

T.P. Optical pumping

This practical work presents a spectroscopy experiment. This experiment will allow us to observe the electronic energy levels of Rubidium 85 and Rubidium 87 in their vapor form inside of an enclosure. A simple measurement of its optical transparency as a function of a radio-frequency radiation allows to probe matter in its finest details. We will be able to detect the fine and hyper-fine levels of valence electrons.

I. INTRODUCTION

Optical pumping is a process of polarization of the electronic spins through their interaction with a polarized light. It is a foundational experiment in atomic physics that led to major breakthroughs in our understanding of the light-matter interaction and has found many practical applications (atomic clocks, laser, gas MRI for instance). Its invention and its showcase led to the attribution of the Nobel Prize to Alfred Kastler from the Spectroscopie Hertzienne Lab (that has since become the LKB-Laboratoire Kastler Brossel) in 1966. The cooling of atoms with lasers (Cohen-Tannoudji, Nobel Prize 1997) and the measurement of single photons (Serge Haroche, Nobel Prize 2012) are both techniques that have their origin in optical pumping.

After he realized that the polarization of light corresponds to the various photonic spin states making that light, Alfred Kastler suggested a way to transfer that polarization to electronic spins that would then become "hyperpolarized". These hyperpolarised electronic spins would thus have a polarization much larger than the one that would naturally derive from thermal equilibrium. Because this transfer happens through absorption/emission cycles, we use the term "optical pumping".

II. GENERAL PRINCIPLE OF OPTICAL PUMPING

A. Basic principle

1. Zeeman Hamiltonian

Let us consider a particle described by its Hamiltonian \hat{H}_0 , leading to two discrete energy levels E_1 (ground state) and E_2 (excited state), separated by $\Delta E_0 = |E_2 - E_1|$. Let us also consider that the particle has an angular momentum $\hat{\mathbf{J}}$ associated with the quantum number j (Cf. Appendix 1). The associated magnetic momentum is $\mathbf{M} = \gamma\mathbf{J}$ where γ is the gyromagnetic ratio.

The energy level corresponding to the quantum number j has a $2j + 1$ degeneracy level, with $2j + 1$ possible values for the quantum number m_j ($-j \leq m_j \leq j$ by integer steps). This degeneracy is lifted when the particle is placed in a magnetic field \mathbf{B}_0 . Indeed, the Hamiltonian then becomes $\hat{H} = \hat{H}_0 + \hat{H}_z$, where $\hat{H}_z = -\mathbf{M} \cdot \mathbf{B}_0$ is the Zeeman Hamiltonian. The new energy levels of the system are then $E_i + m_j \hbar \gamma B_0$ with $i = 1, 2$ as the eigenvalues

of the angular momentum projected on the quantization axis defined by B_0 (aligned along the \mathbf{e}_z direction in the following) $m_j \hbar$.

Q0: What is the value of \mathbf{J} in the case where the particles are electrons and the angular momentum their spin? Write the eigenvalues of \mathbf{J} along \mathbf{e}_z (eigenvalues of J_z).

Give the mathematical expression of the energy difference $\Delta E_z = -\mathbf{M} \cdot \mathbf{B}_0$ between the various Zeeman levels. The orbital gyromagnetic ratio of the electron is $\gamma_e = \frac{q}{2m}$ (q is the signed charge of the electron and m its mass), that of its spin is $\gamma = g_e \frac{q}{2m}$ (where $g_e = 2$ is the Landé factor of the electron). Give an order of magnitude of ΔE_z for a magnetic field \mathbf{B}_0 of amplitude 10^{-5} T. Compare this value, on one hand, to the thermal energy at room temperature, and on the other hand to the typical energy of optical photons in the visible range.

Assuming that electrons follow the Boltzmann statistics, compute the ratio of populations $\frac{N(m_j=1/2)}{N(m_j=-1/2)}$ for Zeeman levels deriving from the same energy level E_i .

Make a numerical calculation making use of the lab conditions and deduce the electronic distribution between the Zeeman levels of the ground state.

2. Light polarization

Classically, light can be polarized in two ways, circular right (σ^+) or left (σ^-). These polarizations correspond to a rotation of the electromagnetic field in a plan perpendicular to its propagation axis. In quantum mechanics, we introduce the notion of photon, a massless particle associated to the electromagnetic field. As for every particle, the photon has a spin. This spin is an integer because the photon is a boson and is equal to 1. It can be shown in the context of field theory that circular right polarization (resp. left) corresponds to photons whose projection onto the propagation axis is $+\hbar$ with the quantum number $m_{ph} = +1$ (resp. $-\hbar$ with the quantum number $m_{ph} = -1$).

In the rest of this practical work, the propagation axis of the light will be the same as the Zeeman field axis \mathbf{B}_0 and will be called \mathbf{e}_z . Thus, we will use the projections of the electronic and photonic angular momenta on the same quantization axis.

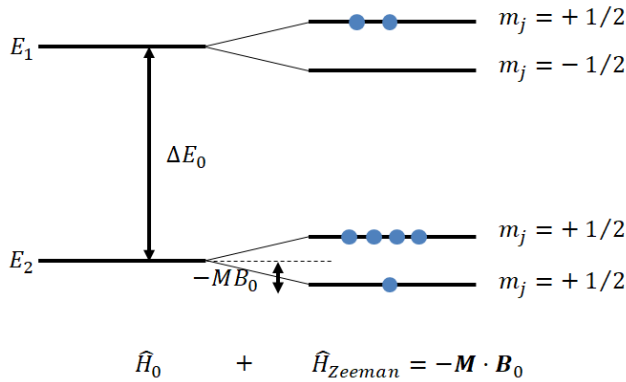


FIG. 1. Possible transitions for a two levels system where the spin degeneracy is lifted by a Zeeman field.

B. Electron-photon interaction

By sending light on electrons, it is possible to generate transitions between the electronic levels E_1 and E_2 by absorbing photons. The necessary condition for this is that the condition $E_{\text{photon}} = E_{\text{ph}} \simeq \Delta E_0$ is satisfied in order to conserve the total energy of the system.

However, the angular momentum must be conserved as well, i.e. the spin of the system. If the light is circular right polarized (σ^+), as it will be in the following, photons are all in a spin state $m_{\text{ph}} = +1$ that will be transferred to the electron in the interaction process. The following condition must then be satisfied $m_j^{\text{final}} - m_j^{\text{initial}} = m_{\text{ph}} = +1$ so that a photon is absorbed.

Once on the excited level, the electron will revert back to the ground state with no defined polarization. The two photon spin states $m_{\text{ph}} = \pm 1$ are allowed, and the condition is now $m_j^{\text{final}} - m_j^{\text{initial}} = m_{\text{ph}} = \pm 1$. The electron thus has a non zero probability to fall back on a level on which it will not be able to absorb any more polarized radiation.

Q1: *Under the effect of a continuous illumination, after many absorption/emission cycles, on which level does the particle necessarily end up? We will assume (and verify) that the width of the spectral line of the incident light is larger than the typical Zeeman splitting used in this practical work (field \mathbf{B}_0 with amplitude from 10^{-5} T to 10^{-4} T).*

If, instead of a single electron, we consider a statistical ensemble, all the electrons will eventually end up in the same Zeeman sub-level, i.e. in the same orientational state for their angular momentum. We call this level the "trap level". The ensemble of the angular momenta of the particles is polarized. This phenomenon is actually in a dynamical equilibrium with the thermodynamical

deexcitations that tend to redistribute the electrons according to the Boltzmann statistics. It is this special equilibrium that distributes in a non-thermodynamical way the particles in the energy levels that we call optical pumping.

Q2: *Explain through a series of diagrams, similar to that of fig. 1, the transition between a thermodynamical distribution of the electrons and the distribution induced by optical pumping.*

This situation is a very exotic one: the polarization is obtained via the interaction of the electrons with the light and does not correspond to the usual situation of thermodynamical equilibrium. The role of the external magnetic field is simply to lift the degeneracy and its amplitude does not affect (in first approximation) the final polarization level. The fact that we are able, thanks to optical pumping, to establish polarizations independently of the Boltzmann statistics will allow us to observe the Zeeman effect even for very small fields and at high temperature.

III. DESCRIPTION OF THE EXPERIMENTAL SETUP: EVIDENCING OPTICAL PUMPING

We will check experimentally the effect of optical pumping on an energetically quantized system, similar to the one shown in fig. 1. This system is a vapor of atoms whose electronic levels can, in first approximation, be described by this diagram. In practice, it is a Rubidium (Rb) vapor, an alkali species with a single valence electron, whose electronic structure is close to that of hydrogen (Cf. appendix 3). The density of this vapor is controlled by the temperature of the cell to which it is confined ($\approx 50^\circ\text{C}$). This cell is placed in between current polarized coils that generate the magnetic field \mathbf{B}_0 parallel to \mathbf{e}_z . The experiment will consist in sending a circular polarized light σ^+ on the system. That light will be emitted by the same type of atoms than those in the cell such that the energy conservation condition is satisfied and will be detected by a photodiode placed opposite to the lamp. The circular polarization is obtained by inserting a polarized/analyzed system with an angle of 45° on the optical path. The setup is shown in Fig 2.

The "TeachSpin" system provides all the necessary elements in order to perform the experiment in a single box, from the heating of the Rb cell, the power supply of the lamp, that of the magnetic coils and the amplifier used to read the photodiode signal. In this practical work we will use all the functions, exception made of the generation of the magnetic fields that will be provided by external generators.

Principle of the measurement: The electronic transitions between the various energy levels of the atomic systems are deduced from the transparency T of the bulb containing the gas. We measure the transparency us-

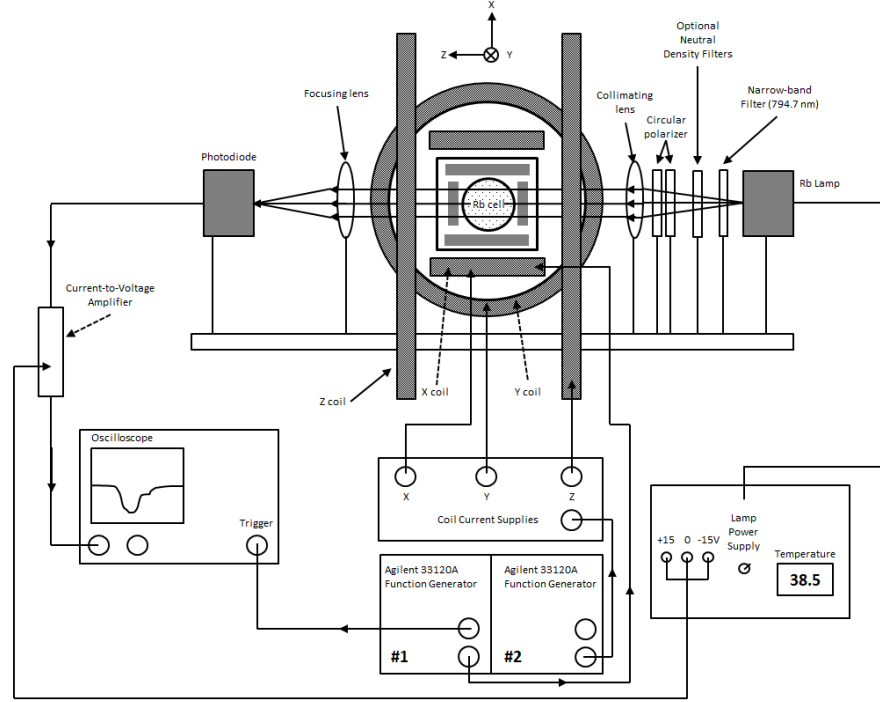


FIG. 2. Diagram of the experimental for optical pumping: The Rb lamp (on the right) creates photons that are first filtered (interferential filter) in order to only select one type of transition. They are then polarized circularly before being sent to the Rb cell whose temperature is controlled by a Peltier effect heater. They are then detected by the photodiode on the left. The coils are powered by the DC current generator or the GBF to generate magnetic fields. Table 1 gives the values of voltage that should not be exceeded when powering the coils.

ing a photodiode placed behind the bulb. This photodiode delivers an electric signal proportional to the incident photon flux that we visualize on the oscilloscope after amplification. When σ^+ (or σ^-) polarized photons induce electronic transitions, they do not exit the bulb and the transparency decreases. Inversely, when no electronic transition is induced by the polarized photons anymore, the transparency comes back to its initial state. All the measurements made in this practical work are transparency measurements of the bulb as a function of time.

The Zeeman field \mathbf{B}_0 and in the following the radio-frequency field are produced by external power supplies, plugged on the coils described on Fig. 2. The maximal values of voltages and currents are indicated in table I.

Zeeman coils (field generated along \mathbf{e}_z)	RF coils
$V_{\max} = 40 \text{ V}, I_{\max} = 3 \text{ A}$	$V_{pp\max} = 10 \text{ V}$

TABLE I. Voltage values not to be exceeded on the coils terminals.

A. Experiment: Dehmelt effect

The Zeeman field \mathbf{B}_0 defines the quantization axis \mathbf{e}_z of the experiment. Under illumination, the electrons in the system are in the trap level. We abruptly reverse the Zeeman field (now aligned with $-\mathbf{e}_z$). We observe a temporary fall of the cell transparency. This change in the transparency of the cavity with the inversion of the magnetic field is called "Dehmelt effect".

Q3: Using diagram 1, explain this effect qualitatively.

Experiment

- Apply the voltage bias at least 10 minutes before the first manipulation so that the temperature of the lamp and that of the cell are stabilized.
- Check roughly the alignment of the optical elements on the optical axis, making sure not to change the orientation of the bench.
- Plug the Low Frequency Generator (GBF) to the coils aligned along the \mathbf{e}_z axis and apply a low frequency square signal (dozen of Hz) with $V_{pp} = 10 \text{ V}$.

- Plug the output of the amplifier of the photodiode on the oscilloscope.
- Synchronize the oscilloscope with the square signal of the GBF. You must observe a figure of same period and in phase with the magnetic field inversion.

Remarks: The photodiode signal is amplified by an amplifier that is on the main part of the experiment (see Fig. 3). The offset should be adjusted in order to work as close to zero as possible. It will be useful to adjust the time constant according to the characteristic times of the experiment.

Q4: Record the data from the oscilloscope and explain the observations. Estimate the characteristic time of the phenomenon. Decrease the Zeeman amplitude. What do you observe? Explain.

Q5: From a series of observations, estimate the local value of the residual magnetism (mostly due to the earth magnetic field) in the \mathbf{e}_z direction.

Elements:

- The field created by a coil of radius R at a distance R from the axis is given by:

$$\mathbf{B}(M) = \frac{\mu_0 I}{2} \frac{R^2}{(z^2 + R^2)^{3/2}} \mathbf{e}_z \quad (1)$$

- The two Zeeman coils are made out of 20 individual coils, powered in such a way that their fields add vectorially.
- The total resistance of the coils is $11.735 \, \Omega$.

IV. ENERGY LEVELS OF RUBIDIUM, REMINDER ON THE FINE AND HYPERFINE STRUCTURE

Up to this point we have considered a two levels system in which each level is made up of two sub-levels with spins $\pm \frac{1}{2}$. The structure of the energy levels of rubidium is actually more complex than the two-level system studied up to now and the following experimental observations require the knowledge of its fine and hyperfine structure. In practice, the bulb contains rubidium vapor which has two isotopes with similar abundance: $\approx 72\%$ for ^{85}Rb and $\approx 28\%$ for ^{87}Rb , as well as a buffer gas, Argon, magnetically neutral, in order to avoid Rb-Rb collisions that induce parasitic transitions.



FIG. 3. Photodiode signal amplifier. The gain is set in the top right corner (usually we keep it at the maximum). An offset is applied in order to measure around 0 set both roughly and finely. An integration constant allows to average the signal (bottom right).

A. Main structure: atomic orbitals

The main Hamiltonian of the valence electron of an alkali element such as Rubidium (a single electron on the outer shell) is similar to that of hydrogen. It contains a kinetic energy term $\hat{P}^2/2m$ (\hat{P} is the momentum and m is the electron mass) and an electrostatic interaction term between the electron and the nucleus, screened by the other electrons $V(R)$:

$$\hat{H}_0 = \frac{\hat{P}^2}{2m} + V(R). \quad (2)$$

The energy levels are then quantized by the principal quantum number n :

$$E_n = -\frac{E_I}{n^2} \quad (3)$$

where E_I is the first ionization energy. The corresponding states have a $\sum_{l=0}^{n-1} (2l+1)$ degeneracy level and are described by the quantum numbers n and l (Cf. appendix 3).

This description is rigorous for the hydrogen atom that only has one electron. For atoms with more than two electrons, and thus for alkali, an electronic interaction term must be added to the Hamiltonian. This leads to energy levels slightly more complex, making use of both

quantum numbers n and l . For this reason we will observe transitions between levels with the same number n but with different l (2s2p transitions).

B. Fine structure: spin-orbit coupling

The fine structure takes into account the relativistic corrections to the Schrödinger equation (which is then called the Dirac equation). The expansion of the Hamiltonian to the first order in v/c leads to

$$\hat{H} = \hat{H}_0 + \hat{H}_f \quad (4)$$

where $\hat{H}_f = \hat{H}_{mv} + \hat{H}_D + \hat{H}_{so}$. \hat{H}_{mv} is the energy correction due to the relativistic variation of the mass with the velocity. \hat{H}_D is the energy correction due to the non-locality of the interactions with the electron (the electron is sensitive to its environment, not only to the electric field at its position). \hat{H}_{so} is the energy correction due to the coupling between the magnetic moment of the electron and the magnetic field "seen" by the electron because of its movement in the electrostatic field of the proton. Indeed, when a charge moves in an electrostatic field with a velocity \mathbf{v} , it "experiences" a field \mathbf{B} such that $\mathbf{B} = -\frac{1}{c^2} \mathbf{v} \wedge \mathbf{E}$. \hat{H}_{so} is the only term out of the three that lifts the degeneracy of the energy levels when the system is put in an external magnetic field, just like what we did in section 2. The other terms of the Hamiltonian only move the energy levels altogether. If $\hat{\mathbf{L}}$ is the orbital angular momentum of the electron and $\hat{\mathbf{S}}$ its spin, we can show that

$$\hat{H}_{so} = f(\mathbf{r}) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad (5)$$

where $f(r)$ is a function of the position r and

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{\hat{J}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2}{2} \quad (6)$$

with $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. We remind the reader that this definition of $\hat{\mathbf{J}}$ leads to $|l - s| \leq j \leq l + s$ where j varies by integer steps (Cf. appendix 2). From geometrical considerations we can show that if $\{\hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z\}$ realizes a complete set of commuting variables (ECOC in French), then so does $\{\hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z\}$. However, this set has the advantage of defining a vector basis $\{|n, k, s, j, m_j\rangle\}$ that are common eigenvectors to \hat{H}_0 and \hat{H}_{so} . As such, the state of the system is fully described by the quantum numbers n, l, s, j and m_j . When applying a field \mathbf{B}_0 , the degeneracy of the energy levels is (partially) lifted due to the different values of j .

For an alkali such as Rubidium, there is only one electron on the valence shell ($n = 2$). The only relevant spin quantum number is thus $s = \frac{1}{2}$. For the ground state $l = 0$ (level 2s in s, p, d, f... spectroscopic notation) there is thus only one possible value for j which is $j = \frac{1}{2}$ and no degeneracy lifting of the ground state under the effect

of spin-orbit coupling. We simply refer to this level as $2s_{1/2}$. However, for the first excited state we have $l = 1$ and thus two possible values for j : $j = \frac{1}{2}$ and $j = \frac{3}{2}$. We thus have a partial degeneracy lifting into two levels $2p_{1/2}$ and $2p_{3/2}$. We can therefore refine our description from the "general principle" section. There is not only one but two possible transitions $D1$ and $D2$ between the fundamental (level 2s) and first excited (level 2p) state:

$$\begin{aligned} D1 : 2s_{1/2} &\rightarrow 2p_{1/2}, \\ D2 : 2s_{1/2} &\rightarrow 2p_{3/2}. \end{aligned} \quad (7)$$

Q6: Draw a diagram of the energy levels of Rubidium under a Zeeman field of amplitude B_0 aligned with the \mathbf{e}_z axis.

C. Hyperfine structure: contact term

When taking into account the spin of the nucleus and the associated magnetic momentum $\hat{\mathbf{M}}_I$ there are many more corrections that disrupt the fine structure. Here, we will only consider the "contact" term which is the most important one.

Reminder: In general, the following relation between the angular momentum of a charged particle and its corresponding magnetic momentum is always valid: $\hat{\mathbf{M}}_L = \gamma \hat{\mathbf{L}}$ where γ is the gyromagnetic ratio. We remind the reader that for an electron, the orbital gyromagnetic ratio is $\gamma_e = \frac{q}{2m}$. The spin angular momentum associated with the electron is $\hat{\mathbf{M}}_S = g_e \gamma_e \hat{\mathbf{S}}$, where g_e is the Landé factor that can be computed using the Dirac equation and which is equal to $g = 2$. For protons, we define the gyromagnetic ratio $\gamma_p = \frac{-q}{2M}$, where $-q$ is the charge of the proton and M its mass. We can then write the associated spin angular momentum $\hat{\mathbf{M}}_I = g_p \gamma_p \hat{\mathbf{I}}$, where $\hat{\mathbf{I}}$ is the spin of the proton and g_p its Landé factor which is approximately equal to 5.585.

Because $\gamma_p \ll \gamma_e$ (because of the mass difference between the proton and the electron) nuclear magnetism is much smaller than electronic magnetism (taken into account in the fine structure). The corrections that we will take into account in the calculation of the hyperfine structure are those due to nuclear magnetism, both in the case of hydrogen (a single proton) and in the case of Rubidium studied here. If we consider the total spin of a nucleus \hat{I} (quantum number i), we can show that the only term of the hyperfine Hamiltonian \hat{H}_{hf} that has an influence on the degeneracy lifting of the energy levels is the so-called "contact" term. It actually refers to the interaction between $\hat{\mathbf{M}}_S$ and the magnetic field from within the inside of a proton.

The full Hamiltonian will thus be

$$\hat{H} = \hat{H}_0 + \hat{H}_f + \hat{H}_{hf}. \quad (8)$$

Just as before, we can write

$$\hat{H}_{hf} = A \hat{\mathbf{J}} \cdot \hat{\mathbf{I}} \quad (9)$$

where A is a constant. The analysis is similar to that of the fine structure. We write the total angular momentum $\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} + \hat{\mathbf{I}}$. $\hat{\mathbf{F}}$ is diagonal in the coupled basis $\{|n, l, s, j, i, f, m_f\rangle\}$ and, furthermore

$$\hat{\mathbf{J}} \cdot \hat{\mathbf{I}} = \frac{\hat{F}^2 - \hat{J}^2 - \hat{I}^2}{2}. \quad (10)$$

\hat{H}_{hf} is thus also diagonal in this basis

$$A\hat{\mathbf{J}} \cdot \hat{\mathbf{I}} |j, i, f, m_f\rangle = \frac{A\hbar^2}{2} [f(f+1) - i(i+1) - j(j+1)] |j, i, f, m_f\rangle \quad (11)$$

where $|j - i| \leq f \leq j + i$ by integer steps.

In the case of Rb, we have $i(^{87}\text{Rb}) = \frac{3}{2}$ and $i(^{85}\text{Rb}) = \frac{5}{2}$.

Q7: Draw a clear diagram of the possible energy levels for ^{87}Rb and ^{85}Rb for $n = 2$ in its principal, fine and hyperfine structure while indicating the values of the various quantum numbers.

V. ZEEMAN EFFECT AND OPTICAL PUMPING

A. Zeeman effect

We saw previously that it is necessary to apply a magnetic field in order to lift the orientational degeneracy. However, the situation is now more complex due to the many angular momenta susceptible to couple to the external field. We must thus first describe correctly the Zeeman effect (degeneracy lifting by application of a magnetic field) in an alkali atom.

First, we can forget about the electrons which are not valence electrons. These electron are indeed paired and do not contribute to the angular momentum. Second, one must distinguish the separate effects of atomic and nuclear Zeeman effects because nuclei and electrons have very different gyromagnetic ratios. In the case of a non-zero electronic angular momentum we can thus neglect the nuclear Zeeman term.

The total electronic angular momentum is the sum of its orbital momentum $\gamma\hat{\mathbf{L}}$ and of its spin momentum $\gamma g_e\hat{\mathbf{S}}$. We will thus write the Zeeman Hamiltonian as

$$\hat{H}_Z = \gamma_e \mathbf{B}_0 \cdot (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \quad (12)$$

If the magnetic field is along \mathbf{e}_z

$$\hat{H}_Z = \gamma_e \hat{B}_0 (\hat{L}_z + 2\hat{S}_z). \quad (13)$$

The direction O_z is not arbitrary anymore as it corresponds to that of the external magnetic field that defines the magnetic interaction energies with the field. We call this axis the Zeeman energy quantization axis. We

notice that the eigenvectors of the hyperfine structure $\{|n, l, s, j, i, f, m_f\rangle\}$ are not eigenvectors of \hat{H}_Z . We will leave to the students the ungrateful task of diagonalizing the full Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_F + \hat{H}_{hf} + \hat{H}_Z$ and we will rather place ourselves in an experimental situation in which it is possible to treat the Zeeman effect as a second order perturbation, i.e. we will apply a sufficiently small field \mathbf{B}_0 . We will also use one of the consequences of the Wigner-Eckart theorem.

B. Wigner-Eckart theorem

Let us consider a system of angular momentum $\hat{\mathbf{J}}$. The Wigner-Eckart theorem concerns the vectorial operators.

Definition: An observable $\hat{\mathbf{V}}$ is vectorial if it verifies the following commutation relations

$$[\hat{J}_x, \hat{V}_x] = 0, \quad [\hat{J}_x, \hat{V}_y] = i\hbar \hat{V}_z, \quad [\hat{J}_x, \hat{V}_z] = -i\hbar \hat{V}_y \quad (14)$$

Theorem: Let \mathbf{V} be any vectorial operator restricted to the sub-space $\mathcal{E}(n, j)$ with j the quantum number associated to the angular momentum $\hat{\mathbf{J}}$. We then have

$$\hat{\mathbf{V}} = \frac{\langle \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} \rangle_{n,j}}{\langle \hat{J}^2 \rangle_{n,j}} \hat{\mathbf{J}}. \quad (15)$$

This theorem is also called the projection theorem.

Let us now come back to the problem we are trying to solve. In a perturbative calculation one only has to diagonalize the perturbing Hamiltonian in the degeneracy subspaces of the perturbed Hamiltonian. Here, the degeneracy corresponds to the orientational degeneracy (for the different possible values of m_f) because, as long as we have not applied a magnetic field, all the directions are equivalent. However, the quantum numbers that characterize the norms of the angular momenta are fixed (the numbers l, s, f, i and j) as they come up in the calculation of the eigen-energies of the fine and hyperfine structure. To conclude, in the subspaces that come into play in the first order perturbation calculation, the norms are fixed and the validity conditions of the Wigner-Eckart theorem are fulfilled. Finally, after a few line of calculus, for a first order perturbation analysis of the Zeeman term (and only in this framework) we can write

$$\hat{L}_z + 2\hat{S}_z = \frac{\langle \hat{\mathbf{J}} \cdot \hat{\mathbf{F}} \rangle}{\langle \hat{F}^2 \rangle} \left[\frac{\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{J}} \rangle}{\langle \hat{J}^2 \rangle} + 2 \frac{\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{J}} \rangle}{\langle \hat{J}^2 \rangle} \right] \hat{F}_z = g_F g_J \hat{F}_z. \quad (16)$$

The g_J and g_F coefficients are called Landé factors.

Q8: Compute the Landé factors for the ground states of the hyperfine structure of ^{87}Rb and ^{85}Rb .

In the case where the applied directing field is weak it is therefore possible to approximate the Zeeman Hamiltonian by

$$\hat{H}_Z \simeq \hat{H}_Z^{(1)} = \gamma_e g_F g_J B_0 \hat{F}_z. \quad (17)$$

From this we can directly see that the application of an external magnetic field lifts, through the Zeeman effect, the orientational degeneracy. This could be physically anticipated but the interesting point is that this degeneracy lifting is directly proportional to m_F . The Zeeman sub-levels of the hyperfine structure of alkalis are thus, in a first order approximation, equidistant (as it is a consequence of the Wigner-Eckart theorem whose condition of application are only valid in the first order).

C. Absorption of polarized light and relaxation in the case of rubidium

If the light is circular right polarized, we are dealing with a flux of photons prepared in an angular momentum state $m_{ph} = +1$. Their absorption will thus follow the rule $\Delta m_f = +1$ (conservation of angular momentum). However, their desexcitation can happen with $\Delta m_f = \pm 1$. In the experimental setup, an interferential filter is inserted between the lamp and the cell that contains the Rubidium such that D2 transitions do not happen. Here we will thus only consider D1 type transitions.

Q9: On the energy diagrams of ^{87}Rb and ^{85}Rb that you drew previously, indicate the trap energy level (give the associated quantum numbers) after optical pumping by a circular right polarization.

As in the simplified example studied before, the polarization achieved through optical pumping is not in a thermodynamical equilibrium state. Thermal agitation will tend to constantly re-equilibrate the populations according to Boltzmann statistics. Experimentally, the final polarization that we obtain is thus the result of a dynamical equilibrium between optical pumping and relaxation.

VI. SPECTROSCOPY

A. First order time dependent perturbation

We will now study the hyperfine structure of Rubidium atoms and do the spectroscopy of the levels we previously calculated. For that purpose, we need to realize inter-level transitions and thus send photons whose energy correspond to these various levels. A good order of magnitude was calculated in the framework of the simplified diagram (question Q0). Because this energy is very small compared to the other characteristic energies

of Rubidium, we will use the time dependent perturbation theory to describe this process. The photons correspond to an electromagnetic field generated by the coils in which an alternating current of pulsation ω_{RF} circulates (RF stand for "Radio-Frequency").

We then apply a second magnetic field, oscillating and perpendicular to the directing field (thus along \mathbf{e}_x or \mathbf{e}_y). Indeed, in order to achieve non-zero transition probabilities between the energy levels of the hyperfine Hamiltonian (whose degeneracy is lifted by the Zeeman Hamiltonian), time dependent perturbation theory shows that we must have non-zero terms outside of the diagonal of the hyperfine Hamiltonian. However the hyperfine basis is (in its short version) $\{|f, m_f\rangle\}$ in relation to the ECOC (in short version as well) \hat{F}^2, \hat{F}_z . We thus need terms containing \hat{F}_x or \hat{F}_y , hence a field along \mathbf{e}_x or \mathbf{e}_y . The total Hamiltonian of the system will therefore now be $\hat{H} = \hat{H}_0 + \hat{H}_F + \hat{H}_{hf} + \hat{H}_Z + \hat{H}_{RF}$. Just as we did previously, we can approximate the effect of this magnetic field by the Hamiltonian

$$\hat{H}_{RF} = -\gamma_e B_1 \cos \omega_{rf} t \mathbf{e}_x \cdot (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) = -\gamma_e g_J g_F B_1 \cos \omega_{RF} t \hat{F}_x. \quad (18)$$

If this interaction can be treated in the framework of first order time dependent perturbation of the Zeeman effect, we can show that it induces transitions for $\Delta m_f = \pm 1$ (this selection rule about the absorption of the radio-frequency electromagnetic radiation should not be confused with the one we have discussed before that relates to the absorption of polarized light). Thus, when we satisfy

$$\hbar \omega_{RF} = |\Delta E_{\text{Zeeman}}(\Delta m_f = \pm 1)| = |\hbar \gamma_e B_0 g_F g_J|, \quad (19)$$

the RF field induces electronic transitions from the $2s_{1/2}$ level ($m_f = 2$) for ^{87}Rb ($2s_{1/2}$ ($m_f = 3$) for ^{85}Rb) that does not absorb circular right polarized light to the others that do absorb the light (we note that in this first order approximation the levels for different m_f are equidistant). The transparency of the cell will thus drop. A measure of the transparency of the cell during a RF frequency sweep will thus allow to identify the resonance conditions of each Rubidium isotope. We will observe two peaks, one per isotope.

In the following, we will realize a set of experiments aimed at studying the hyperfine spectrum of Rubidium atoms by varying the relative intensity of the Zeeman and RF fields.

B. Manipulation: Weak Zeeman field, weak RF field

In a first step, we place ourselves in a situation in which both magnetic fields are weak and constitute small perturbations to the principal Hamiltonian. A first order perturbative expansion will be sufficient to explain our results.

- The directing coils are powered by a current stabilized power supply. The value of this current must remain low (roughly below 0.2 A) so that the Zeeman term remains a first order perturbation of the hyperfine coupling.
- The "small" coils perpendicular to the directing coils ("RF coils" on the TeachSpin setup) are powered by a GBF in sinusoidal mode. In a first step, the voltage is at its maximum (do not exceed $V_{pp} = 10$ V) in order to maximize the absorption/emission probability associated to the time dependent perturbation.
- By using the GBF in sweeping mode, we will observe the fall of the transparency when the frequency corresponds to the resonance criterion (equation 19). We will sweep fast enough (hundred of ms) to visualize the spectrum directly on the oscilloscope by synchronizing it to the reference signal of the GBF. Possible starting values: sweep from $f_{\min} = 10$ kHz to $f_{\max} = 900$ kHz in $T_{\text{sweep}} = 300$ ms, the current in the direction coils must be gradually increased by hand starting from 10 mA until resonance peaks are observed. Be careful not to go beyond the coil maximum current (3 A).
- Sweep slower (5s is a reasonable value). Lower the intensity of the GBF in order to come back to the first order time dependent perturbation with respect to the Zeeman effect. You will have to find a compromise between a satisfactory signal to noise ratio and the sharpness of the resonance peak.
- Adjust the frequency sweep window in order to observe with the highest precision possible the two resonance frequencies.

Q9: Do a data acquisition. Check that the frequency ratio corresponds to the ratio of the Landé factors of the two Rubidium isotopes. Redo the experiment for a dozen different values of the directing field and check the linearity of the current/frequency relation that is expected in the first order. Do not forget to write down the sweeping values f_{\min} , f_{\max} and T_{sweep} in order to reconstruct the scale a posteriori. Write down the value of the directing field.

C. Manipulation: Strong Zeeman field, weak RF field

If the Zeeman effect is too intense to be analyzed in the first order perturbation theory framework, we cannot use the Wigner-Eckart theorem any longer. By increasing the amplitude of the directing field, the Zeeman sub-levels

are not equidistant anymore and we can, for each isotope, observe as many resonances as there are adjacent intervals between energy levels corresponding to different m_f .

- Increase the directing field by a factor 10 (approximately 1 A for the Zeeman coils).
- Observe the peaks corresponding to both isotopes (that are thus at higher frequency) by using a strong RF field if needed if the signal to noise ratio is unfavorable.
- Come back to the case of a weak RF excitation (approximately below $2 V_{pp}$).
- Zoom on one of the two peaks. Narrow the sweep until you are able to see the sub-peaks corresponding to transitions between hyperfine levels.
- It can sometimes be difficult to observe sub-peaks. Two strategies are then possible: (i) sweep fast in frequency ($T_{\text{sweep}} \approx 100$ ms) with a small time integration constant, or (ii) sweep very slowly ($T_{\text{sweep}} \approx 5$ s) with a larger integration constant. In both cases do not forget to average with the oscilloscope.

Q10: Do an acquisition of the sub-peaks you got, one per isotope. Explain the observed number of peaks. Inverse the polarization by tilting the polarizing plate by 90° ; the relative intensities must change.

The intensities must decrease as we get detuned from the transition involving the level on which the electrons get pumped (the other levels are populated through relaxation processes).

D. Second order time dependent perturbations

If we now increase the amplitude of the radio-frequency field, it cannot be considered as a first order perturbation any longer and the selection rule $\Delta m_f = \pm 1$ is not valid anymore. By taking the calculation to the second order in perturbation, we can determine a new selection rule: $\Delta m_f = \pm 2$ and thus show that there are transitions at the following frequencies

$$\hbar\omega_{RF} = \frac{1}{2} [\Delta E(m_f = 1 \leftrightarrow m_f = 2) + \Delta E(m_f = 0 \leftrightarrow m_f = 1)] \quad (20)$$

(the same rule applies for all the other combinations for which we have a total of $\Delta m_f = \pm 2$). From a corpuscular point of view this means that two RF photons at $\nu_{RF} = \frac{\nu_1 + \nu_2}{2}$ are absorbed in order to realize a $\Delta m_f = \pm 2$ transition (energy conservation). We will talk about *two quanta* transition.

Remark: We also have conservation of the angular momentum as we use two photons σ^\pm and thus $2m_{ph} = \pm 2 = \Delta m_f$.

E. Manipulation: two quanta transitions, strong Zeeman and strong RF

The settings are those of the previous experiment. The difference is that we now increase gradually the intensity of the radio-frequency field, i.e. the output voltage of the GBF, until we can observe additional peaks in between those of the spectrum of a single quantum.

Q11: *Make an acquisition of the new peaks obtained, one per isotope. Comment on the results.*

F. Manipulation: Time dependent perturbation at higher orders

If we accept that radio-frequency fields can lead to several quanta transitions, nothing should in principle prevent this to also happen between adjacent levels, meaning $\Delta m_f = \pm 1$. This can indeed be demonstrated (see Cohen-Tannoudji, volume 2... obviously). Experimentally, this must lead to transitions for integer fractions of the one quantum transition. Because the radio-frequency field oscillates, it corresponds to a straight polarization, meaning the superposition of a circular right and left polarization. From a corpuscular point of view, it is thus made up of photons either in the $m_{ph} = +1$ or $m_{ph} = -1$ state. It is therefore impossible to conserve the angular momentum while realizing a $\Delta m_f = \pm 1$ transition by absorbing two photons (we would either get $\Delta m_f = \pm 2$ if both photons have the same polarization, or $\Delta m_f = 0$ if they have opposite polarization but never $\Delta m_f = \pm 1$). However nothing stands in the way of three quanta transitions or, in general, of transitions involving an odd number of quanta n . They correspond to fractional energies of the single quantum transitions $|\Delta E_{\text{Zeeman}}(\Delta m_f = \pm 1)|/n$.

In order to observe this effect, one must maximize the relative amplitude of the radio-frequency field with respect to that of the directing field. To do so, a minimal current is set on the directing coils (a few mA or even no current at all, using the ambient field). In the same time, the GBF voltage is set to its maximum (≈ 10 V).

Q12: *Try to observe n quanta peaks ($n = 3$ or even $n = 5$) that correspond to both isotopes. Make an acquisition and indicate the frequency of the peaks.*

VII. RABI OSCILLATIONS

We will now observe the dynamics of the system under a sinusoidal time dependent perturbation (see appendix 4), which, in this case, is the radio-frequency field. It produces transitions between the eigenstates of the system. We can show that the system oscillates periodically from

one state to the other with a frequency called the "Rabi frequency", that depends on the amplitude of the perturbation as well as on its gap in frequency with respect to the energy difference between the levels considered. This oscillation happens as long as the system is coherent on the quantum level. If it exchanges energy with its environment in a non-coherent way, the amplitude of the oscillations decreases and they cannot be observed any longer.

We will carry out an observation of the "Rabi oscillations" of Rubidium atoms from the cell by placing ourselves in a weak Zeeman field, such that the corresponding levels are equidistant. For that purpose, we will send a periodic sinusoidal signal at a relatively low frequency (a few dozen of Hz) at the frequency corresponding to the transition between adjacent Zeeman levels. If the coherence time is long enough, we will be able to observe Rabi oscillations created by the application of the RF signal.

A. Manipulation: Rabi oscillations

- Place yourself in a relatively weak field \mathbf{B}_0 (DC current of the order of 0.1 to 0.2 mA).
- Do a frequency sweep in order to find the two peaks corresponding to ^{87}Rb and ^{85}Rb (cf. manipulation 6.2).
- Choose a peak and restrict the sweep between f_{\min} and f_{\max} in order to zoom on it.
- We now want to know the resonance frequency as precisely as possible, i.e. find the one that gives the minimum transparency of the cell. Stop the sweep and look for the frequency f_0 between f_{\min} and f_{\max} by hand such that it minimizes the transparency of the bulb.
- Send a sinusoidal signal at the frequency f_0 whose amplitude is modulated by a low frequency square signal (10 to 100 Hz). Synchronize the oscilloscope on the square and zoom in on the beginning of a square.
- Play with the frequency f_0 in order to maximize the Rabi oscillations. If you do not observe them, it is possible that the frequency at which the Rabi oscillations should be observed has shifted (temperature drift). In this case, do another sweep to once again determine the frequency f_0 .

Q13: *Make an acquisition. Measure the period of the oscillations and the characteristic decay time that corresponds to the quantum coherence time. How do those two parameters vary if f_0 and the amplitude of the RF field are changed?*

Appendix A: Reminders on the angular momentum

1. Orbital angular momentum

In classical mechanics the angular momentum is defined by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. If the potential to which a particle is submitted is a central one, meaning of the form $V(r)$ with r the norm of the position of the particle, then the resulting force due to this potential is $\mathbf{f} = -\frac{dV}{dr} \frac{\mathbf{r}}{r}$. In that case, according to the angular momentum theorem, \mathbf{L} is constant (zero) with respect to the origin of the chosen frame of reference. We say that it is a constant of the motion. It is an important quantity in classical mechanics as well as in quantum mechanics.

The immediate quantum transposition of the angular momentum is the orbital angular momentum $\hat{\mathbf{L}}$ (we use the symbol $\hat{}$ because it is an operator and in bold symbol because it has three components \hat{L}_x , \hat{L}_y and \hat{L}_z). In Cartesian coordinates, the components of $\hat{\mathbf{L}}$ are:

$$\begin{cases} \hat{L}_x = \hat{Y}\hat{P}_z - \hat{Z}\hat{P}_y \\ \hat{L}_y = \hat{Z}\hat{P}_x - \hat{X}\hat{P}_z \\ \hat{L}_z = \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x \end{cases} \quad (\text{A1})$$

Because $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$ we have $[\hat{L}^2, \hat{\mathbf{L}}] = \mathbf{0}$, and in particular

$$[\hat{L}^2, \hat{L}_z] = 0. \quad (\text{A2})$$

This means that there exists a common eigenvector basis to \hat{L}^2 and \hat{L}_z . By looking at the effect of the orbital angular momentum on the wavefunction $\psi(r, \theta, \phi)$ in spherical coordinates we find:

$$\begin{cases} \langle r | \hat{L}_z | \psi \rangle = -i\hbar \frac{d\psi}{d\phi} \\ \langle r | \hat{L}^2 | \psi \rangle = -\hbar^2 \left(\frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right) \end{cases} \quad (\text{A3})$$

We can see that neither \hat{L}_z nor \hat{L}^2 depend on r (the norm of the position vector \mathbf{r}), but only on θ and ϕ . The eigenfunctions common to \hat{L}_z and \hat{L}^2 are thus independent of r and are written as $Y_l^m(\theta, \phi)$ and called spherical harmonics.

2. Angular momentum, general definition

In quantum mechanics there exists other angular momenta than the orbital one $\hat{\mathbf{L}}$. Those do not have any classical counterparts. The spin is one of those. In general, we define an angular momentum operator in quantum mechanics as $\hat{\mathbf{J}} = \hat{J}_x \mathbf{e}_x + \hat{J}_y \mathbf{e}_y + \hat{J}_z \mathbf{e}_z$ such that

$$[\hat{J}_i, \hat{J}_k] = i\hbar \epsilon_{ijk} \hat{J}_j, \quad (\text{A4})$$

where $\epsilon_{ijk} = 1$ for $i \neq j \neq k$. We also define $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ and we thus have the relation

$$[\hat{J}^2, \hat{J}_z] = 0. \quad (\text{A5})$$

There is therefore a common eigenvector basis to \hat{J}^2 and \hat{J}_z . We can show that the eigenvalues of \hat{J}^2 are $j(j+1)\hbar^2$, where j is an integer (as for $\hat{\mathbf{L}}$) or half-integer (no classical equivalent) positive or equal to zero. We can also show that the eigenvalues of \hat{J}_z are $m\hbar$ with $m = -j, -j+1, \dots, j$. We write $|j, m\rangle$ the eigenvector of \hat{J}^2 and \hat{J}_z associated to the previously mentioned eigenvalues in the common basis.

Finally we define $\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y$ and we can show that

$$\hat{J}_{\pm} |j, m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1\rangle \quad (\text{A6})$$

First remark: (\hat{J}^2, \hat{J}_z) is not, in general, an ECO as this ensemble is not complete.

Second remark: A quantum system without charge or mass can still have an angular momentum, which is impossible in classical mechanics.

Appendix B: Reminder on the composition of angular momenta

Let us consider a quantum system made up of two sub-systems, with angular momentum $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ respectively and the associated quantum numbers j_1 and j_2 . For each of them, we consider the operators that commute between each other \hat{J}_i^2 and \hat{J}_{zi} ($i = 1, 2$) where \mathbf{e}_z is a quantization axis. For the first one, the associated eigenvalues are $j_1(j_1+1)\hbar^2$ and $j_2(j_2+1)\hbar^2$ respectively. For the second, the $2j_1+1$ eigenvalues associated are $m_1\hbar$ with $-j_1 \leq m_1 \leq j_1$ by integer steps and the $2j_2+1$ eigenvalues associated are $m_2\hbar$ with $-j_2 \leq m_2 \leq j_2$ by integer steps.

The total angular momentum is $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. The operators \hat{L}^2 and \hat{L}_z commute. The associated quantum numbers are j and m . We can show that they satisfy the following conditions

$$|j_1 - j_2| \leq j \leq (j_1 + j_2) \quad (\text{B1})$$

$$-j \leq m \leq j \quad (\text{B2})$$

where j and m change by integer steps.

The eigenvectors common to \hat{L}^2 and \hat{L}_z can be calculated from the initial eigenvectors

$$|j, m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2 | j, m \rangle \quad (\text{B3})$$

where $\langle j_1, j_2; m_1, m_2 | j, m \rangle$ are the Clebsch-Gordan coefficients.

Appendix C: Reminder on the energy levels of the hydrogen atom

1. Writing the Hamiltonian

In the case of the hydrogen atom, in the frame of reference of the center of mass, the potential to which the electron is subjected is central, of the form

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (C1)$$

The Hamiltonian of the system is then

$$\hat{H} = \frac{\hat{P}^2}{2m} + V(r) \quad (C2)$$

where $\hat{\mathbf{P}}$ is the electron momentum and m its mass.

The Schrödinger equation can be written in the case of a central potential (only dependent on r) as

$$\left[-\frac{\hbar^2}{2m} \Delta + V(r) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (C3)$$

where $\psi(\mathbf{r})$ is the electron wavefunction.

We are looking for the eigen-elements (eigenvalues E and eigenvectors ψ) of this equation. However in spherical coordinates, $\Delta\psi = \frac{1}{r} \frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2} \left[\frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right]$. We can recognize in the second item, the $\langle \mathbf{r} | \hat{L}^2 | \psi \rangle$ term from equation A3. By replacing it in the Hamiltonian we have

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2mr^2} \hat{L}^2 + V(r). \quad (C4)$$

As \hat{L}^2 does not depend on r we then have

$$[\hat{H}, \hat{L}^2] = 0. \quad (C5)$$

There is thus a common basis of eigen vectors to \hat{H} and \hat{L}^2 . However the spherical harmonics $Y_l^m(\theta, \phi)$ are already an eigenvector basis for \hat{L}^2 . Actually $g(r)Y_l^m(\theta, \phi)$ with any g is a basis of \hat{L}^2 . We must thus find $g(r)$ such that $g(r)Y_l^m(\theta, \phi)$ is also a basis for \hat{H} .

2. Solving the Schrödinger equation

a. Eigen energies

We look for ψ such that $\psi(r, \theta, \phi) = \frac{1}{r} u(r) Y_l^m(\theta, \phi)$. As $\hat{L}^2 |\psi\rangle = \hbar^2 l(l+1) |\psi\rangle$ the Schrödinger equations reads as

$$\frac{d^2 u}{dr^2} - \left[\frac{l(l+1)}{r^2} - \frac{K}{r} \right] u(r) = \epsilon^2 u(r) \quad (C6)$$

where $K = \frac{2\mu}{\hbar^2} \frac{e^2}{4\pi\epsilon_0}$ and $\epsilon^2 = -\frac{2\mu E}{\hbar^2}$. We write $u(r) = v(r)e^{-\epsilon r}$ and equation C6 becomes

$$\frac{d^2 v}{dr^2} - 2\epsilon \frac{dv}{dr} - \left[\frac{l(l+1)}{r^2} - \frac{K}{r} \right] v = 0. \quad (C7)$$

We will be looking for $v(r)$ as an integer series expansion: $v(r) = \sum_{k=0}^{\infty} C_k r^k$. Then we have

$$[(k+2)(k+1) - l(l+1)] C_{k+2} = [2\epsilon(k+1) - K] C_{k+1}, \quad (C8)$$

with $C_0 = 0$. Thus $\lim_{k \rightarrow \infty} \frac{C_{k+2}}{C_{k+1}} \simeq \frac{2\epsilon}{k+2}$ following a $1/k$ behavior. But if this is valid then $\lim_{k \rightarrow \infty} v(r) \approx e^{2\epsilon r}$ diverges, which is not acceptable from a physical point of view (the wavefunctions must be normalized). Thus there is an index k_0 such that

$$2\epsilon(k_0+1) - K = 0, \quad (C9)$$

meaning $\epsilon = \frac{K}{2(k_0+1)}$. Hence, by replacing by E

$$E = E_n = -\frac{E_i}{n^2}, \quad (C10)$$

where $n \in \mathbb{N}^*$ ($n = k_0 + 1$) and $E_I = \frac{1}{2} \frac{m}{\hbar^2} \left(\frac{e}{4\pi\epsilon_0} \right)^4$ is the first ionization energy for the electron (of charge e). The eigen energies of the hydrogen atom are thus quantized. We call n the principal quantum number.

b. Eigenstates

If $l = 0$ then $C_0 = 0, C_1 \neq 0, \dots, C_k \neq 0$ for $k \leq k_0 + 1$. If $l = 1, C_0 = 0, C_1 = 0, C_2 \neq 0, \dots, C_k \neq 0$ for $k \neq k_0 + 1$. Thus

$$v(r) = \sum_{k=l+1}^{k_0+1} C_k r^k \quad (C11)$$

and we can write the eigenstates of the hydrogen atom in the following form

$$\psi_{n,l,m}(r, \theta, \phi) = Y_l^m(\theta, \phi) e^{-\frac{r}{na_0}} \sum_{k=l}^{n-1} C_k r^k, \quad (C12)$$

where $a_0 = 5.3 \cdot 10^{-11}$ is the Bohr radius.

c. Denegeracy

We always have $l \leq n-1$ and $m = -l, \dots, l$ ($2l+1$ possible values). As such, the fixed n energy levels are $\sum_{l=0}^{n-1} (2l+1)$ times degenerated. This leads to

- For $n = 1, l = 0$ and $m = 0$. The energy level at $n = 1$ is not degenerated and is written as "1s".
- For $n = 2, l = 0$ and $m = 0$ (level "2s") or $l = 1$ and $m = -1, 0$ or 1 (level "2p"). The levels 2s and 2p have the same energy. The $n = 2$ level is 4 times degenerated.

And so on.

d. The alkali case

Appendix D: Reminder on time dependent perturbations and Rabi oscillations

1. Time dependent perturbations

We consider a system that can be described by the Hamiltonian \hat{H}_0 whose eigenstates and eigenvalues are $|\varphi_n\rangle$ and E_n . For simplicity, we consider that the states are discrete and not degenerated. At time $t = 0$ we apply a time dependent perturbation $\hat{W}(t)$, whose amplitude is small compared to \hat{H}_0 . The new Hamiltonian is then $\hat{H}(t) = \hat{H}_0 + \hat{W}(t)$.

Before the application of the perturbation ($t < 0$), the system is in an eigenstate of the non perturbed Hamiltonian $|\psi(t=0)\rangle = |\varphi_i\rangle$, where the index i stands for *initial*. We can compute the probability to find it at time t in another eigenstate of the $|\psi(t)\rangle = |\varphi_f\rangle$, where the index f stands for *final*. This probability is equal to

$$\mathcal{P}_{if}(t) = |\langle\varphi_f|\psi(t)\rangle|^2. \quad (\text{D1})$$

We now introduce the Bohr pulsation

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \quad (\text{D2})$$

that corresponds to the energy difference between the initial state E_i and the final state E_f . The matrix element that couples these two states via the perturbation is

$$W_{fi}(t) = \langle\varphi_f|\hat{W}(t)|\varphi_i\rangle. \quad (\text{D3})$$

We can then show that

$$\mathcal{P}_{if}(t) = \frac{1}{\hbar^2} \left| \int_0^t \exp(i\omega_{fi}t') W_{fi}(t') dt' \right|^2. \quad (\text{D4})$$

One important case, that we do use in the practical work, is that of a sinusoidal perturbation $\hat{W}(t) =$

$\hat{W} \cos(\omega t)$. In that case, we can show that

$$\mathcal{P}_{if}(t) = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - \exp(i(\omega_{fi} + \omega)t)}{\omega_{fi} + \omega} + \frac{1 - \exp(i(\omega_{fi} - \omega)t)}{\omega_{fi} - \omega} \right|^2. \quad (\text{D5})$$

The first term corresponds to a photon emission and the second to a photon absorption that resonate around $\omega = \omega_{fi}$. Close to the resonance, we can write the absorption probability as

$$\mathcal{P}_{if}(t; \omega - \omega_{fi}) = \frac{|W_{fi}|}{4\hbar^2} \left[\frac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right]^2 \quad (\text{D6})$$

This first order perturbative calculation is valid if $t \ll \frac{\hbar}{|W_{fi}|}$, and obviously if $t \gg 1/\omega$ so that it acts over a time longer than its period.

2. Rabi oscillations

We can compute the transition probability between two levels under the influence of resonant sinusoidal perturbation for times longer than the previously mentioned constraint $t \ll \frac{\hbar}{|W_{fi}|}$. If we place ourselves exactly at the resonance $\omega = \omega_{fi}$ we can show that

$$\mathcal{P}_{if}(t; \omega = \omega_{fi}) = \sin^2 \left(\frac{|W_{fi}|t}{2\hbar} \right). \quad (\text{D7})$$

In the vicinity of the resonance $\omega \approx \omega_{fi}$, we have

$$\mathcal{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{|W_{fi}|^2 + \hbar^2(\omega - \omega_{fi})^2} \sin^2 \left[\sqrt{\frac{|W_{fi}|^2}{\hbar^2} + (\omega - \omega_{fi})^2} \frac{t}{2} \right] \quad (\text{D8})$$

The system thus oscillates periodically with a pulsation that depends on the amplitude of the perturbation (via $|W_{fi}|$) and of the frequency gap with the Bohr pulsation ω_{fi} (Rabi oscillations).