole approximation for W, and introduce the energy density of the e.-m. field, $w_{EM} = 2\varepsilon_0\left|\vec{E}\right|^2$.

c) We introduce now the energy density per Hz $\rho_{rad}(\nu)$, related to the energy density by $w_{em}(\nu) = \rho_{rad}(\nu)d\nu$. For a transition into a *discrete* state, but accounting for a large number of photon states, expressed by $\rho_{rad}(\nu)$, with energies in the range of E_{fi} to $E_{fi} + dE$, one finds

$$T_{i\rightarrow f} = \frac{1}{6\varepsilon_0\hbar^2}\left|\langle i|\vec{\mu}|f\rangle\right|^2 \rho_{rad}\left(\nu = E_{fi}/h\right)$$

Compare this expression with the transition rates for absorption found in the Einstein equations. Justify that

$$B_{i\rightarrow f} = \frac{\left|\langle i|\vec{\mu}|f\rangle\right|^2}{6\varepsilon_0\hbar^2}$$

, and that $B_{i\text{-}f} = B_{f\text{-}i}$.

d) We now relate the molecular transition rate to the reduction of ρ_{rad} due to absorption. To this end, use Lambert-Beer's Law to express the change of light intensity dI due to absorption over a sample of length dz , containing N_i molecules with an absorption cross section α. Write the same equation in terms of $d\rho_{rad}$, using the relation $I = \frac{c}{n}\rho_{rad}(\nu)$.

e) Express the intensity of light as the surface photon density n_{ph}. Relate the molecular transition rate due to absorption to the change in the surface photon density n_{ph}/dt. Show that $B_{if} = \frac{c}{n}\frac{\alpha(\nu)}{h\nu}$, or for molecules in solution using the molar extinction coefficient $\varepsilon(\nu)$:

$$B_{if} = \frac{ln10c}{hnN_A}\frac{\varepsilon(\nu)}{\nu}$$

NB : Lambert-Beer's law using molar extinction coefficient $\varepsilon(\nu)$: $I(z) = I_0 10^{-\varepsilon(\nu)Cz}$, with C, the molar concentration (Mol/L).

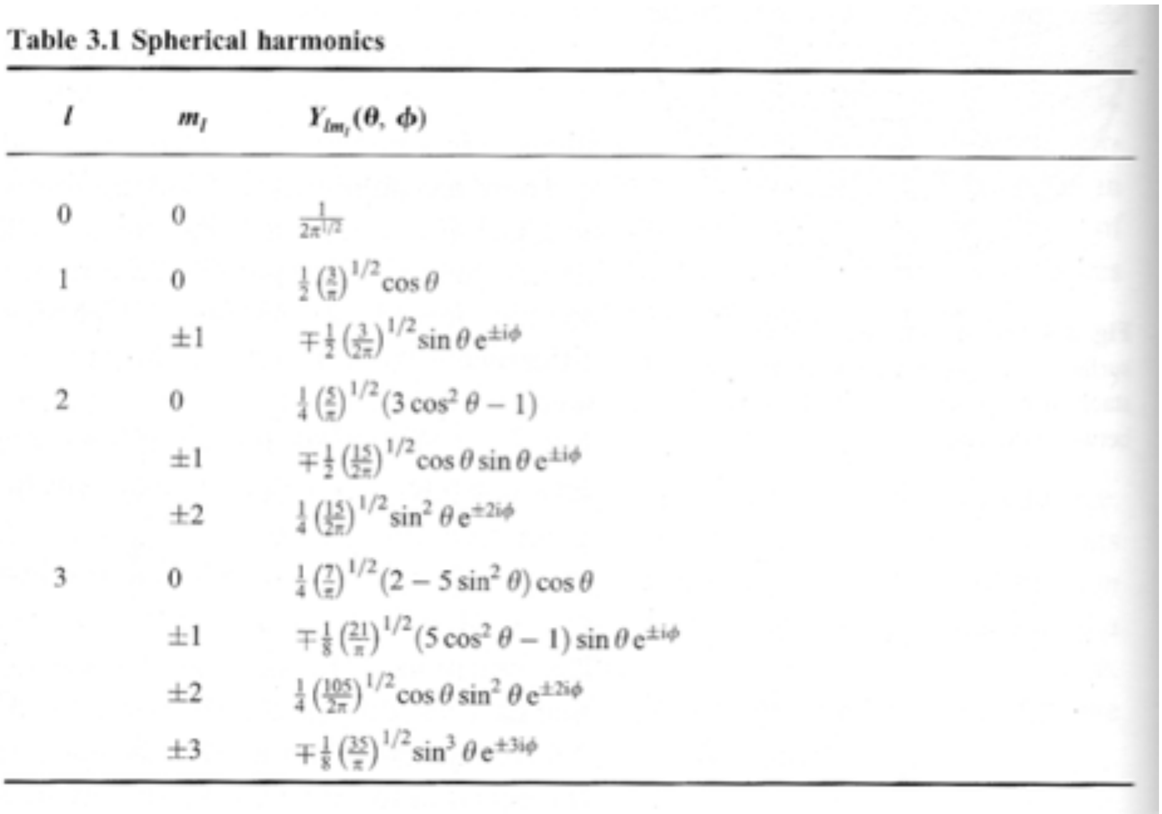


Table 3.1 Spherical harmonics

l	m_l	$Y_{lm_l}(\theta, \phi)$
0	0	$\frac{1}{2\pi^{1/2}}$
1	0	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}(3\cos^2\theta - 1)$
	±1	$\mp\frac{1}{2}\left(\frac{15}{2\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\frac{1}{4}\left(\frac{15}{2\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}(2 - 5\sin^2\theta)\cos\theta$
	±1	$\mp\frac{1}{8}\left(\frac{21}{\pi}\right)^{1/2}(5\cos^2\theta - 1)\sin\theta\, e^{\pm i\phi}$
	±2	$\frac{1}{4}\left(\frac{105}{2\pi}\right)^{1/2}\cos\theta\sin^2\theta\, e^{\pm 2i\phi}$
	±3	$\mp\frac{1}{8}\left(\frac{35}{\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

$$\rho = (2Z/na_0)r$$

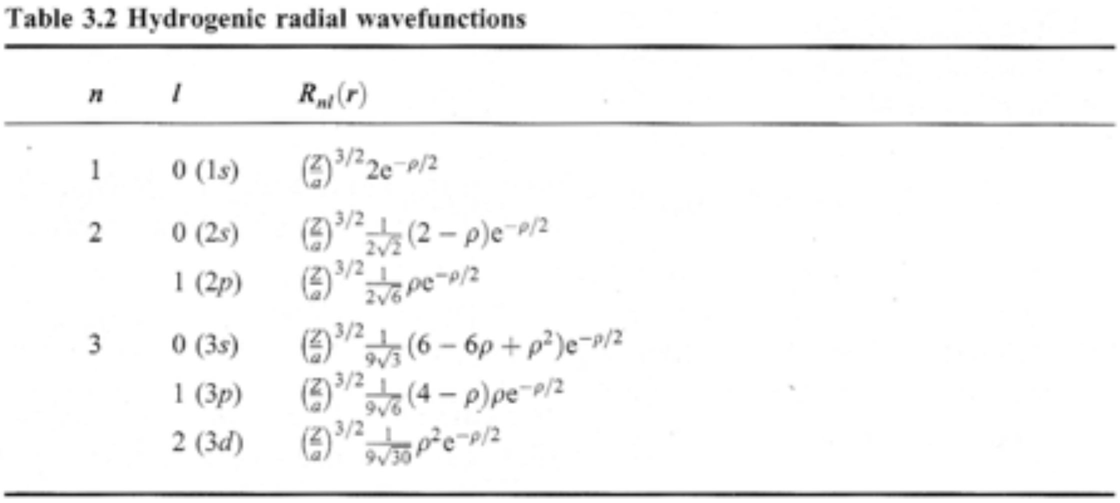


Table 3.2 Hydrogenic radial wavefunctions

n	l	$R_{nl}(r)$
1	0 (1s)	$\left(\frac{Z}{a}\right)^{3/2} 2e^{-\rho/2}$
2	0 (2s)	$\left(\frac{Z}{a}\right)^{3/2}\frac{1}{2\sqrt{2}}(2 - \rho)e^{-\rho/2}$
	1 (2p)	$\left(\frac{Z}{a}\right)^{3/2}\frac{1}{2\sqrt{6}}\rho e^{-\rho/2}$
3	0 (3s)	$\left(\frac{Z}{a}\right)^{3/2}\frac{1}{9\sqrt{3}}(6 - 6\rho + \rho^2)e^{-\rho/2}$
	1 (3p)	$\left(\frac{Z}{a}\right)^{3/2}\frac{1}{9\sqrt{6}}(4 - \rho)\rho e^{-\rho/2}$
	2 (3d)	$\left(\frac{Z}{a}\right)^{3/2}\frac{1}{9\sqrt{30}}\rho^2 e^{-\rho/2}$

The sun’s Hα line : The 3p → 2s transition in hydrogen

A. Determine the transition frequency, given the formula for energy levels (1)

$$h\nu = -13{,}6\,\text{eV}\left(\frac{1}{3^2}-\frac{1}{4}\right) = 1{,}904\,\text{eV} = 3{,}046\times 10^{-19}\,\text{J}\,.$$

And thus ν = 4.57 x 10^{14} Hz.

B. Show that the transition dipole moment is $\mu_z = -e\int\int\int \psi^*_{3p_z}\, z\,\psi^*_{2s}\, r^2 \sin\theta\, d\varphi d\theta\, dr = -Cea_0$ and determine C.

The definition of the z-component of the transition dipole moment gives

$$\langle 3p|\mu_z|2s\rangle = -e\int\int\int \psi^*_{3p_z}\, z\,\psi^*_{2s}\, r^2 \sin\theta\, d\varphi d\theta\, dr$$

with the real-valued wavefunctions given for $3p_z$ and the 2s state,

$$\psi *_{3p_z} = \psi_{3p_z} = Y_{l=1,ml=0}(\theta,\varphi)R_{3,1}(r) = \frac{1}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{2}} \cos\theta \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \frac{1}{9\sqrt{6}}\left(4-\frac{2r}{3a_0}\right)\frac{2r}{3a_0}\,e^{-\frac{r}{3a_0}}$$

$$\psi_{2s} = Y_{l=0,ml=0}(\theta,\varphi)R_{2,0}(r) = \frac{1}{2\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} \frac{1}{2\sqrt{2}}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$$

We find, after multiplying all the prefactors,

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^*_{3p_z}\, z\,\psi^*_{2s}\, r^2 \sin\theta\, d\varphi d\theta\, dr =$$

$$-\frac{2\pi}{72\times 2\pi}\frac{e}{a_0^3}\int_0^{\pi}\cos^2\theta \sin\theta\, d\theta \int_0^{\infty} r^3\left(4-\frac{2r}{3a_0}\right)\left(2-\frac{r}{a_0}\right)\frac{2r}{3a_0}e^{-5r/6a_0}\,dr$$

, where the 2π comes from the integral over ϕ.

The integral over θ is 2/3, so that

$$\langle 3p_z|\mu_z|2s\rangle = -\frac{e}{72}\frac{2}{3}\int_0^{\infty}\left(8-\frac{16}{3}\frac{r}{a_0}+\frac{2}{3}\left(\frac{r}{a_0}\right)^2\right)\frac{2}{3}\frac{r^4}{a_0^4}\,e^{-5r/6a_0}\,dr$$

After variable transformation

$$\langle 3p_z|\mu_z|2s\rangle = -\frac{ea_0}{9\times 18}\int_0^{\infty}\left(8-\frac{16}{3}u+\frac{2}{3}u^2\right)u^4 e^{-5u/6}du$$

With $\int_0^{\infty} u^n e^{-au}\,du = \frac{1}{a^{n+1}}n!$ it follows that

$$\langle 3p_z|\mu_z|2s\rangle = -\frac{ea_0}{9\times 18}\left(\frac{6}{5}\right)^5 4!\left\{8-\frac{16}{3}\frac{6}{5}\times 5+\frac{2}{3}\frac{36}{25}\times 30\right\}$$

We thus obtain for the z-component of μ: $\mu_z = -1{,}769\, ea_0$. This is indeed a dipole moment (charge x distance) with the right order of magnitude.

C. Show that the TDM of the 3s –> 2s is zero.

For the 3s → 2s transition, the integral over θ vanishes, and therefore $\langle 3s|\mu_z|2s\rangle = 0$. In more general terms, if the integral goes over a function $f(\overrightarrow{r})$ with an odd symmetry, with respect to the sign inversion of $\vec{r}$, $f(-\overrightarrow{r}) = -f(\overrightarrow{r})$, then the integral is zero.

D. Is the emission due to stimulated or spontaneous emission ?

1) Evaluate the transition rate for stimulated emission given by $T_{i\to f} = B_{3p\to 2s}\,\rho_{rad}(\nu)$. Here, the Einstein coefficient B_{3p-2s} is related to the total TDM by $B_{i\to f} = \frac{\left|\langle i|\vec{\mu}|f\rangle\right|^2}{6\varepsilon_0\hbar^2}$, and the spectral power density of the sun, approximated by a black body is $\rho_{\mathrm{rad}} = \frac{8\pi \mathrm{h}\nu^3/\mathrm{c}^3}{\exp\left(\frac{\mathrm{h}\nu}{\mathrm{kT}}\right)-1}$. Use 5400 K for the T of the sun's photosphere.

The total transition dipole moment $|\langle i|\vec{\mu}|f\rangle|^2 = \mu_x^2 + \mu_y^2 + \mu_z^2 = 3\mu_z^2$ since the atom is spherical.

Hence, the Einstein coefficient is $B_{3p-2s} = \frac{\left|\langle i|\vec{\mu}|f\rangle\right|^2}{6\varepsilon_0\hbar^2} = 1.16\ 10^{21}\ \mathrm{J^{-1}\ m^3\ s^{-2}}$.

For T= 5400 K, and $\nu = 4.57 \times 10^{14}$ Hz, we find $\rho_{\mathrm{rad}} = 1.037\ 10^{-15}$ J/(Hz m^3).

It follows for the transition rate of **stimulated emission** $T_{SE} = B_{3p-2s}\rho_{rad}$= 1.20 10^6 s^{-1}.

2) Compare this rate to the one of spontaneous emission given by $A_{3p\to 2s} = B_{3p\to 2s}\frac{8\pi h\nu^3}{c^3}$

Indeed, spontaneous emission does not involve the radiation field, and the transition rate is simply $T_{sp} = A_{3p-2s}$.
We find $\frac{8\pi h\nu^3}{c^3} = 5.87\ 10^{-14}$ Jsm^{-3}, and thus A_{3p-2s} =6.82 10^7 s^{-1}.
T_{sp} is roughly 50 times higher than T_{SE} ! The atoms recombine more frequently by spont. emission than by stim. emission. This is true in general, unless the radiation field is very intense and enhances stim. emission, as it is the case in a laser (the laser cavity creates a very high energy density).

The average lifetime of the atoms in the 3p level can therefore be deduced from the simple relation: $\tau = \frac{1}{T_{sp}} = 14.7$ ns. This is a typical order of magnitude for radiative lifetimes of atoms and molecules (2-20 ns for allowed an intense transitions).

Master MCN

Light-Matter interactions – Exercise classes

Sessions No. 6&7, Dec 2 & 16, 2021

S. Haacke & M. Gallart

Vibrational mid-IR spectroscopy - Franck-Condon principle – Franck-Condon factors for vibronic transitions – absorption spectra of polyatomic molecules

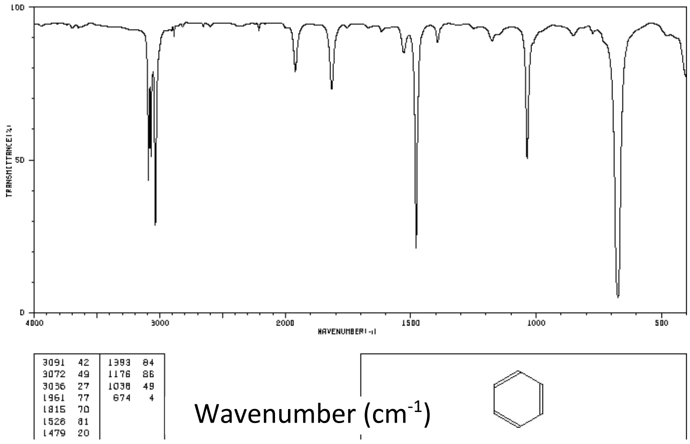
Background and motivation

What determines the spectral width of absorption and emission spectra of polyatomic molecules ? Many examples like figure 2 exist, where the spectra are periodically modulated.

Task 1: Selection rules in vibrational mid-IR spectroscopy – the harmonic oscillator

The IR absorption spectrum of benzene (below, https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi) shows only one peak for the C=C vibration (1479 cm^{-1}), although many transitions n=0 → n', called "overtones", are energetically possible. For a harmonic oscillator, these should appear at 2 x 1479 cm^{-1}, 3x 1479 cm^{-1} and so on. Why aren't they observed ?

a) Find out (Google) where this energy scale in cm^{-1} comes from. In spectroscopy, this unit is called "wave numbers" or "inverse centimeters".
b) What are the different peaks in the spectrum due to ?
c) Derive the selection rules for IR absorption (transitions in the ground state harmonic oscillator), by using the recursion and orthogonality properties of Hermitian polynomials (cf. lecture).

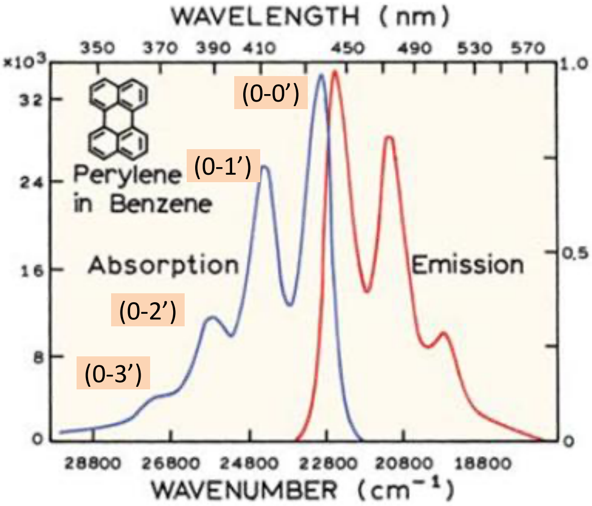


3091	42	1393	84
3072	49	1176	86
3036	27	1038	49
1961	77	674	4
1815	70		
1526	81		
1479	20		

Figure 1: Mid-IR transmission spectrum of benzene in gas phase. Energy scale in cm^{-1} ("wave numbers").

Task 2 : Vibronic progressions in UV/VIS spectra

Calculate approximately the energy difference of the peaks labeled (0-0'), (0-1'), (0-2'), (0-3'), and determine the corresponding average frequency (in cm^{-1}). What kind of molecular excitation does this frequency correspond to ?



https://chemistry.stackexchange.com/questions/76942/calculating-the-uv-vis-spectrum-of-perylene

Figure 2: Absorption and emission spectra of perylene in the solvent benzene.

The absorption and emission transitions occur between electronic states (cf. fig. 3), the potential energy surfaces of which are bound potentials. These can be approximated by harmonic potentials describing the molecular vibrations along specific bonds (e.g. C=C, or C-C). These molecular vibrations are quantized, with eigenenergies $E_\nu = \hbar\omega(\nu + 1/2)$, according to the quantum number ν, and with the wavefunction $\varphi_\nu\left(\vec{R}\right) = N_\nu H_\nu\left(\sqrt{\alpha}x\right)e^{-\alpha x^2/2}$, with α defined by the relevant reduced mass μ and the spring constant k: $\alpha = \frac{\sqrt{\mu k}}{\hbar}$, and H$_\nu$($\sqrt{\alpha}$x) the Hermitian polynomials. The normalization constant is $N_\nu = \left(\frac{1}{2^\nu \nu!}\sqrt{\frac{\alpha}{\pi}}\right)^{1/2}$.

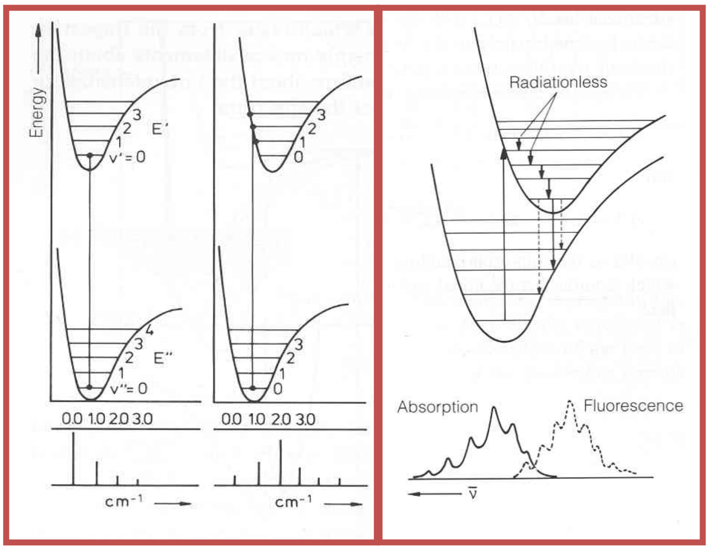


Figure 3: Schematic of the vibronic transitions in absorption (left) and emission (right).

More in detail the total wavefunction is described by an electronic and a vibrational part:

$$\left|\Psi\right\rangle = \left|\varepsilon,\nu\right\rangle$$

$\Psi\left(\vec{r},\vec{R}\right) = \psi_\varepsilon\left(\vec{r},\vec{R}\right)\varphi_\nu\left(\vec{R}\right)$, with ε indexing the electronic state. This is the **Born-Oppenheimer approximation**, based on the fact that nuclei move much slower than electrons.

The transition dipole moment then reads:

$$\left\langle \varepsilon',v'\middle|\vec{\mu}\middle|\varepsilon,v\right\rangle = \int \varphi^*_{v'}\left(\vec{R}\right)\left\{\int \psi^*_{\varepsilon'}\left(\vec{r},\vec{R}\right)\vec{\mu}\psi_{\varepsilon}\left(\vec{r},\vec{R}\right)d^3\vec{r}\right\}\varphi_{v}\left(\vec{R}\right)d^3\vec{R}$$

The Franck-Condon principle, assumes that during light absorption the atoms do not move (**R**= const.), leading to factorisation of the integrals:

$$\left\langle \varepsilon',v'\middle|\vec{\mu}\middle|\varepsilon,v\right\rangle = \left\{\int \psi^*_{\varepsilon'}\left(\vec{r},\vec{R}\right)\vec{\mu}\psi_{\varepsilon}\left(\vec{r},\vec{R}\right)d^3\vec{r}\right\}\int \varphi^*_{v'}\left(\vec{R}\right)\varphi_{v}\left(\vec{R}\right)d^3\vec{R}$$

$$= \left\{\int \psi^*_{\varepsilon'}\left(\vec{r},\vec{R}\right)\vec{\mu}\psi_{\varepsilon}\left(\vec{r},\vec{R}\right)d^3\vec{r}\right\}\times F(v',v)$$

The electronic part includes the selection rules (symmetry of electronic wavefunctions), while *F(*ν*',* ν*)*, the Franck-Condon factor, modulates the transition strength giving rise to the periodic modulations observed in fig.2. We will explicitely calculate them in the following.

Task 3: Calculate the FC factors *F(*ν*',* ν*)*

a) ν'=0 → ν=0. The ν'=0 vibrational state in the electronic ground state is $\varphi_{v'=0}\left(\vec{R}\right)=\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\alpha\left(R-R_e\right)^2/2}$, with R_e, the equilibrium bond length in the electronic ground state, and $\varphi_{v=0}\left(\vec{R}\right)=\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\alpha\left(R-Q_e\right)^2/2}$, the one for the excited state with Q_e, the excited state equilibrium bond length (fig. 2). We assume the same α, meaning the same restoring force constant k in both electronic states. Show that $F\left(0',0\right)=e^{-\alpha\left(R_e-Q_e\right)^2/4}$

For this use $\int_{-\infty}^{\infty}e^{-ax^2}dx=\sqrt{\frac{\pi}{a}}$. Plot $F(0',0)$ as a function of $\Delta=\sqrt{\alpha}\Delta R=\sqrt{\alpha}\,(R_e-Q_e)$ and justify its shape.

b) ν'=0 → ν=1. The ν=1 vibrational state in the electronic excited state is

$$\varphi_{v=1}(R)=\frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4}H_1(R-Q_e)e^{-\frac{\alpha(R-Q_e)^2}{2}}=\sqrt{2}\left(\frac{\alpha}{\pi}\right)^{1/4}\sqrt{\alpha}\,(R-Q_e)\,e^{-\frac{\alpha(R-Q_e)^2}{2}}.$$

Show that $F\left(0',1\right)=\frac{\sqrt{\alpha}}{2}\left(R_e-Q_e\right)e^{-\alpha\left(R_e-Q_e\right)^2/4}$, and discuss its shape as a function of Δ compared to $F(0',0)$.

c) If we introduce the displacement of the two potential energy curves $\Delta=\sqrt{\alpha}(R_e-Q_e)$, and the **Huang-Rhys factors** as $S=\Delta^2/2$, one can show that for transitions to higher vibrational states, the square of the Franck-Condon factors are $\left|F(0',v)\right|^2=\frac{S^v}{v!}e^{-S}$. Justify this result on the basis of the form of the Hermitian polynomials.

d) For the **emission process**, the transitions occur from ν=0 → ν' (fig. 2), since vibrational relaxation in the excited state leads to population only of ν=0 (in the limit $\hbar\omega \gg k_BT$).

Justify that $\left|F(0',v)\right|^2=\left|F(0,v')\right|^2$.

e) Optional: Show that $\sum_{v} |F(0',v|^2 = 1$, by using the fact that the vibrational wavefunctions form a complete orthonormal basis set.

Task 4: Building a theoretical absorption spectrum including the FC factors

Figure 4a displays the situation for S=1, for the displaced harmonic oscillators. Figure 4b gives a schematic absorption spectrum. Determine the energy (in cm^{-1}) of the main parameters used: the electronic transition energy $\Delta E = E(S_1 - S_0)$, and the vibrational quantum $\hbar\omega$.

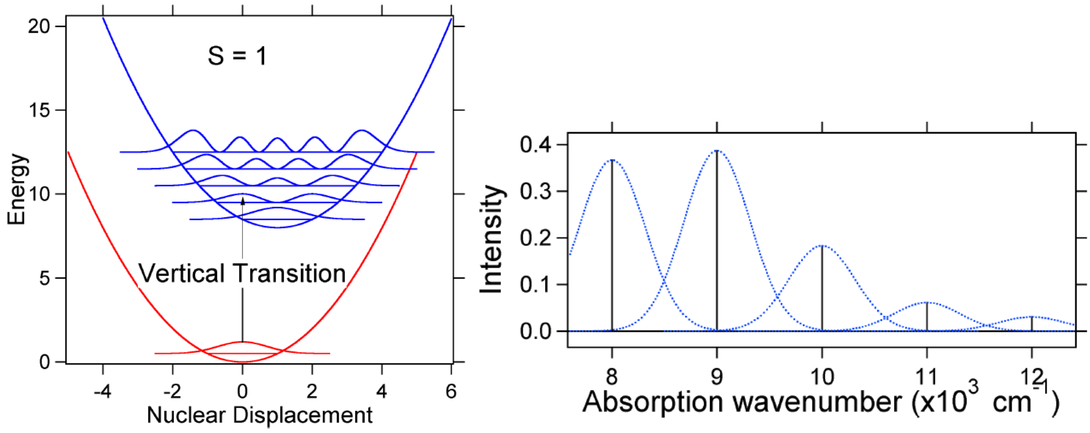


Figure 4: a: Alignment of excited and ground state harmonic potentials for S=1; b: Schematic absorption spectrum for the situation depicted in (a). The vibronic transitions are broadened by a Gaussian function.

- **a)** Build the absorption and emission spectra using the same parameters, but for S=2.
- **b)** Determine the Stokes shift, the difference between the maximum of absorption and emission spectra (cf. lecture), for S=2.

11.4 Normal mode frequencies

- Vibrational frequencies are chemical fingerprints

  The lighter the elements, the higher the frequency

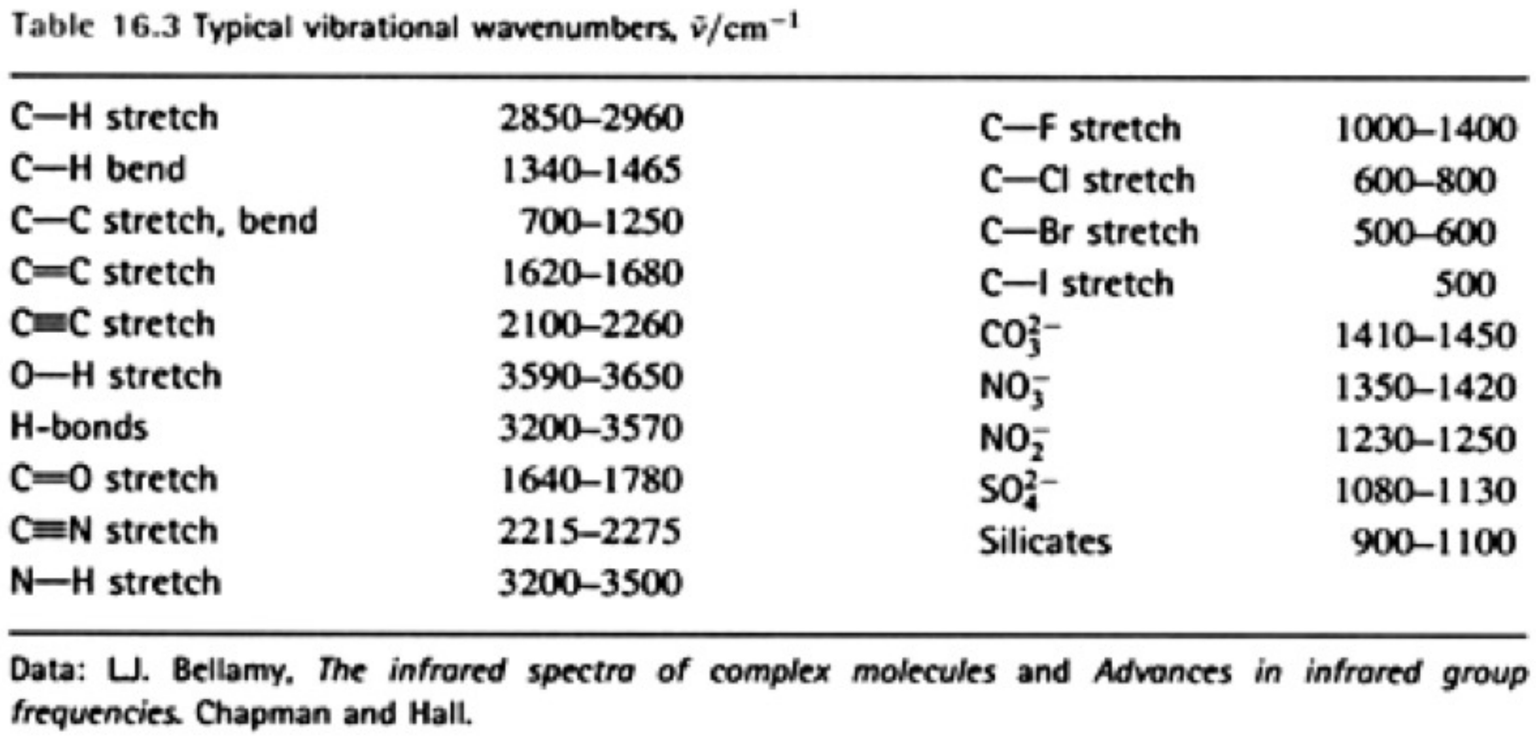


Table 16.3 Typical vibrational wavenumbers, $\tilde{\nu}/\text{cm}^{-1}$

C—H stretch	2850–2960	C—F stretch	1000–1400
C—H bend	1340–1465	C—Cl stretch	600–800
C—C stretch, bend	700–1250	C—Br stretch	500–600
C═C stretch	1620–1680	C—I stretch	500
C≡C stretch	2100–2260	CO_3^{2-}	1410–1450
O—H stretch	3590–3650	NO_3^-	1350–1420
H-bonds	3200–3570	NO_2^-	1230–1250
C═O stretch	1640–1780	SO_4^{2-}	1080–1130
C≡N stretch	2215–2275	Silicates	900–1100
N—H stretch	3200–3500		

Data: L.J. Bellamy, *The infrared spectra of complex molecules* and *Advances in infrared group frequencies*. Chapman and Hall.

Master MCN

Light-Matter interactions – Exercise classes

Sessions No. 8, Dec 6, 2022

S. Haacke & M. Gallart

Rotational & Vibrational mid-IR spectroscopy

Background and motivation
Understand the rotational fine structure observed in mid-IR absorption of a di-atomic molecule in a dilute gas.

Figure 1 presents the mid-IR absorption spectrum of H-Cl in diluted gas phase, with increasing energy from right to left. Every peak appears as a doublet. The spectral lines are determined in cm^{-1}. The values for the four central peaks are ν = 2906,24 ; 2904,11 ; 2865,10 ; 2863,02 cm^{-1}

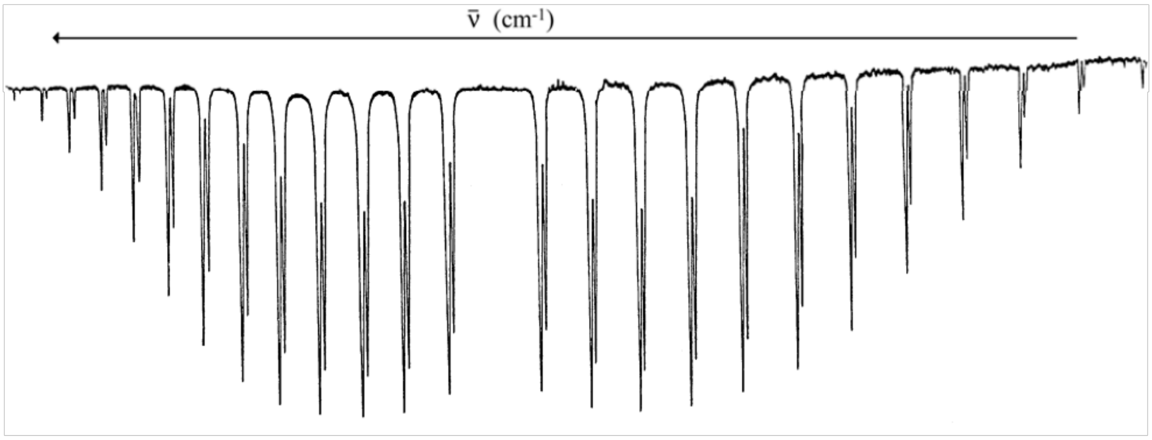


Figure 1: Mid-IR transmission spectrum of HCl in gas phase. Energy scale in cm^{-1} ("wave numbers").

Question 1: Explain the origin of the absorption peaks

The spectral range is in the mid-infrared (3-30 μm), which means that the photon energy is not large enough to induce transitions between electronic states. The observed transitions are between quantum states in the electronic <u>ground state only.</u>

a) Recall the eigenergies of a di-atomic molecule including the vibrational and rotational eigenstates, using the quantum numbers n (harmonic oscillator) and J (rotation of a molecule with moment of inertia I). Make a schematic diagram of the quantum levels involved in the spectral transitions.

b) Within the dipolar approximation, recall the selection rules for vibrational and rotational transitions, between the eigenstates.

c) The "R branch" corresponds to transitions with ΔJ=+1 and the "P branch" to ΔJ=-1. Where are these branches located in the spectrum ?

d) The origin of the doublet structure is due to an "isotope effect". Indeed Cl is present in both the ^{35}Cl and ^{37}Cl isotopes. How does the isotope effect change the transition energies ?

e) The intensity of the peaks is given by the absorption A=1 -T. And A is proportional to the number of molecules in the ground state: N (n=0) = f(J). Find a formula expressing N(J) as a function of temperature T and the degeneracy of the rotational levels g_J. What is the origin of the decreasing peak intensity on both sides of the spectrum ?

f) What spectral resolution $\Delta\lambda/\lambda$ is required to resolve the doublet structure ?

Question 2 : Determine the molecular parameters

a) Show that, for the intense peaks in the doublets, the rotational constant $B = \frac{h^2}{8\pi^2 I}$ is equal to 10,28 cm^{-1}. What is the value of the moment of inertia I ?

b) Calculate the reduced mass for ^{35}Cl and calculate the interatomic radius r from the value of I.

c) From the vibrational frequency ω, show that the force constant k is equal to 476 Nm^{-1}. N.B. Use the first peak of the R band to determine the vibrational transition frequency $\hbar\omega$.

Master Nanophysics & Condensed Matter January 25, 2022

Exam in "Light-matter interactions"

S. Haacke & M. Gallart

Test duration: 3 hours

I- Spectroscopy of the tetracene monomer

The figure below displays the normalized steady state absorption (black) overlapped with the steady state fluorescence (red) of the tetracene monomer. In this part, we will interpret these experimental results by using what we know about the spectroscopy of diatomic molecules.

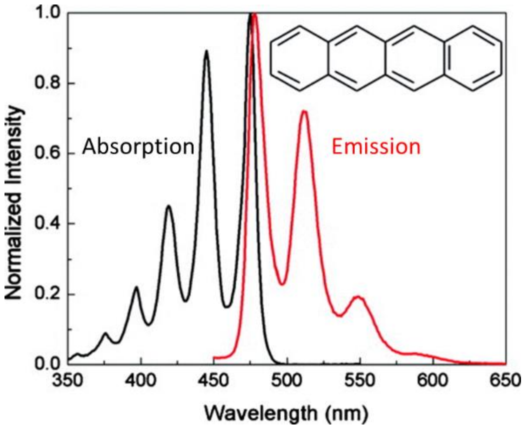


Figure 1 :Absorption(black line) and emission (red line) of tetracene in a toluene solution[1]*.*

1- Give the formal expression of the wavefunctions associated with the electronic states of a diatomic molecule. Which quantum numbers label each component of the total wavefunction and of which degree of freedom are they characteristic?

2- Describe the initial and final states that are implied in the optical transitions responsible for the spectra presented in the figure 1. Draw a sketch of these energy levels labeled with the right quantum numbers.

3- Explain in few words what is the Franck-Condon approximation. Using the simple theoretical model that you know, outline the concept and general formulas by which the intensity of each individual spectral line can be calculated, both in absorption and emission.

4- The individual lines within each spectrum are split by a constant amount of energy $\hbar\omega_0$. What is this energy quantum characteristic of? Describe now qualitatively the scenario leading, after light-absorption from the molecular ground state, to light emission from an excited state. Specify which relaxation processes or transitions between the quantum states are radiative or non-radiative. How can one explain the mirror symmetry between both spectra of figure 1?

---

[1] Burdett, Jonathan & Mueller, Astrid & Gosztola, David & Bardeen, Christopher. (2010). Excited state dynamics in solid and monomeric tetracene: The roles of superradiance and exciton fission. The Journal of chemical physics. 133. 144506. 10.1063/1.3495764.

II- Einstein equations and perturbative approach

The Einstein model of light-matter interaction is a phenomenological model that describes the radiation of a two-level system at the thermal equilibrium. We consider here an ensemble of N two-level atoms with ground and excited states E_a and E_b, respectively, and such as E_b - E_a = $\hbar\omega_0$. We denote the corresponding populations N_a and N_b. The rate equation describing the time evolution of the excited population in interaction with a thermal field, with spectral density $u(\omega)$, is:

$$\frac{dN_b}{dt} = -AN_b - B_{ba}u(\omega_0)N_b + B_{ab}u(\omega_0)N_a \tag{1}$$

1- Explain the meaning of the different terms occurring in equation (1) and indicate their respective units. Write the condition of population conservation (closed system).

2- In the stationary regime, express the ratio N_b/N_a at the thermal equilibrium. Then, find the temperature dependent general relation between A, B_{ba}, B_{ab}. First, consider the limit of high temperatures when $k_BT >> \hbar\omega_0$ to deduce that $B_{ba} = B_{ab} \equiv B$. Then, use this result and the fact that the field is thermal to write the equation connecting A and B.

We remind the spectral density of the black body radiation as a function of ω:

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1}$$

3- According to the time-dependent perturbation theory, the probability of transition between an initial state$|i\rangle$ with energy E_i and a final state $|f\rangle$ with energy E_f, when a perturbation W is applied for a duration t is:

$$P_{if}(t) = \frac{1}{\hbar^2}\left|\int_0^t dt'\langle f|W(t')|i\rangle\, e^{i(E_f-E_i)t'/\hbar}\right|^2$$

Express the transition probability per unit frequency dP_{ab} from a to b under the influence of the electric dipole operator related to an electric field $\boldsymbol{E}(\omega)$ linearly polarized along the **z**-direction. Assume the resonant approximation and discuss its validity.

4- By integrating dP_{ab} over all the frequencies ω and by averaging the dipole orientation over all the directions of space, show that the time-dependent probability of transition is

$$P_{ab} = \frac{\pi q^2 r_{ba}^2}{3\varepsilon_0\hbar^2}u(\omega_0)t$$

We give:

$$\lim_{t\to\infty}\left[\frac{\sin(\omega_0-\omega)\,t/2}{(\omega_0-\omega)t/2}\right]^2 = 2\pi t\delta(\omega_0-\omega)$$

5- Express the absorption probability per unit time. By drawing a parallel between the present probability and the phenomenological constant of the Einstein's rate equations, deduce the expression for the spontaneous emission rate of the two-level system.

III- Mid-IR spectroscopy: Vibrational and rotational-vibrational spectroscopy

Figure 2 shows the mid-IR absorption spectrum of CO in the gas phase, measured with poor spectral resolution. It shows two broad bands, one centered at 2143 cm^{-1} and a second at 4260 cm^{-1}.

1- Convert these energies into wavelengths and energies in Joule.

We will use cm^{-1} as the energy scale for the following questions.

2- What is the selection rule for transitions between quantum states of an harmonic oscillator? Indicate possible reasons for the observation of the second absorption band at 4260 cm^{-1}.

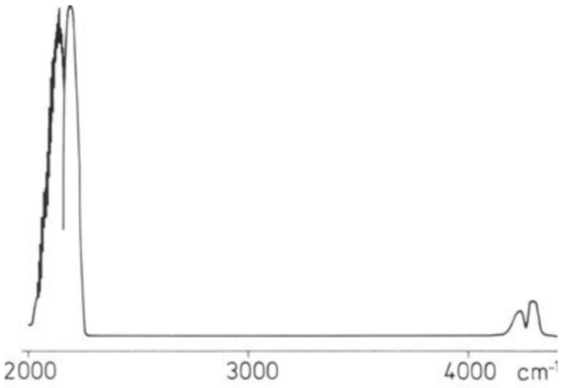


Figure 2: Absorption spectrum of CO in the gas phase

Figure 3 shows the mid-IR transmission spectrum of HBr. The two central peaks are found at 2539.5 and 2570.4 cm^{-1}.

3- Make a schematic drawing of the quantum states and energy levels involved in these transitions. Distinguish vibrational and rotational quantum states, and recall the precise formulas for their energies as a function of ν, the vibrational quantum number, and J, the rotational quantum number.

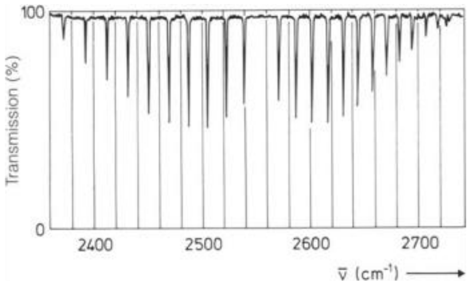


Figure 3: Mid-IR transmission spectrum of HBr in gas phase.

4- Recall the selection rules for rotational transitions, and explain the origin of the observed peaks.

5- Give the formula for the transition energies observed, as a function of the vibrational quantum $\hbar\omega$ and of the rotational constant B.

6- Determine B (in cm^{-1}), and translate it into $\hat{B} = Bhc$, the rotational constant in Joule. Here h is Planck's constant (6.62 x10^{-34} Js) and c the speed of light in cm/s. The molar masses are M_H = 1,008 g/mol, and M_{Br} = 79,94 g/mol. Deduce the atomic masses m_H and m_{Br}, and determine the interatomic distance $R_{\text{H-Br}}$ from $\hat{B}$.

7- Determine the energy of the vibrational quantum $\hbar\omega$ (in cm^{-1}). Translate it into Joule, outline the formulas for determining the molecules spring constant k.

8- How would the shape of the spectra change when the temperature is lowered to T= 4 K? How would the ratio $R = \frac{T(2539.5\ cm^{-1})}{T(2377\ cm^{-1})}$ of the peaks in the center and at the far-left change? Justify your answer.

Avogadro constant: N_A = 6,02 x10^{23}

Master Nanophysics & Condensed Matter January 27, 2021

Exam in “Light-matter interaction”

S. Haacke & M. Gallart

Test duration: 3 hours

I- Bloch vector representation of a two-level system

1. The most general form of a two-level system eigenstate is:

$$|\psi\rangle = cos\left(\frac{\vartheta}{2}\right)e^{+i\frac{\Phi}{2}}|a\rangle + sin\left(\frac{\vartheta}{2}\right)e^{-i\frac{\Phi}{2}}|b\rangle.$$

We note $\hat{\sigma}$ the corresponding density matrix operator.

Let us consider the so-called *Bloch vector* $\boldsymbol{U}\begin{pmatrix} u \\ v \\ w \end{pmatrix}$, the coordinates of which are defined as

$$\begin{cases} u = \frac{1}{2}(\sigma_{ab} + \sigma_{ba}) \\ v = \frac{1}{2i}(\sigma_{ab} - \sigma_{ba}) \\ w = \frac{1}{2}(\sigma_{aa} - \sigma_{bb}) \end{cases}$$

By using the general expression of $|\psi\rangle$, compute the expression of u, v and w as a function of θ and ϕ. Show that the extremity of $\overrightarrow{U}$ spans the surface of a sphere with radius ½. Draw a sketch displaying the angles θ and ϕ.

2. Now, we assume that $|\psi\rangle$ describes the eigenstate of a two-level system interacting with a sinusoidal electromagnetic field with angular frequency ω. The optical Bloch equations, in the absence of relaxations, are:

$$\begin{aligned} \dot{\sigma}_{aa} &= -i\frac{\Omega_1}{2}\left(\sigma_{ba}e^{+i\omega t} - \sigma_{ab}e^{-i\omega t}\right) \\ \dot{\sigma}_{bb} &= +i\frac{\Omega_1}{2}\left(\sigma_{ba}e^{+i\omega t} - \sigma_{ab}e^{-i\omega t}\right) \\ \dot{\sigma}_{ab} &= +i\omega_0\sigma_{ab} - i\frac{\Omega_1}{2}e^{+i\omega t}(\sigma_{bb} - \sigma_{aa}) \\ \dot{\sigma}_{ba} &= -i\omega_0\sigma_{ba} + i\frac{\Omega_1}{2}e^{-i\omega t}(\sigma_{bb} - \sigma_{aa}) \end{aligned}$$

where Ω_1 is the Rabi frequency and ω_0 is the Bohr frequency of the transition.
Use the rotating frame transformation to eliminate the rapid time-dependence in the previous equation set. What is the physical meaning of this transformation?

3. By use of the results obtained in question 2, write the differential equations that are obeyed by $\widetilde{u}$, $\widetilde{v}$ and $\widetilde{w}$, the three components of $\widetilde{\boldsymbol{U}}$ in the rotating frame. Show that $\widetilde{\boldsymbol{U}}$ undergoes a precession around a vector $\boldsymbol{\Omega}$ whose coordinates will be given. What is the frequency of this precession?

4. We focus on the case where the electric field frequency is resonant with the Bohr frequency of the transition, with the system initially in the ground state $|a\rangle$. Give the equation of motion of $\widetilde{\boldsymbol{U}}$. How is the precession modified as compared to the case treated in question 3? What is its new frequency? What is the time evolution of the excited state population?

II- Optical pumping

We will study in this exercise the effect of “optical pumping” of an atom. We will show that the selection rules governing the interaction of an atom with **circularly polarized light** lead, under continuous illumination of the ground-to-excited state transition, to a non-equilibrium distribution of population among the sub-levels of the ground state.

We consider an atomic transition between a ground state of total angular momentum $J_a = ½$ and an excited state with total angular momentum $J_b = ½$. In the absence of incident light, the two ground-state sub-levels, which have the same energies, are equally populated: half of the atoms are initially in each of the states $m_a = -½, +½$. The quantization axis is chosen to be along the z direction.

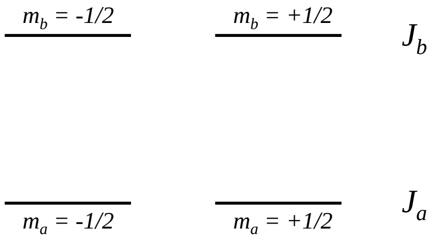


Figure 1 : diagram of ground and excited states of the studied atom/

1. The population of atoms interacts with a σ^+ circularly polarized light, the frequency of which is resonant with the $J_a = 1/2 \rightarrow J_b = 1/2$ transition. Which one of the two possible excited states is populated through light absorption? Justify your answer by discussing the optical selection rules.

2. We assume that atoms can relax from the excited state determined in question **2** to their ground state by spontaneous emission. What are the possible final ground-states of the relaxation? What is the polarization of the emitted light?

3. Under continuous illumination with σ^+ circularly polarized light a steady state is reached. Experimentally it is found that the incoming light is no longer absorbed. The progress towards the steady state can be monitored by measuring the transmission of the pumping light (see figure below). As a consequence, the σ^+ circularly polarized emission goes to zero intensity. What does this suggest for the population of the ground state levels? Explain the absorption-emission process that is responsible for the evolution of the system towards this non-equilibrium optically pumped distribution in the ground state?

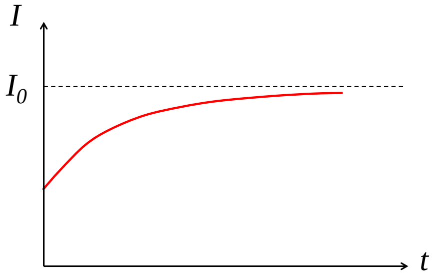


Figure 2 : Temporal evolution of the transmitted light intensity. In the steady-state the absorption goes to zero, i.e. $I=I_0$.

III- Rotation-vibration spectrum Diatomic molecules

The nuclear Hamiltonian of a diatomic molecule is written:

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{\hbar^2}{2\mu r^2}L^2+V(r)$$

where r is the inter-nuclear distance, and μ is the reduced mass of the two-body system. L is the angular momentum operator and $V(r)$ is the potential energy of interaction that is assumed to be harmonic.

1. By looking for the solution of the corresponding Schrödinger equation under the form:

$$\chi_{n,l,m}(r,\vartheta,\varphi)=\frac{1}{r}u_n(r)Y_l^m(\vartheta,\varphi)$$

where $u_n(r)$ is the eigenfunction of a one-dimensional harmonic oscillator and $Y_l^m(\vartheta,\varphi)$ is a spherical harmonic, compute the expression of the energy eigenvalues $E_{n,l}$ (assume that the centrifugal energy does not depend on r and is equal to its value evaluated at the average inter-nuclear distance r_0). Identify the vibrational and rotational terms. Make a schematic diagram of the energy spectrum.

2. Within the dipolar approximation, recall the selection rules for vibrational and rotational transitions, between the eigenstates labelled by n (harmonic oscillator) and l (rotation of a molecule with moment of inertia I).

3. The figure below displays the infrared absorption spectrum of HBr. Label the absorption lines with vibrational and rotational quantum numbers.

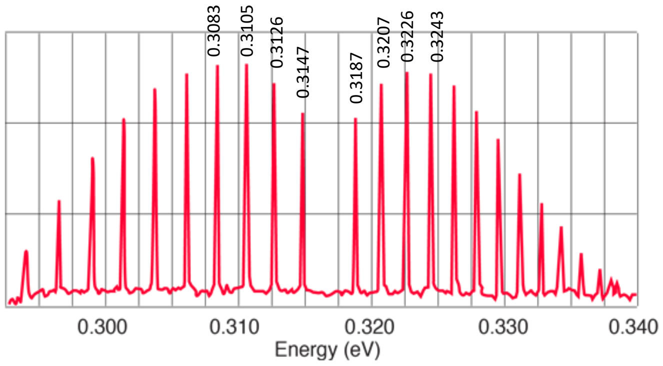


Figure 3 : Sketch of the vibration-rotation spectrum of HBr

4. What is the origin of the decreasing peak intensity on both sides of the spectrum?

5. Show that, for the intense peaks in the doublets, the rotational constant $B=\frac{\hbar^2}{2I}$ is equal to ≈ 1 meV. What is the value of the moment of inertia I?

6. Calculate the reduced mass and calculate the interatomic radius R_0 from the value of I.

7. From the vibrational frequency ω, show that the force constant k is equal to 379 $\mathrm{Nm^{-1}}$(use the first peak of the R band to determine the vibrational transition frequency $\hbar\omega$).
M_{Br} = 80 u; M_H = 1 u with 1 u = 1.66×10^{-27} kg

Exam in "Light-matter interaction"

S. Haacke & M. Gallart

Test duration: 2 hours

I- Coherent transients and π/2-pulses

We consider a two-level system which stationary eigenenergies and eigenstates are noted $\{E_2, E_1\}$ and $\{|1\rangle, |2\rangle\}$ respectively. We set $E_2 - E_1 = \hbar\omega_0$, E_1 being the ground-state energy. The system is in interaction with a quasi-resonant electromagnetic field $E_0 cos(\omega t)$. The solution of the time-dependent problem is expanded on the basis of the stationary states:

$$|\psi(t)\rangle = \tilde{\boldsymbol{C}}_{\boldsymbol{1}}(\boldsymbol{t}) e^{i\frac{\delta}{2}t}|1\rangle + \tilde{\boldsymbol{C}}_{\boldsymbol{2}}(\boldsymbol{t}) e^{-i\frac{\delta}{2}t} e^{-i\omega_0 t}|2\rangle$$

with

$$\begin{cases} \tilde{C}_1(t) = \boldsymbol{cos}\left(\frac{\boldsymbol{\Omega}}{2}\boldsymbol{t}\right) - \boldsymbol{i}\frac{\boldsymbol{\delta}}{\boldsymbol{\Omega}}\boldsymbol{sin}\left(\frac{\boldsymbol{\Omega}}{2}\boldsymbol{t}\right) \\ \tilde{C}_2(t) = -\boldsymbol{i}\frac{\boldsymbol{\Omega_1}}{\boldsymbol{\Omega}}\boldsymbol{sin}\left(\frac{\boldsymbol{\Omega}}{2}\boldsymbol{t}\right) \end{cases}$$

where $\boldsymbol{\Omega_1}$ is the Rabi frequency, $\boldsymbol{\Omega}$ the generalized Rabi frequency and $\boldsymbol{\delta}$ the detuning.

1- Give the expressions of $\boldsymbol{\Omega}$ and $\boldsymbol{\delta}$.

For the remainder, we assume that the incident field is tuned exactly on resonance.

2- Write the corresponding expressions of $\tilde{\boldsymbol{C}}_{\boldsymbol{1}}(\boldsymbol{t})$, $\tilde{\boldsymbol{C}}_{\boldsymbol{2}}(\boldsymbol{t})$ and $|\psi(t)\rangle$.

We consider the situation described in 2 but we suppose now that the electromagnetic field is applied under the form of a $\frac{\pi}{2}$-pulse switched on at $t = 0$, the system being initially in the ground-state.

3- *Define what a* $\frac{\pi}{2}$-pulse is. Calculate the numerical values of $\tilde{\boldsymbol{C}}_{\boldsymbol{1}}(\boldsymbol{t})$ and $\tilde{\boldsymbol{C}}_{\boldsymbol{2}}(\boldsymbol{t})$ that characterize the new state of the system after the interaction with the $\frac{\pi}{2}$-pulse. What are the probabilities for the system to be in state $|1\rangle$, in state $|2\rangle$? Conclusion?

The system is still in the state prepared in 3. The operator associated with the electric dipole moment is written $\hat{D} = \begin{pmatrix} 0 & d \\ d & 0 \end{pmatrix}$.

4- Explain why $\hat{D}$ does not present any diagonal terms. Calculate $\langle\hat{D}\rangle$, the expectation value of $\hat{D}$. How does it evolve in time? Use this result to explain what a coherent transient is.

II- Optical transitions in a bulk semiconductor

We plan to establish the optical selection rules for an optical transition, under the influence of an electric field $E_0 cos\{\omega t - i\vec{k}_0 \cdot \vec{r}\}$, between the valence band (E_v, $|\psi_{v,k_v}(\vec{r})\rangle$) and the conduction band (E_c, $|\psi_{c,k_c}(\vec{r})\rangle$) of a bulk semiconductor that presents a direct bandgap located at $\vec{k} = 0$. For simplicity, we assume that the potential seen by electrons in the crystal lattice is invariant under a translation of vector $\vec{a}$ along the three directions of space.

1- What is a direct bandgap semiconductor? What is an indirect bandgap semiconductor?

The periodic parts of the wave-functions are noted $u_{v,\vec{k}_v}(\vec{r})$ and $u_{c,\vec{k}_c}(\vec{r})$ for the valence band and the conduction band respectively.

2- Write the total wave-functions $|\psi_{c,k_c}(\vec{r})\rangle$ and $|\psi_{v,k_v}(\vec{r})\rangle$ associated with the electronic bands considered here. What are the properties of$u_{v,\vec{k}_v}(\vec{r})$ and $u_{c,\vec{k}_c}(\vec{r})$? How are expanded the corresponding energies E_c and E_v in the reciprocal space ?

We denote $|W_{cv}|$ the matrix element of the dipole moment operator $-qE_0\hat{r}\cdot exp\{-i\vec{k}_0\cdot\vec{r}\}$ evaluated between $|\psi_{v,k_v}(\vec{r})\rangle$ and$|\psi_{c,k_c}(\vec{r})\rangle$.

3- What is the general definition of optical selection rules associated with the transition between two electronic states?

4- Describe qualitatively the main steps of the procedure that is used to write $|W_{cv}|$ in a factorized form:

$$|W_{cv}| \propto f(\vec{k}_v,\overrightarrow{k}_c) \times g\left(u_{v,\vec{k}_v},u_{c,\vec{k}_c}\right)$$

Where $f(\vec{k}_v,\overrightarrow{k}_c)$ and $g\left(u_{v,\vec{k}_v},u_{c,\vec{k}_c}\right)$ will be made explicit. What properties of the wave-function enable one to obtain this result? What approximations are made?

We assume that the wavelength of the incident light is in the visible spectral range.

5- Discuss the possibility of a transition between the valence band and the conduction band as a function of the initial and final electronic wave-vectors. What are the practical consequences when comparing optical properties of indirect and direct bandgap semiconductors?

We are now interested in a transition occurring at $\vec{k} \approx 0$. In this case, $u_{v,\vec{k}_v}(\vec{r})$*and* $u_{c,\vec{k}_c}(\vec{r})$ *are eigenstates of the total angular momentum operator:* $u_{v,\vec{k}_v=\vec{0}}(\vec{r}) = |j;j_z\rangle$ and $u_{c,\vec{k}_c=\vec{0}}(\vec{r}) = |s;s_z\rangle$. The incident light is circularly polarized in the plane perpendicular to the direction of quantization. The initial state is a valence state characterized by$|j;j_z\rangle$, the final state is a conduction state characterized by $|s;s_z\rangle$.

6- What are the possible values of s_z as a function of j_z and of the light helicity?

The valence band presents a *p*-like ($\ell = 1$) symmetry while the conduction band is *s*-like ($\ell = 0$). This results in the existence of 6 valence states and 2 conduction states.

7- Draw a sketch of the different states at $\vec{k} = 0$ with the corresponding values of $|j;j_z\rangle$ and $|s;s_z\rangle$. Indicate the allowed transitions in the case of a circularly polarized light.

Master Nanophysics & Condensed Matter January 24, 2019

Exam in “Light-matter interaction”

Test duration: 2 hours

I- Course evaluation

1- Vibronic transitions

Figure I-1 presents absorption and emission spectra of a molecule for different values of the so-called Huang-Rhys factor S.

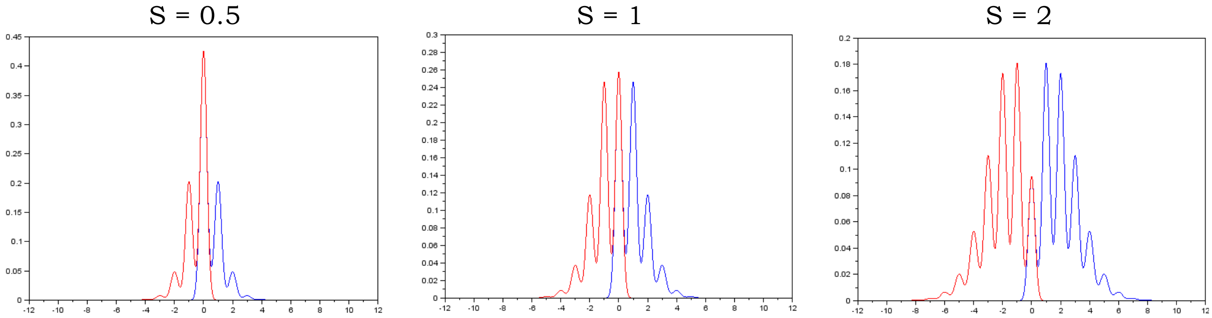


Figure I-1

What are vibronic transitions? What are the quantum states implied in these transitions? Draw a sketch of these states. What is the form of the related wave-functions? Give an outline of the calculation of the transition probability. What is the Franck-Condon principle? What the spacing between the sharp lines in the spectrum is related to? What is characterized by the Huang-Rhys factor S? Comment the evolution of spectra with S. What would the spectrum look like if S = 0.

2- Rotation vibration

Figure I-2 shows the vibration absorption spectrum of HBr

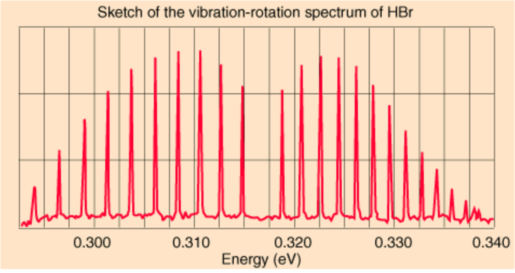


Figure I-2

What are the molecule states that are implied if the transitions presented in figure 2. How are they calculated? Plot a sketch of these states labelled with the corresponding quantum numbers. Detail the physical meaning of these quantum numbers. What are the eigen energies? What is the condition for observing optically induced rotation-vibration transitions in a diatomic molecule? When this condition is satisfied, what are the optical selection rules? Draw the corresponding allowed transitions in the previous sketch of the energy spectrum.

II- Exercise

Quantum wells with infinite barrier – selection rules for dipolar transitions

We consider a heterostructure made of an alternation of nanometric layers of semiconductor materials with different bandgaps. This artificial edifice presents discontinuities in the band profile where the high band gap material defines barriers along the growth direction *z* (cf. figure II-1). Electrons and holes are confined in the so-formed quantum wells, but they are free to move in the (x,y) plane. Electrons are confined in the QW formed in the conduction band and holes form similar quantum states in the valence band of the low band gap material.

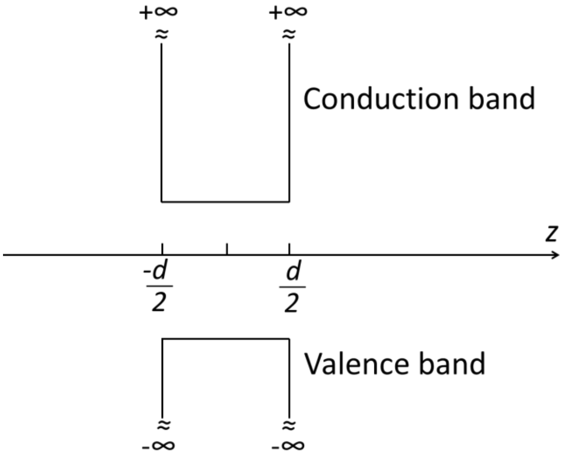


Figure II-1

a) Justify that electron and hole wave-functions can be approximated by the solutions of the stationary Schrödinger equation of a QW with infinite barriers:

$$\psi(\vec{r}) = N\varphi_n(z)\, e^{ik_x\cdot x} e^{ik_y\cdot y}$$

$$\varphi_n(z) = \begin{cases} \sqrt{(2/d)}\cos(k_n z) & \text{If } n \text{ odd} \\ \sqrt{(2/d)}\sin(k_n z) & \text{If } n \text{ even.} \end{cases} , x \in [0, d]\,;\ \varphi_n(z) = 0 \text{ elsewhere}\,;\ k_n = \frac{\pi}{d} n$$

b) The effective mass of electrons m_e^* is smaller than the one of hole m_h^*. Draw the energy levels of electrons and holes.

c) Compute the selection rules for interband transitions between the highest hole subband n_h=1 and all the electron levels $n_e \geq 1$.

$$\langle \mu_z \rangle = e\,\langle \varphi_{n_h=1}(z_h)\,|z|\varphi_{n_e}(z_e)\rangle$$

d) Under the application of an electric field, the QW potential energies change as indicated in the fig. II-2.

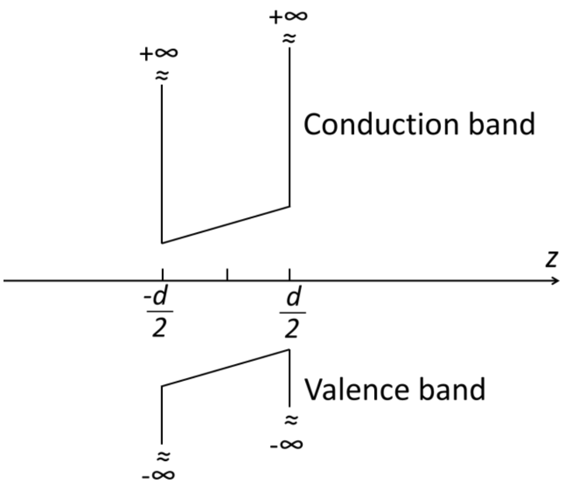


Figure II-2

a. Discuss qualitatively how the E-field induced asymmetry will change the shape of the envelope functions $\varphi(z)$ and consequently, the selection rules.

b. Will the dipole moment of the $n_h=1$ to $n_e=1$ transition increase?

c. Will new transition appear in the absorption spectrum?

Master Nanophysics & Condensed Matter June 19, 2020

Exam in “Light-matter interaction”

S. Haacke & M. Gallart

Test duration: 2 hours

I- Atom and two-level system: lifetime of an exited state

We consider an atom, located at $\boldsymbol{r} = \boldsymbol{r_0}$, approximated by a two-level system whose stationary eigenenergies and eigenstates are noted $\{E_1, E_2\}$ and $\{|1\rangle, |2\rangle\}$ respectively. We set $E_2 - E_1 = \hbar\omega_0$, E_1 being the ground-state energy and $\omega_0 > 0$. The system is in interaction with a quasi-resonant electromagnetic field $E_0 sin(\omega t)$. The matrix element of the electric dipole Hamiltonian between $|1\rangle$ and $|2\rangle$ is $W_{21} = -\langle 2|\hat{\boldsymbol{D}}.\boldsymbol{\varepsilon}|1\rangle E(\boldsymbol{r_0}) = -dE(\boldsymbol{r_0}) = \hbar\Omega_1$.

1- What is the physical meaning of Ω_1? Why does W_{21} depend only on $\boldsymbol{r_0}$ and not on the spatial extension of the atom?

2- The system is initially in the ground state $|1\rangle$. Use the first-order time dependent perturbation theory to express the probability $\mathrm{P}_{12}(\mathrm{t}, \omega)$ for the atom to be in the state $|2\rangle$ after an interaction of duration t with the field. You will use the resonant approximation, discuss its validity.

3- Draw a sketch of $N_2 \propto \mathrm{P}_{12}(\mathrm{t}, \omega)$ as a function of ω, and for a given value of t. What is the physical cause of the broadening $\Delta\omega$ of this curve? Discuss its evolution with the interaction time t.

4- Now, to take into account the lifetime of the excited sate, we consider that the population N_2 of level $|2\rangle$ can decay to level $|1\rangle$ by an irreversible coupling to a continuum of states. We are interested here neither in the nature nor in the modeling of this continuum, but only on the consequence of its existence on the population of the excited state. So, we suppose that the EM-field is switched off at time $t = 0$, so that $N_2(t)$ evolves only because of the coupling with the continuum with an initial condition $N_2(0) = 1$ at $t = 0$. Supposing that the decay probability per unit time is constant and denoted Γ, write and integrate the rate equation to obtain the explicit form of the function $F(t)$ that expresses the evolution of $N_2(t)$ in the absence of absorption.

5- We come back to the full problem where the population N_2 is fed by light absorption from the ground state with probability $\mathrm{P}_{12}(\mathrm{t}, \omega)$ and decays with a probability per unit time Γ. Show that, in the stationary regime, $N_2 = \int_0^{+\infty} \mathrm{P}_{12}(\mathrm{t}', \omega)\ F(t')dt' \propto \frac{1}{2}\frac{\Omega_1^2}{(\omega-\omega_0)+\Gamma^2}$. Plot N_2 as a function of ω. Comment the differences between this solution and the result obtained in question 3. What is the physical cause of the resonance broadening?

6- The same problem can be solved with a non-perturbative treatment. A similar reasoning leads to $N_2 \propto \frac{1}{2}\frac{\Omega_1^2}{(\omega-\omega_0)+\Gamma^2+\Omega_1^2}$. What new parameter acts now on the width of the resonance? What are the limiting values of N_2 when $(\omega - \omega_0) + \Gamma^2 \gg \Omega_1^2$ and $(\omega - \omega_0) + \Gamma^2 \ll \Omega_1^2$. For large values of Ω_1, what physical process appears here that was absent in the perturbative description? Comment.

7- Use your answers to questions 5 and 6 to illustrate the different results for N2 obtained with the perturbative and the non-perturbative methods, and discuss when one or the other should be used.

II- Optical transitions in a two-dimensional quantum well

A- Square quantum well

Growth techniques such molecular beam epitaxy allows to synthetize semiconductors quantum wells, made of nanometric layers of compounds with different bandgap energies, in which electrons and holes are confined along the growth axis. The carriers are free to propagate in the (x, y) plane but are submitted to a square potential well in the z-direction that arises from the band discontinuities between the involved materials (Figure 1). One can show that the wavefunctions can be written

$$\left|\psi^n_{c,k_c}\right\rangle = Ne^{-i\vec{k}^c_\parallel\cdot\vec{\rho}}\, f^n_c(z)\, u_{k_c}(\vec{r}) \text{ and } \left|\psi^p_{v,k_v}\right\rangle = Ne^{-i\vec{k}^v_\parallel\cdot\vec{\rho}}\, f^p_v(z)\, u_{k_v}(\vec{r})$$

for the conduction and valence bands respectively, where the index *n*(*p*) is the quantum number associated with *n*th(*p*th) confined state in the well while $f_n(z)$ $(f_p(z))$is the so-called envelope function that describes the spatial localization of the corresponding charge carrier in the quantum well. To simplify the problem and to handle analytical expressions, we choose to make the assumption that the barrier height is infinite.

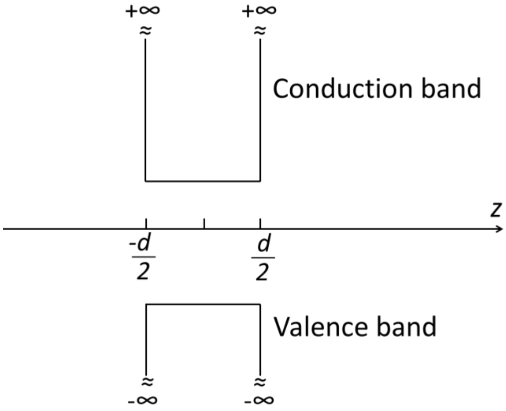


Figure 1

1- The envelope function introduced above is the solution of the Schrödinger equation of a single particle in a square quantum well with infinite barriers. Write and solve the equation to express $f^n_c(z)$and $f^p_v(z)$ with the right boundary conditions. Deduce the eigen-energies $E^n_c(\vec{k}^c_\parallel)$ and $E^p_v(i\vec{k}^v_\parallel)$ of electrons and holes, respectively.

2- We plan to establish the optical selection rules for an optical transition, under the influence of the electric field of light $E_0 cos\{\omega t - i\vec{k}_0\cdot\vec{r}\}$, between a state $E^p_v(\vec{k}^v_\parallel)$ in the valence band and a state $E^n_c(\vec{k}^c_\parallel)$ in the conduction band of this quantum well. By following the same procedure as the one used in the lecture for direct-bandgap bulk semiconductors, express the quantum well selection rules related to an initial state $(p, \vec{k}^v_\parallel)$ and a final state $(n, \vec{k}^c_\parallel)$. Highlight the fact that some transitions are strictly forbidden for reasons of symmetry.

B- Quantum well in a static electric field

Under the application of an external static electric field, the QW potential energies change as indicated in the Figure 2.

1- Describe qualitatively the new profile of the envelope functions $f_c^n(z)$and $f_v^p(z)$. Draw a sketch of these wavefunctions for the two first confined state in the quantum well. How are the optical selection rule that connect n and p modified? Do any forbidden transitions still exist?

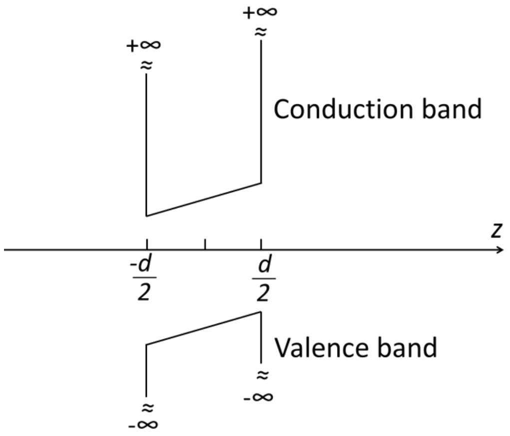


Figure 2

2- We wish to draw a parallel between this problem and the optical properties of diatomic molecules as they were described during the lecture. Draw a sketch of the ground and excited electronic states of a diatomic molecule and indicate how optical transitions occur between vibronic states. Give a picture of the possible spectra for absorption and emission of light.

3- By comparing your answers to B-1 and B-2, can you deduce any similarities between the optical transitions in a quantum well submitted to a static electric field and the optical transitions between the vibronic states of a diatomic molecule.