# Chapter 4

# Light from atoms: spectroscopy

Spectroscopy is the analysis of the wavelength composition of the light emitted by a system under scrutiny. It is a very powerful technique, which allows the study of the internal structure of atoms (energy levels, cross sections...) as well as of their external environment (magnetic field, temperature...). Furthermore, it doesn't requiring any physical contact: all that is needed is to collect the light emitted by the sample, and spectroscopy can be used to study stars light-years away from Earth.

In this chapter, we will set a basic framework for spectroscopy, using models and ideas introduced before. The objectify is twofold: learn a powerful and elegant technique which has very broad applications in physics, and help us understand more accurately some of the ingredients we have included in previous models. In the framework of the previous lecture, the aim of this chapter is to estimate the light-matter interaction cross section $\sigma(h\nu)$. To do so, we will discuss the basic ingredients to estimate the location of the lines of an atomic spectrum, we will investigate the actual shape of these lines, and see how the environment can affect the spectrum.

**Note** In this chapter, we will consider not only the internal degrees of freedom $(\mathbf{r}, \mathbf{v})$ corresponding to the relative motion of the electron around the nucleus, but also the external degrees of freedom $(\mathbf{R}, \mathbf{V})$ corresponding to the motion of atomic center of mass - ie of the nucleus.

## 4.1 Atomic spectrum: a bar code for atoms

In this first section, we will address the following question: if we consider an ensemble of atoms, can we estimate the light that this ensemble is actually emitting - or the light that these atoms could possibly absorb ? In the most simple version of this question, can we estimate the wavelength at which these atoms are emitting / absorbing radiations?

We already have some insights on this question from the familiar hydrogen atom - remember how the Bohr model allows to recover the Rydberg formula for the hydrogen spectrum. In a more general picture, the radiation which is actually being emitted by an ensemble of atoms depends on 3 key ingredients, which we will details in the coming pages:

1. The energy eigenstates for the atom
2. The properties of light corresponding to transitions between these states
3. The population of these different states

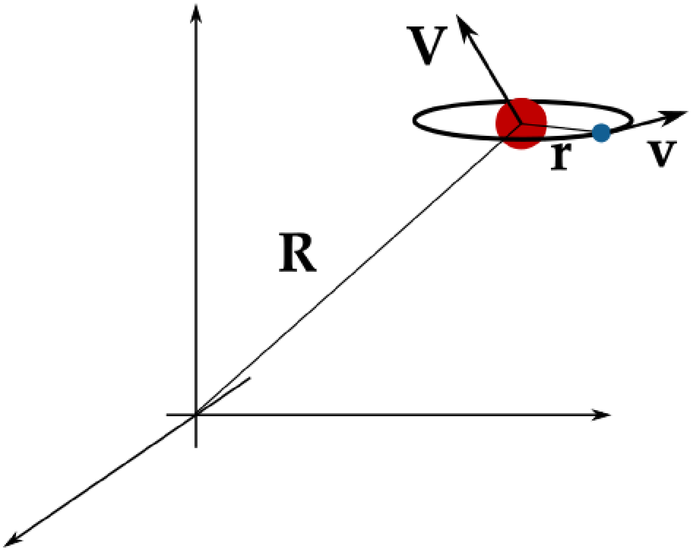

Figure 4.1: Internal (**r**, **v**) and external (**R**, **V**) degrees of freedom.

**Note for the future**

In a quantitative quantum treatment, we would show that the number of absorption processes per second at a given energy $h\nu$ is proportional to:

$$R(h\nu) \propto \sum_{i,j\neq i} \left|\langle\psi_j| - e\hat{\mathbf{r}}.\mathbf{E}\,|\psi_i\rangle\right|^2 \delta\left(E_j - E_i - h\nu\right)\ p_i\left(1-p_j\right) \tag{4.1.1}$$

where we see the three ingredients mentioned above.

### 4.1.1 Atomic states

The energy eigenstates should be derived from the total Hamiltonian of the atom, which is usually separated into two terms: the internal Hamiltonian, which only depends on the relative coordinates **r** of the electron with respect to the nucleus and the external Hamiltonian, which depends on the position **R** of the atom in space.

**Internal structure** $H_{\text{int}}$ (full derivation in chapter 6)

In its simplest form, the internal Hamiltonian accounts for the kinetic energy and the Coulomb potential of the electrons. Calculations can be carried analytically for atoms with one single electron (Schrodinger model), and will derive explicitly the key results of this model in Lecture 6. For now, we will simply recall these results: in the Schrodinger model, quantum states can be entirely described with three integer numbers:

- The primary quantum number $n \in \mathbb{N}^*$ is directly related to the energy of the state, through the Rydberg relation:
$$E_n = -E_0/n^2 \tag{4.1.2}$$
- The secondary quantum number $l \in [0, n-1]$ gives the modulus of the orbital angular momentum of the state:
$$L^2 = l(l+1)\hbar^2 \tag{4.1.3}$$

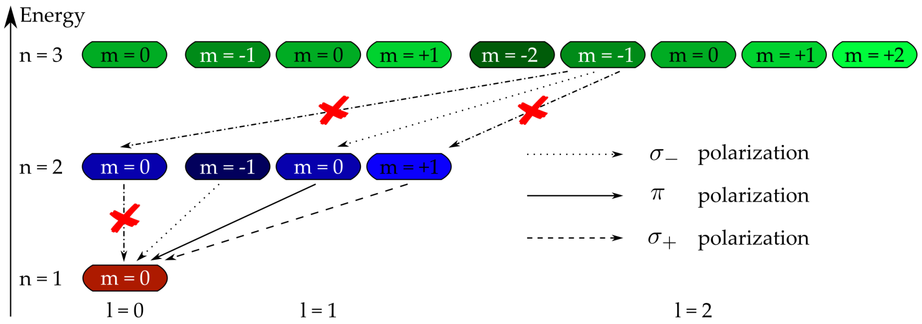

Figure 4.2: Energy levels and some corresponding allowed and forbidden transitions. The forbidden transitions illustrate three selections rules : $|\Delta l| \leq 1$, $|\Delta m_L| \leq 1$ and no transitions from $l = 0$ to $l' = 0$.

- The azimuthal quantum number $m_L \in [-l, l]$ gives the direction of the angular momentum - or at least its projection onto a reference axis (usually z):

$$L_z = m_L \hbar \tag{4.1.4}$$

Each value of the energy is thus degenerated $\sum_{l=0}^{n-1} \sum_{m_L=-l}^{l} 1 = n^2$ times (see Fig. 4.2)

This simplest model can be refined with additional features. The most common are:

- Including the notion of *spin* - considering that each electron can have a spin “up” or “down” adds one more degree of freedom, and brings the degeneracy of each level to $2n^2$
- Including spin-orbit coupling - considering that electrons with spin up or down don’t have exactly the same energy, leading to the fine-structure of the atom
- Including the nucleus spin and its coupling to the electron, leading to the hyper-fine structure of the atom

To account for other atoms than Hydrogen (or ionized Helium...), this model has to be adapted to account for several electrons and their interactions. The problem becomes quickly too complex to allow analytical solutions, but the idea of discrete energy levels given by the basic properties of the atom remains.

**External environment $H_{\text{ext}}$**

The environment surrounding the atom will affect the energy levels - leading to shifts of the energy levels, which can possibly lift degeneracy. We will discuss this in more details in section 4.3.

### 4.1.2 Allowed and forbidden light - selection rules

For a radiative transition between two levels to occur, these two levels should be coupled through light. This is possible only if the constraints set by the transition are compatible with the basic properties of light.

You already have an intuitive notion of this idea from energy conservation. You know that for an atom to decay from a state with energy $E_e$ to a state with energy $E_g$, it has to emit a photon with energy $h\nu = E_e - E_g$. The same kind of consideration should be applied to other conserved quantities, and especially to angular momentum along the $z$ axis: for an atom to decay from a state with angular momentum $m_e\hbar$ to a state with angular momentum $m_g\hbar$, it has to emit a photon with angular momentum $L_{z,\text{photon}} = m_e\hbar - m_g\hbar$.

| | *Before emission* | *After emission* |
|---|---|---|
| | *Atom in* $\vert e\rangle$<br>*0 photon* | *Atom in* $\vert g\rangle$<br>*1 photon* |
| Energy | $E_e$ | $E_g + h\nu$ |
| Angular momentum $L_z$ | $m_e\hbar$ | $m_g\hbar + L_{z,\text{photon}}$ |

However, photons can only have three possible values for angular momentum : $-\hbar$ (corresponding to a $\sigma_-$ polarized beam), 0 (corresponding to a $\pi$ polarized beam) or $+\hbar$ (corresponding to a $\sigma_+$ polarized beam). Consequently, no radiative transition between two states with $\Delta m > 1$ can exist.

This is a very simple example of a *selection rule*. The most generic approach is to consider under which conditions the matrix element $\langle\psi_j|\,\hat{\mathbf{r}}.\mathbf{E}\,|\psi_i\rangle$ can be non-zero, and requires at least a semi-classical treatment (quantum atom). For now, we will simply consider the orbital selection rules

$$\begin{cases} \Delta m_L = -1,\, 0\,\text{or}\, +1 \\ \Delta l = -1,\, 0\,\text{or}\, +1 \\ l_e \neq 0\,\text{or}\, l_g \neq 0 \end{cases} \tag{4.1.5}$$

**Remark: absorption and emission**

We have mostly discussed from the emission perspective, but the exact same rules apply on absorption processes. You will never drive a $m_L = -2 \rightarrow m_L = 0$ transition, because you will never find a photon with the corresponding momentum. The connection between absorption and emission is actually very deep and the ability of a system to absorb light is directly related to its ability to emit this light. From a quantum perspective, this connection comes from the fact that both processes depend on the same matrix element $\langle\psi_j|\,\hat{\mathbf{r}}.\mathbf{E}\,|\psi_i\rangle$. For a more classical derivation, see Kirchhoff law in appendix.

### 4.1.3 Populations

Atomic states and selection rules will give you which transitions can possibly take place - which is sufficient to estimate the interaction cross section $\sigma$. But to estimate which light is *actually* emitted among all the possible transitions, we need to know how the different states are populated. For a emission process to occur, we need an atom in a high energy state, and we need an empty low energy state (remember that Pauli principle prevents two electrons from being in the exact same state).

To stimulate the emission of an ensemble of atoms (ie to produce luminescence), we need to bring energy to the system so as to promote atoms to excited states, and let them relax by emitting a photon. There are many different ways of bringing energy to the system, which will define several types of luminescence:

- Photo-luminescence: excite the system by sending light
- Electro-luminescence: excite the system by injecting electrons
- Cathodo-luminescence: excite the system by shooting electrons
- Thermo-luminescence (or incandescence): excite the system by increasing the temperature

The only difference between these different experiments is how atoms are excited, and which distribution of atoms among the different energy levels is reached.

## 4.2 Line width

Atomic spectra are not simply given by the value of the spectral lines - if we zoom in, we see that these lines have a finite width. This profile comes from two convoluted contributions: the intrinsic width of the line (ie the profile the line would have if the atom was alone in the vacuum) and the extrinsic width (resulting from the environment).

### 4.2.1 Intrinsic width: Lorentzian profile

We will discuss three ways of describing the intrinsic line-width of an atomic transition.

**Qualitative approach: Heisenberg principle**

When an atom is brought to the excited state, it won't stay there forever. Due to spontaneous emission, it relax to the ground state at some point. The time it will take for this transition to happen is not fixed, but the spontaneous decay rate $\Gamma$ gives a typical estimation. The uncertainty $\Delta t$ on the time it will take to see this transition occurring scales with $\Gamma^{-1}$: if the atom remains typically a nano-second in the excited state, then we can expect the decay within few nanoseconds after the atom reached the excited state - so the uncertainty is indeed of the order of nano-seconds as well. When the atom decays, the photon it emits has a typical energy $\hbar\omega = E_e - E_g$ corresponding to the atomic transition, but this photon can have slightly more or slightly less energy than this typical value. The Heisenberg principle states that the smaller the uncertainty on time, the larger the uncertainty on energy - and we can therefore estimate the spread of the photon energy

$$\Delta E \, \Delta t \gtrsim \hbar \Rightarrow \Delta\omega \gtrsim \Gamma \tag{4.2.1}$$

This relation tells us that transitions with a very short lifetime will give a broad spectral line - and vice versa.

**Statistical approach: Wiener-Khintchine theorem**

A more quantitative description of the spectral line has been discussed in the previous lecture, using the Wiener-Khintchine theorem to account for the wave-train model. We simply recall here the final result: if an ensemble of atoms emit a "monochromatic" radiation with frequency $\omega_0$ with random phase jumps occurring with a $\Gamma/2$ probability per second, then the spectrum takes a Lorentzian shape with a typical spread $\Gamma$:

$$I_{\text{atom}}(\omega) = \frac{2}{\mu_0 c}\frac{1}{2\pi}\int d\tau \, \langle \mathcal{E}^*(t)\mathcal{E}(t+\tau)\rangle \, e^{i\omega\tau} = I_0 \frac{4}{\pi\Gamma}\frac{1}{1+4\left(\frac{\omega-\omega_0}{\Gamma}\right)^2} \tag{4.2.2}$$

**Quantitative approach: Wigner-Weisskopf model**

In the previous two approaches (and since the beginning of this course), the spontaneous decay time $\Gamma$ is taken as an input parameter of the model. If we want to estimate this parameter from more basic quantities, we need to go to a quantum model. But a simple quantum model of the atom such as the Schrödinger model is not sufficient, as we can see pretty easily. In the Schrödinger model, atomic orbitals are eigenstates of the Hamiltonian. So if we put an atom in an excited state, the Schrödinger equation tells us the atom should stay there forever - the wavefunction simply acquires a phase over time. So why are the atom actually decaying to the ground state ?

This decay means the atomic levels are *not* the real eigenstates of the full Hamiltonian - which means something is missing in the problem. There is something from the environment which should be included in there - like collision between atoms. But if the atom is alone in the middle of vacuum, what is the external perturbation that will make the atom decay ? The correct answer to this question requires a quantum treatment of light, which is out of the scope of this lecture. The full derivation reaches an analytical expression for the spontaneous decay rate:

$$\Gamma = \frac{\left|\langle g|\,\hat{\mathbf{D}}\,|e\rangle\right|^2 \omega_{eg}^3}{3\pi\epsilon_0\hbar c^3} \tag{4.2.3}$$

If we consider an ensemble of atoms, the line width discussed here is the same for all atoms - it is an *homogeneous* broadening of the line.

### 4.2.2 Extrinsic width: pressure effect (optional)

In the previous section, we considered the emission of an isolated atom. If we now consider a population of atoms, collisions between atoms can make them decay from excited to ground state, triggering an emission with a random initial phase. This effect will lead to a Lorentzian shape as described with the Wiener-Khintchine theorem, but with a larger phase-jump rate than the intrinsic profile. It is the so-called *collisionnal* broadening, or pressure broadening (as the typical time between two collisions in a gas depends on the pressure).

### 4.2.3 Extrinsic width: thermal effect

If we observe the spectral emission of an ensemble of atoms (see Fig. 4.3), we observe several difference with the intrinsic line width devised above. Notably, the shape is more Gaussian then Lorentzian, the width is significantly larger than $\Gamma$ and depends on the temperature of the sample...

These features come from the thermal motion of the atoms. Each of them emits the intrinsic spectrum (eq. 4.2.2) but as the move in all directions, the perceived radiation is the superposition of this intrinsic spectrum shifted by Doppler effect. In this section, we will recall the Doppler effect and show that it leads to the observed Gaussian profile.

**Doppler shift**

Consider an emitter producing "beeps" periodically with frequency $2\pi/\omega_0$. The signal is being recorded by a receiver. The initial distance between emitter and receiver is $d_0$ (this distance will play no role in the end) and the emitter moves away from the reciever at velocity $V$ (see Fig. 4.4).

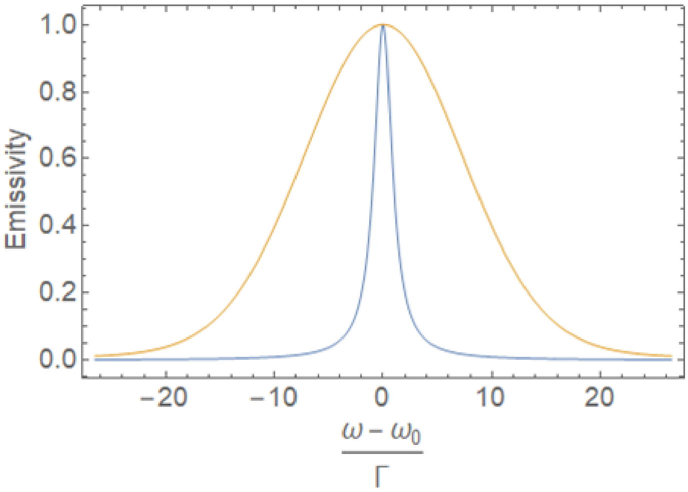

Figure 4.3: Typical intrinsic line width (blue) ; line shape actually observed with an ensemble of atoms (yellow).

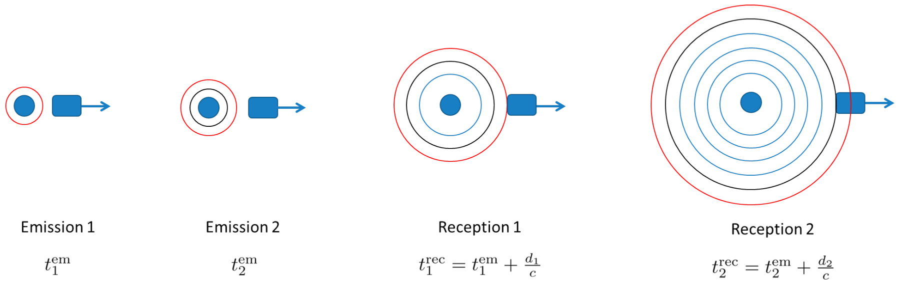

Figure 4.4: Time definitions for the Doppler effect.

- At time $t_1^{\text{em}}$, the emitter produces a first "beep".
- At time $t_2^{\text{em}}$, the emitter produces a second "beep".
- The receiver captures the first "beep" at time $t_1^{\text{rec}}$ such that $d_0 + V\,t_1^{\text{em}} = c\left(t_1^{\text{rec}} - t_1^{\text{em}}\right)$ ie $t_1^{\text{rec}} = \left(1 + \frac{V}{c}\right) t_1^{\text{em}} + \frac{d_0}{c-V}$
- The receiver captures the first "beep" at time $t_2^{\text{rec}}$ such that $d_0 + V\,t_2^{\text{em}} = c\left(t_2^{\text{rec}} - t_2^{\text{em}}\right)$ ie $t_2^{\text{rec}} = \left(1 + \frac{V}{c}\right) t_2^{\text{em}} + \frac{d_0}{c-V}$

The frequency measured by the receiver is thus

$$\omega_{\text{measured}} = \frac{2\pi}{t_2^{\text{rec}} - t_1^{\text{rec}}} = \frac{2\pi}{\left(t_2^{\text{em}} - t_1^{\text{em}}\right)\left(1 + \frac{V}{c}\right)} = \frac{\omega_0}{1 + \frac{V}{c}} \tag{4.2.4}$$

### Thermal broadening

We want to estimate the amount of light measured at a given frequency $\omega$ from a thermal ensemble of atoms. This light has been emitted at frequency $\frac{\omega}{1-\frac{V}{c}}$ by atoms moving at velocity $V$, and the Doppler shift makes it a frequency $\omega$ for the observer. Noting $n_{\text{at}}(V)\,dV$ the number of atoms with a velocity between $V$ and $V + dV$, we get

$$I_{\text{tot}}(\omega) = \int_{-\infty}^{+\infty} dV \, I_{\text{at}}\left(\omega\left(1 + \frac{v}{c}\right)\right) n_{\text{at}}(V) \tag{4.2.5}$$

and the thermal distribution is given by Boltzmann equation

$$n_{\text{at}}(V) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{1}{2}\frac{mv_x^2}{k_B T}\right) \tag{4.2.6}$$

**Gaussian profile ($k_B T \gg \hbar\Gamma$)**

If the intrinsic width $\hbar\Gamma$ is much smaller than the spread of the thermal distribution $k_B T$, we can consider that atoms only emit at their resonant frequency $\omega_0$ - ie $I_{\text{at}}(\omega) \simeq I_0 \delta(\omega - \omega_0)$ and the measured radiation takes a Gaussian profile[1]

$$I_{\text{tot}}(\omega) = I_0 \int_{-\infty}^{+\infty} dV \, \delta\left(\omega\left(1 + \frac{V}{c}\right) - \omega_0\right) n_{\text{at}}(V) \tag{4.2.7}$$

$$\propto I_0 \int_{-\infty}^{+\infty} dV \, \delta\left(V - c\frac{\omega - \omega_0}{\omega}\right) n_{\text{at}}(V) \tag{4.2.8}$$

$$\simeq \frac{I_0}{\sqrt{2\pi\Delta\omega^2}} \exp\left(-\frac{(\omega - \omega_0)^2}{2\Delta\omega^2}\right) \tag{4.2.9}$$

with a typical width

$$\Delta\omega = \omega_0 \sqrt{\frac{k_B T}{mc^2}} \tag{4.2.10}$$

This is the key result of this section: an ensemble of atoms, each of which emits a very sharp line around $\omega_0$, produce a Gaussian spectrum with a width increasing with temperature. This is a typical case of inhomogeneous broadening, as discussed in Chapter 2.

**Voigt profile** (optional)

The rigorous derivation is the convolution of a Gaussian and Lorentzian profile - it is called a Voigt profile.

## 4.3 Line shift

The environment in which atoms are located can change their energy levels, and thereby the light they can absorb or emit. If we can relate spectral shifts to the environmental conditions (magnetic field, electric field...), then we can estimate these conditions simply by looking at the atomic spectrum. In this section, we will focus on the Zeeman shift - ie the spectral shift induced by an external magnetic field.

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[1] Using the basic properties of the Dirac function: $\delta(ax) = |a|^{-1}\delta(x)$

### 4.3.1 Zeeman shift - classical approach

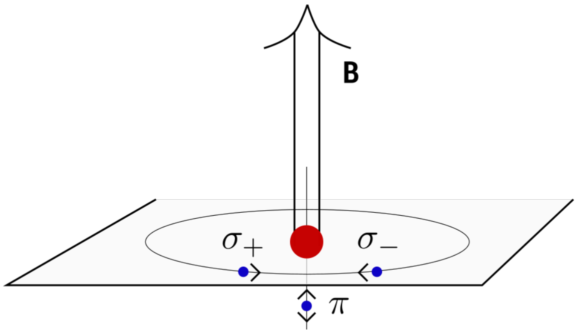
Consider a hydrogen atom (for the sake of simplicity) place in an external magnetic field **B**. How are the energy levels (and thus the spectrum) modified by the presence of the field?

#### Classical approach

We can get a first idea from the classical Lorentz model. We consider a spring-like force and add the Lorentz force corresponding to the influence of the external field onto the electron:

$$m\ddot{\mathbf{r}} = -m\omega_0^2\mathbf{r} - q\mathbf{v} \times \mathbf{B} \tag{4.3.1}$$

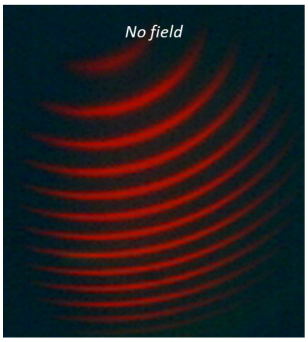
In the absence of magnetic field, the resonant frequency $\omega_0$ is the same regardless of the actual trajectory of the electron. We can demonstrate analytically (see appendix) that with the magnetic field, we now have three different resonant frequencies depending on whether the electron oscillates along the field direction ($\omega_0$), or along direct or indirect circular orbits within the transverse plane ($\omega_0 \pm \frac{qB}{2m}$).

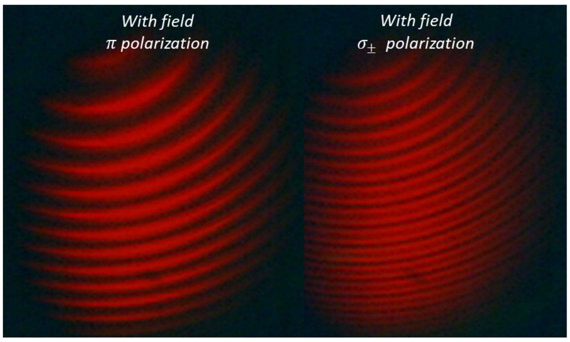


These three orbits will be excited by light with the corresponding polarization - so we expect that the atom will emit linearly polarized light at frequency $\omega_0$ and circularly polarized light at frequency $\omega_0 \pm \frac{qB}{2m}$. So from one single spectral line in the absence of magnetic field, we expect to see 3 different lines with a splitting increasing with $B$ and with different polarization.

#### Limitations of the classical model

The classical model does account very well for the emission of some atoms, such as Cadmium. Experimentally, we can see the 640 nm line split into three polarized components as a magnetic field is turned on.





However, some atoms such as Mercury show a splitting into *more than three* lines. This so-called anomalous Zeeman effect can't be explained with a classical model, and requires a more sophisticated description.

### 4.3.2 Zeeman shift - quantum approach

To derive a semi-classical model (quantum atom, classical fields), we need to find a Hamiltonian $\hat{H}_{\text{Zeeman}}$ to account for the interaction between the electron and the magnetic field. The total Hamiltonian will the be

$$\hat{H}_{\text{tot}} = \hat{H}_0 + \hat{H}_{\text{Zeeman}} \tag{4.3.2}$$

1. To do so, we start be identifying the classical expression of the potential energy resulting from this interaction. Considering that the electron forms a circular orbit around the nucleus, it can be considered as a loop of current of radius $r$. The corresponding current $I$ can be estimated by counting the amount of charge passing at any point of the loop every second - ie the charge of the electron times the number of round trips per second:

$$I = -q\,\frac{v}{2\pi r} \tag{4.3.3}$$

   A loop of current is equivalent to a magnet, with magnetic dipole

$$\boldsymbol{\mathcal{M}} = I\,\mathbf{S} = -q\,\frac{v}{2\pi r}\,\pi r^2\,\mathbf{u_z} = \frac{-q}{2m}\,\mathbf{L} \tag{4.3.4}$$

   and the corresponding potential energy is

$$E_p = -\boldsymbol{\mathcal{M}}.\mathbf{B} = \frac{q}{2m}\,\mathbf{L}.\mathbf{B} \tag{4.3.5}$$

2. We then use this expression to construct the Zeeman Hamiltonian:

$$\hat{H}_{\text{Zeeman}} = -\left(\frac{q}{2m}g_e\right)\,\hat{\mathbf{L}}.\mathbf{B} \tag{4.3.6}$$

   where we have transformed the angular momentum $\mathbf{L}$ into the operator $\hat{\mathbf{L}}$, and we have added a small correction factor $g_e$ called the Landé factor, which comes from the full rigorous quantum derivation. The Landé factor depends on whether the alignment of spin and orbital momentum and can be calculated explicitly for each energy level.

3. We must now estimate the influence of this additional term on the energy spectrum of the atom. The key ingredient here is the *perturbation theory* (technical details in appendix). The main idea is the following one: if there was no mag field, then the Hamiltonian would simply by $H_0$ and we know very well the corresponding eigenstates $\left|\psi_i^{(0)}\right\rangle = |n_i, l_i, m_i\rangle$ (see section 4.1.1). If we switch on the mag field, then the Hamiltonian changes to include $\hat{H}_{\text{Zeeman}}$, and the former eigenstates $\left|\psi_i^{(0)}\right\rangle$ are not eigenstates of the total Hamiltonian anymore. But keep it very small, then the new eigenstates corresponding to the total Hamiltonian should still be pretty close to the former eigenstates. Perturbation theory tells us that the new energy levels

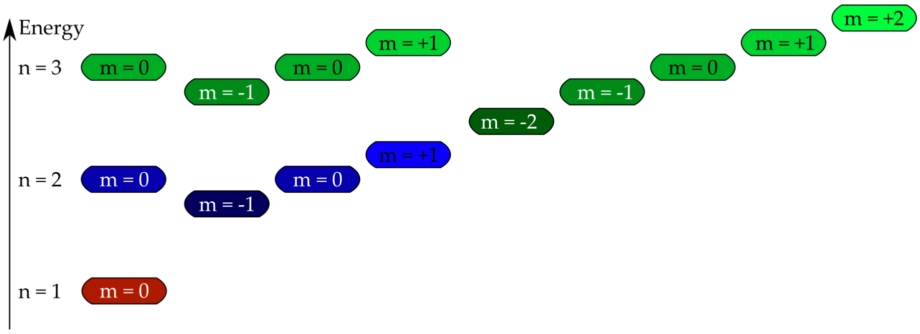


Figure 4.5: Energy shift due to the Zeeman effect, assuming the same Landé factor $g_e$ for all states.

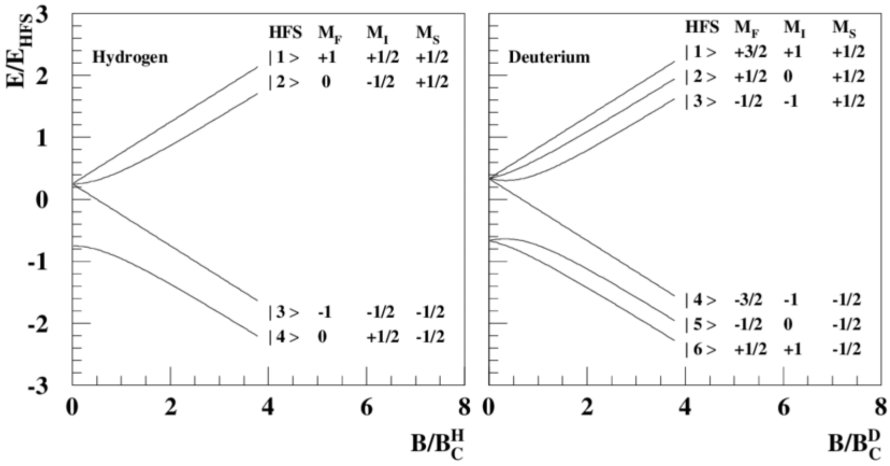
are shifted with respect to the previous ones by an amount:

$$\begin{aligned}\delta E(m_z) &= \left\langle \psi_i^{(0)} \middle| H_{\text{Zeeman}} \middle| \psi_i^{(0)} \right\rangle \\ &= \frac{q\hbar}{2m} g_e \times m_i \times B \qquad (4.3.7)\end{aligned}$$

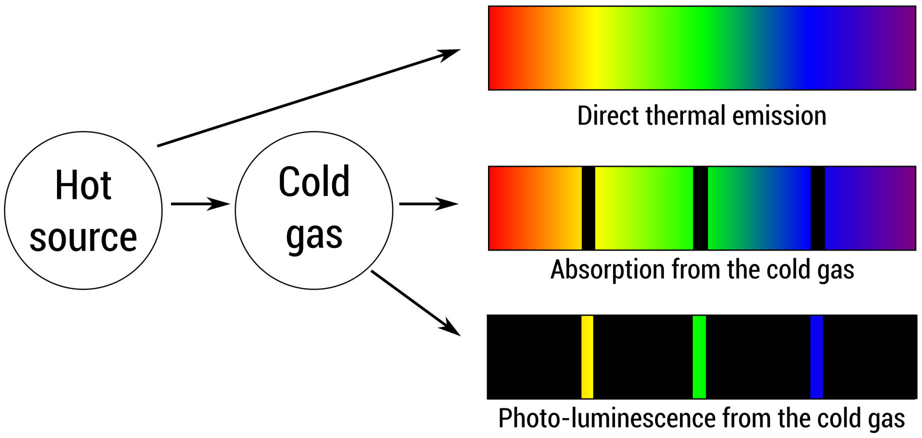
So the Zeeman effect lifts (partially) the degeneracy by shifting the energy levels according to the azimuthal quantum number (see Fig. 4.5).

This semi-quantum model is able to capture the anomalous Zeeman effect, considering that the initial and final state don't necessarily have the same Landé factor.

Note that this linear behavior only holds at low field (perturbative approach). It can be shown that at high field (Paschen-Back regime), the energy shift is also linear with respect to the field - but with a different slope than at low field!



### 4.3.3 Application: magnetometry



### 4.3.4 Other usual shifts

Simply mentioned for scientific culture.

**External electric field: Stark shift**

To account for an external electric field applied onto the atom, we consider a Hamiltonian corresponding to the potential energy of an electric dipole:

$$H_{\text{Stark}} = -q\hat{\mathbf{r}}.\mathbf{E_0} \tag{4.3.8}$$

The energy shifts are slightly more difficult to estimate than the Zeeman shift, as they do not simply depend one single quantum number. For instance, the energy shift of the hydrogen ground state is zero up to the second order of perturbation theory (ie $\delta E(\psi_{n=0})$ scales with the square of the electric field) ; for the first excited state, the first order perturbation of $|n = 2, l = 1, m = \pm 1\rangle$ is zero as well, while the energy shifts for $|n = 2, l = 1, m = 0\rangle$ and $|n = 2, l = 0, m = 0\rangle$ are the same. We will not derive these results here, it is a classical quantum mechanics homework.

**External light field: Light shift**

We will show in chapter 5 that when a beam of light with frequency $\omega_L$ is shone onto a 2 level atoms, if the laser frequency is far enough from the atomic resonance $\omega_{eg}$, then the ground state of the atom is shifted by an amount

$$\delta E(\mathbf{R}) \propto \frac{I_L(\mathbf{R})}{\omega_L - \omega_{eg}} \tag{4.3.9}$$

This light-induced energy shift is the basic idea allowing fine manipulation of atoms with lasers, such as optical tweezers.

## 4.4 Take home message

- The ability of an ensemble of atoms to absorb or emit light depends
  - The energy states (with internal and external degrees of freedom)

  - The coupling between these states (selection rules)
  - The population of these states

- The spectral profile has an intrinsic width (Lorentz), but the emission of a thermal ensemble of atoms is broadened by the Doppler effect to a Gaussian profile $\Delta\omega = \omega_0 \sqrt{\frac{k_B T}{mc^2}}$.
- The external environment can lead to a shift of the atomic levels, sometimes lifting degeneracies. This shift can be estimated with perturbation theory. For an magnetic field, the Zeeman effect leads to $\delta E = \frac{q\hbar}{2m} g_e m_i B$.

## 4.5 Appendix to lecture 4

### 4.5.1 Perturbation theory (/!\ important /!\)

We start from an unperturbed situation corresponding to a Hamiltonian $H_0$ - which we know very well. In particular, we will consider that we know the eigen elements $\{\epsilon_N, |\phi_{n,r}\rangle\}$ of $H_0$:

$$H_0 \, |\phi_{n,r}\rangle = \epsilon_n \, |\phi_{n,r}\rangle \tag{4.5.1}$$

We turn on a small perturbation, such that the total Hamiltonian is now $H = H_0 + \lambda H_1$, and we look for the eigen elements $\{E_n, |\psi_{n,r}\rangle\}$ of this new situation

$$H \, |\psi_n\rangle = E_n \, |\psi_n\rangle \tag{4.5.2}$$

The main idea is to consider a series expansion of the new elements

$$|\psi_n\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda \left|\psi_n^{(1)}\right\rangle + \lambda^2 \left|\psi_n^{(2)}\right\rangle + ... \tag{4.5.3}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \tag{4.5.4}$$

leading to an order-by-order resolution:

$$\begin{array}{lrl} 0^{th} \text{ order} & H_0 \left|\psi_n^{(0)}\right\rangle & = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle \\ 1^{st} \text{ order} & H_0 \left|\psi_n^{(1)}\right\rangle + H_1 \left|\psi_n^{(0)}\right\rangle & = E_n^{(0)} \left|\psi_n^{(1)}\right\rangle + E_n^{(1)} \left|\psi_n^{(0)}\right\rangle \\ ... & & \end{array} \tag{4.5.5}$$

**$0^{th}$ order**

The $0^{th}$ order equation recovers the eigen elements of $H_0$:

$$\left|\psi_n^{(0)}\right\rangle = |\phi_{n,r}\rangle \qquad E_n^{(0)} = \epsilon_n \tag{4.5.6}$$

This simply means that in the absence of perturbation, the eigen elements of $H$ are the eigen elements of $H_0$ (which is trivial).

**$1^{st}$ order**

Considering the $1^{st}$ order equation, we project onto $\langle\phi_{n,r}|$ to obtain

$$\langle\phi_{n,r}| \, H_0 \left|\psi_n^{(1)}\right\rangle + \langle\phi_{n,r}| \, H_1 \, |\phi_{n,r}\rangle = \epsilon_n \, \langle\phi_{n,r} \left|\psi_n^{(1)}\right\rangle + E_n^{(1)} \, |\langle\phi_{n,r} \; \phi_{n,r}\rangle \tag{4.5.7}$$

leading to

$$\lambda E_n^{(1)} = \langle \phi_{n,r} | \, \lambda H_1 \, | \phi_{n,r} \rangle \tag{4.5.8}$$

which tells by how much the energy levels are shifted (up to the first order).

### 4.5.2 Kirchhoff law of radiation

The direction averaged Kirchhoff law of radiation $\alpha(E) = \epsilon(E)$ can be obtained from a careful energy balance. Let's consider a body with emissivity $\epsilon_1(E)$ and absorptivity $\alpha_1(E)$. The energy balance for the body exposed to a thermal radiation of radiance $L_T(\lambda)$ imposes

$$\int dE \, M_E^{BB}(E)\epsilon_1(E) = \int dE \, M_E^{BB}(E)\alpha_1(E) \tag{4.5.9}$$

which is not enough to conclude on the identity between emissivity and absorptivity at all wavelength.

Let's now put the body inside a cavity, the radiative behavior of which is characterized by $\epsilon_2$, $\alpha_2$. We assume thermal equilibrium at temperature $T$ between the body and the cavity.

The spectral irradiance arriving on the body is $\phi_{\text{in}}(E) = M_E^{BB}(E)\epsilon_2(E) + (1 - \alpha_2(E))\,\phi_{\text{out}}(E)$ where the spectral irradiance reaching the cavity is expressed as $\phi_{\text{out}}(E) = M_E^{BB}(E)\epsilon_1(E) + (1 - \alpha_1(E))\,\phi_{\text{in}}(E)$.

Solving this simple system leads to

$$\begin{aligned}
\phi_{\text{in}}(E) &= M_E^{BB} \frac{\epsilon_2 - \epsilon_1(1-\alpha_2)}{1 - (1-\alpha_1)(1-\alpha_2)} \\
\phi_{\text{out}}(E) &= M_E^{BB} \frac{\epsilon_1 - \epsilon_2(1-\alpha_1)}{1 - (1-\alpha_1)(1-\alpha_2)}
\end{aligned}$$

and the energy balance requires

$$\int dE \, \phi_{\text{in}}(E) = \int dE \, \phi_{\text{out}}(E) \Rightarrow \int dE \, M_E^{BB} \frac{\alpha_1\alpha_2}{1-(1-\alpha_1)(1-\alpha_2)} \left( \frac{\epsilon_1}{\alpha_1} - \frac{\epsilon_2}{\alpha_2} \right) = 0 \tag{4.5.10}$$

The trick is that this relation holds for whatever cavity material, ie whatever $\epsilon_2$, $\alpha_2$. This is possible if and only if $\epsilon \propto \alpha$, and the first equation imposes $\epsilon(E) = \alpha(E)$ for each energy, hence the direction-averaged Kirchhoff law of radiation.

### 4.5.3 Classical derivation of the Zeeman frequency shift

Within Lorentz model, Newton's second law including the Lorentz force induced by the external magnetic field reads:

$$m \begin{pmatrix} \ddot{x} \\ \ddot{y} \\ \ddot{z} \end{pmatrix} = -m\omega_0^2 \mathbf{r} - q\mathbf{v} \times \mathbf{B} = -m\omega_0^2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} - qB \begin{pmatrix} \dot{y} \\ -\dot{x} \\ 0 \end{pmatrix} \tag{4.5.11}$$

**Along the z-axis**

The trajectory along the z-axis is unchanged by the magnetic field (which makes sense, since the Lorentz force has no effect along the field direction)

$$\ddot{z} + \omega_0^2 z = 0 \tag{4.5.12}$$

and the resonant frequency is $\omega_0$.

### Within the transverse plane

To solve the equation of motion within the transverse plane, we introduce the variable $U = x + iy$, which allows us to write

$$\begin{cases} \ddot{x} + \omega_0^2 x + \frac{qB}{m}\dot{y} = 0 \\ \ddot{y} + \omega_0^2 y - \frac{qB}{m}\dot{x} = 0 \end{cases} \Rightarrow \ddot{U} - i\frac{qB}{m}\dot{U} + \omega_0^2 U = 0 \tag{4.5.13}$$

For small fields, the roots of the characteristic equation are

$$r_\pm = \frac{1}{2}\left(i\frac{qB}{m} \pm \sqrt{\left(\frac{qB}{m}\right)^2 - 4\omega_0^2}\right) = i\left(\frac{qB}{2m} \pm \omega_0\right) = \pm i\omega_\pm \tag{4.5.14}$$

$$\omega_\pm = \omega_0 \pm \frac{qB}{2m} \tag{4.5.15}$$

where we stop at first order in $\frac{qB}{m\omega_0}$. The corresponding solutions are $x(t) = \mathrm{Re}(U)$ and $y(t) = \mathrm{Im}(U)$ with $U(t) = U_+ e^{i\omega_+ t} + U_- e^{-i\omega_- t}$. The trajectories corresponding to the resonant frequencies $\omega_+$ and $\omega_-$ are thus circular trajectories traveled in the direct and indirect way respectively.