Q-MECH AND SPECTROSCOPY

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Master MAUCA
January 22, 2019

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Do you remember those happy days?

The foundation of QM comes from some historical experiments and formulations. Some of them are recalled hereafter.
In this chapter you will check your souvenirs.

Answer to all the questions that are in blue.

This is the rule for the entire document

All your calculations have to be written in a \LaTeX{} report that will be marked.

1.1 Maxwell-Boltzmann

Considering a classical collection of particles of mass $m$ in thermodynamical equilibrium at temperature $T$ Boltzman gives the probability that a particle has the energy $E$:

$$
f(E) = Ae^{\frac{E}{k_B T}}$$  \hspace{1cm} (1.1)

($k_B$ Boltzman constant)

No restriction on the number of particles which can occupy a given state.

Determine $A$. Derive the mean energy of a system of particles randomly distributed among the available energy states.

Compute $A$ in the case of $E$ is the 1D kinetic energy and deduce the following Maxwell velocity distribution where $v$ is the modulus of the 3D velocity

Maxwell’s velocity distribution of the particles

$$f(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2k_B T} \right)^{\frac{3}{2}} v^2 \exp\left( -\frac{mv^2}{2k_B T} \right)$$
1.2 Fermi-Dirac

The probability for a fermion (electron for example) to occupy the energy level $E_i$ at temperature $T$ is given by the Fermi Dirac distribution

$$f(E_i, T) = \frac{1}{\exp\left(\frac{E_i - E_F}{k_BT}\right) + 1}$$ (1.2)

What is $E_F$?

Plot (Python) $f$ as a function of $E_i - E_F$ for $T_\star = 0$K, 100K, 1000K, 5000K, 10000K. Comment

1.3 Bose-Einstein

The probability for a boson (photon or He for example) to occupy the energy level $E_i$ at temperature $T$ is given by the Fermi Dirac distribution

$$f(E_i, T) = \frac{1}{\exp\left(\frac{E_i - E_F}{k_BT}\right) - 1}$$ (1.3)

- Considering photon in a 3D cavity (one can consider a cube of volume $L^3$),
- taking into account that photon are bosons of energy $h\nu$, (the average energy per "mode" or "quantum" is then $<E> = \frac{h\nu}{\exp\left(\frac{h\nu}{k_BT}\right) - 1}$),
- applying the limit conditions for the electric field at the edge of the cavity
- using the wave equation for $\vec{E}$: $\Box \vec{E} = \vec{0}$ where $\Box$ is the d’Alembert operator

one can derive the number of photon modes allowed in the cavity, then derive the density of modes leading to the spectral energy density in the cavity.

1.4 Planck

The spectral energy density for a black body (isotropic radiation) at temperature $T$ is given by Planck law:

$$B_\nu(T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right) - 1}$$ (1.4)

Units of $B_\nu(T)$?

Express $B_\nu(T)$ for small frequencies (this is the Rayleigh Jeans formulation). What is the "ultraviolet catastroph:?"

Express $B_\nu(T)$ for high frequencies (this is the Wien formulation). From this formulation show that we can find the Stefan law. Give the expression of $\sigma$ and its value. Is it the value you are used to find? why? (hint: $\int \frac{x^{s-1}}{e^x - 1} \, dx = \Gamma(s)\zeta(s)$ where $\Gamma(x)$ and $\zeta(x)$ are respectively the Euler gamma function and the Riemann zeta function and $\zeta(4) = \pi^4/90$
Show that:

\[ B_\lambda(T) = \frac{8\pi\hbar c}{\lambda^5} \frac{1}{\exp\left(\frac{\hbar c}{\lambda k_B T}\right) - 1} \]  

(1.5)

Plot \( B_\nu \) and \( B_\lambda \) for \( T_{sun} = 5700 \text{ K} \) compare and comment. Plot \( B_\lambda \) for \( T = 2.73 \text{K} \). Why this later plot? comment.

Derive the Wien displacement \( \lambda_{max} T = C_{ste} \). Compute the \( C_{ste} \)

1.5 Atomic Units: a. u.

Redo the historic calculation of Bohr for the hydrogen atom (1 proton + 1 electron) starting from: electron is on circular orbit, its charg is \( q_e \), its mass is \( m_e \). \( E = h\nu \), \( E \) is the total electron energy = \( E_c + E_p \), \( ||\vec{L}|| = n\hbar \) (\( \vec{L} \) electron angular momentum )

Show that \( r = r_n \) the possible electron orbital radii and \( r_n = a_0n^2 \) where \( a_0 \) is the Bohr radius. Express this later as a function of \( \alpha \) the fine structure constant \( \alpha = \frac{q_e^2}{4\pi\varepsilon_0\hbar}\). Look for an interpretation of \( \alpha \) Show that \( E_n = E_1/n^2 \). \( E_n \) being the total energy of the electron on orbit of radius \( r_n \). \( E_1 \) is the fundamental level also called the Rydberg constant \( R_y \). Express \( R_y = f(\alpha, m_e, c) \). Give its value in eV Setting \( 4\pi\varepsilon_0 = 1 \) (CGS unit) show

\[ a_0 = \frac{\hbar}{m_e c \alpha}, q_e^2 = \hbar c \alpha, R_y = \frac{m_e^2 c^2}{2} \]

Atomic units provide a complete integrated unit system in the manner of SI units but with quantities scaled to the dimensions of the atom. In atomic units:

Unit of mass is the electron mass, \( m_e = 1.6605402 \times 10^{-27} \text{ kg} = 1 \text{ a.u.} \)

Unit of electric charge is the electron charge, \( e = 1.602188 \times 10^{-19} \text{ C} \), = 1 a. u.

Unit of length, the Bohr radius \( a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e^2} = 5.29177249 \times 10^{-11} \text{m} = 1 \text{ a. u.} \)

Planck constant divided by \( 2\pi \), \( \hbar = 1 \text{ a.u} \times 1.05457 \times 10^{34} \text{ J.s} \)

Similarly \( 4\pi\varepsilon_0 = 1 \). In this unit system, the atomic unit of energy is known as the Hartree and is denoted \( E_h \). \( 1E_h = 2R_\infty = 27.2113661 \text{ eV} = 4.3597482 \times 10^{-18} \text{ J} \), where \( R_\infty \) is the Rydberg constant. The atomic unit of time is \( 2.41884 \times 10^{-17} \text{ s} \) and the speed of light \( c \) is \( 137.03599 \text{ a.u.} \)

1.6 Equation of Schrödinger

1.6.1 Operators

1.6.1.1 Postulates

1. The state of a system with \( n \) position variables \((q_1, q_2, ... q_n)\) is specified by a state (or wave) function \( \Psi((q_1, q_2, ... q_n)) \). All possible information about the system can be derived from this state function. In general, \( n \) is three times the number of particles in the system. So for a single particle \( n = 3 \), and \((q_1, q_2, q_3)\) may be the Cartesian coordinates \((x, y, z)\), or the spherical polar coordinates \((r, \theta, \phi)\), or some other set of coordinates.

2. To every observable there corresponds a Hermitian operator given by the following rules:
a) The operator corresponding to the Cartesian position coordinate $x$ is $x$ similarly for the coordinates $y$ and $z$,

b) The operator corresponding to $p_x$ the $x$ component of linear momentum, is $\frac{\hbar}{i} \frac{\partial}{\partial x}$ similarly for the $y$ and $z$ components.

c) To obtain the operator corresponding to any other observable, first write down the classical expression for the observable in terms of $x$, $y$, $z$, $p_x$, $p_y$, $p_z$ and then replace each of these quantities by its corresponding operator according to rules (a) and (b).

3. The only possible result which can be obtained when a measurement is made of an observable whose operator is $A$ is an eigenvalue of $A$.

4. Let $\alpha$ be an observable whose operator $A$ has a set of eigenfunctions $\phi_j$ with corresponding eigenvalues $a_j$. If a large number of measurements of $\alpha$ are made on a system in the state $\Psi$, then the expectation value of $\alpha$ for the state $\Psi$ (i.e., the arithmetic mean of the eigenvalues obtained) is given by

$$< A > = \int \Psi^* A \Psi d\tau = \langle \Psi | A | \Psi \rangle$$  \hspace{1cm} (1.6)

where $d\tau$ is an element of volume, and the integral is taken over all space (the right expression is the Dirac bra ket formulation).

5. If the result of a measurement of $\alpha$ is $a_r$; corresponding to the eigenfunction $\phi_r$, then the state function immediately after the measurement is $\phi_r$. This means that in general a measurement changes or disturbs the state of a system. The set of measurements referred to in the 4th postulate are all made on the system in the same state $\Psi$. It is in general necessary to manipulate the system after each measurement to return it to the state $\Psi$ before the next measurement is made.

6. The time variation of the state function of a system is given by

$$i\hbar \frac{\partial \Psi}{\partial t} = H \Psi$$ \hspace{1cm} (1.7)

where $H$ is the operator formed from the classical Hamiltonian of the system.

Note: If the classical expression for an observable contains a product $\alpha \beta$ whose operators $A$ and $B$ do not commute, then the operator corresponding to $\alpha \beta$ is $\frac{1}{2}(AB + BA)$. Examples of this are rare.

1.6.1.2 Deduction of the postulates

A. Probability of result of measurement

Discrete eigenvalues Suppose the eigenvalues $a_j$ of $A$ in postulates 4) and 5) are discrete, and that the state function $\Psi$ and all the eigenfunctions $\phi_j$ of $A$ are normalized. To find the probability $p_r$ that the result of a measurement of the observable $\alpha$ is a particular $a_r$ an expand $\Psi$ in terms of the $\phi_j$ is required i.e. put $\Psi = \sum c_j \phi_j$ (or $\Psi = \sum c_j \langle \phi_j |$) then $p_r = |c_r|^2$

The coefficient $c_r$, is obtained from $c_r = \int \phi_r^* \Psi d\tau$ ($c_r = \langle \phi_r | \Psi \rangle$).
If the coefficients \( c_j \) are known, a convenient expression for the expectation value is
\[
\langle A \rangle = \sum_j p_j a_j = \sum_j \langle c_j \rangle^2 a_j
\]

**Continuous eigenvalues** Let \( \gamma \) be an observable whose operator \( G \) has eigenvalues \( k \) which form a continuous spectrum, i.e. any real value \( k \) is a possible result of a measurement of \( \gamma \). For simplicity we give the results for the one-dimensional case for a system consisting of a single particle. Denote the eigenfunctions of \( G \) by \( \phi(k, x) \). The expansion of \( \Psi(x) \) in terms of \( \phi(k, x) \) is not a sum as above, but an integration which we write in the form
\[
\Psi(x) = \int g(k) \phi(k, x) dk
\]
The significance of the function \( g(k) \) is similar to that of the coefficients \( c_j \) in the previous section. Specifically, \( |g(k)|^2 dk \) is equal to the probability that, if the observable \( \gamma \) is measured; the value obtained lies in the range \( k \) to \( k + dk \).

**Linear momentum** An important example of an observable whose operator has continuous eigenvalues is linear momentum. The eigenfunctions of the operator \( p_x \) are \( \phi(k, x) = c \exp(ikx) \), with eigenvalues \( \hbar k \); \( c \) is a constant. For linear momentum we get: \( \Psi(x) = \int_{-\infty}^{+\infty} g(k) \exp(ikx) dk \).

This equation shows that, for linear momentum, \( g(k) \) is proportional to the Fourier transform of \( \Psi(x) \). The function \( g(k) \) is obtained from \( \Psi(x) \) by the relation:
\[
g(k) \propto \int_{-\infty}^{+\infty} \Psi(x) \exp(-ikx) dx
\]
The constant of proportionality is fixed by the requirement that \( |g(k)|^2 dk \) be equal to the probability of finding \( k \) in the range \( k \) to \( k + dk \); and therefore \( \int_{-\infty}^{+\infty} |g(k)|^2 dk = 1 \).

**B. Time variation of state function** Suppose a one-dimensional system has a Hamiltonian \( H \) that does not vary with time. Then, if the state function \( \Psi(0) \) at time \( t = 0 \) is known, the function at a later time \( t \) is given by \( \Psi(t) = \sum_j c_j u_j \exp(-iE_j t/\hbar) \) where \( u_j \) is an eigenfunction of \( H \) with energy \( E_j \), and the coefficients \( c_j \) are given by
\[
c_j = \int_{-\infty}^{+\infty} u_j^* \Psi(0) dx.
\]
The state function and the eigenfunctions are assumed normalised. These results are for discrete energy values. If the eigenvalues \( E_k \) of the Hamiltonian have a continuous spectrum, with corresponding eigenfunctions \( u_k \) the equations become
\[
\Psi(x) = \int_{-\infty}^{+\infty} g(k) u_k \exp(-iE_k t/\hbar) dk, \text{ where } g(k) = \int_{-\infty}^{+\infty} u_k^* \Psi(x, 0) dx
\]

**C. Time variation of expectation value of observable** The time variation of the expectation value of an observable with operator \( A \) for a system in the state \( \Psi \)
\[
\frac{\partial}{\partial t} \langle A \rangle = \frac{1}{i\hbar} \int \Psi^*(AH - HA) \Psi d\tau
\]
The result assumes that the operator \( A \) does not vary with time.

**1.6.1.3 Some Applications**

- For a certain system, the operator corresponding to the physical quantity \( A \) does not commute with the Hamiltonian. It has eigenvalues \( a_1 \) and \( a_2 \), corresponding to eigenfunctions \( \phi_1 = (u_1 + u_2)/\sqrt{2} \) and \( \phi_2 = (u_1 - u_2)/\sqrt{2} \) where \( u_1 \) and \( u_2 \) are eigenfunctions of the Hamiltonian with eigenvalues \( E_1 \) and \( E_2 \). If the system is in the state \( \Psi = \phi_1 \) at time \( t = 0 \), show that the expectation value of \( A \) at time \( t \) is:
\[
\langle A \rangle = \frac{a_1 + a_2}{2} + \frac{a_1 - a_2}{2} \cos \frac{(E_1 - E_2)t}{\hbar}
\]
• The one-dimensional motion of a particle of mass $m$ in a potential $V(x)$ is represented by the state function $\Psi(x,t)$,

1. Prove that the time variations of the expectation values of position and momentum are given by $\frac{d}{dt} <x> = \frac{<p>}{m}$ and $\frac{d}{dt} <p> = -\frac{dV}{dx}$

2. Explain the physical significance of this result known as Ehrenfest’s theorem

• A particle moving in one dimension has a state function

$\Psi(x) = \frac{1}{(2\pi\Delta^2)^{1/4}} \exp\left(-\frac{x^2}{4\Delta^2}\right)$ where $\Delta$ is a constant. Show the following.

(a) The state function is correctly normalized.

(b) The probability that the particle has linear momentum in the range $p$ to $p + dp$ is $P(p) dp$, where $P(p) = \sqrt{\frac{2\Delta}{\pi}} \frac{\Delta}{\hbar} \exp\left(-\frac{2p^2\Delta^2}{\hbar^2}\right)$

(c) The product of the uncertainties in position and momentum has the minimum value allowed by the uncertainty principle.

1.6.2 1D Schrödinger equation

$H = E_c + E_p = \frac{p^2}{2m} + V$ is the hamiltonian (total energy) of the particle.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (1.8)$$

What represents $\int_a^b |\Psi(x,t)|^2$?

1.6.2.1 1D Well

A particle of mass $m$ moves in a one-dimensional potential which is zero in the region $|x| < a$, and infinite outside this region.

(a) Derive expressions for the normalized solutions of the Schrödinger equation and the corresponding energies.

(b) Sketch (plot) the form of the wave functions for the four lowest energies.

(c) What are the parities of the wave functions? [Notation: $k^2 = \frac{2mE}{\hbar^2}$]

1.6.2.2 1D Harmonic Oscillator

For a one-dimensional oscillator of mass $m$ and angular frequency $\omega$, the Hamiltonian can be expressed as

$$H = \frac{1}{2m}(m^2\omega^2x^2 + p^2)$$

where $x$ is the displacement, and $p$ is the momentum. We define operator $a$ and $a^\dagger$ by

$$a = (2m\hbar\omega)^{-\frac{1}{2}}(m\omega x + ip)$$

and

$$a^\dagger = (2m\hbar\omega)^{-\frac{1}{2}}(m\omega x - ip)$$

A. show:
\[ [p, x] = -i\hbar, \]

\[ aa^\dagger = \frac{H}{\hbar \omega} + \frac{1}{2} \quad \text{and} \quad a^\dagger a = \frac{H}{\hbar \omega} - \frac{1}{2} \]

**B.** It can be shown that the eigenvalues of the Hamiltonian are:

\[ E_n = (n + \frac{1}{2})\hbar \omega \]

where \( n \) is an integer positive or null.

If \( u_n \) is a normalized eigenfunction of the Hamiltonian corresponding to the eigenvalue \( E_n \), then

\[ a u_n = \sqrt{n}.u_n - 1 \quad \text{and} \quad a^\dagger u_n = \sqrt{n + 1}.u_n + 1 \]

These relations show that \( a \) and \( a^\dagger \) act as ladder operators. The operator \( a \) is known as an annihilation operator, and \( a^\dagger \) as a creation operator.

Let's show these results. For this purpose we introduce the operator \( N = a^\dagger a \) so that

\[ H = \hbar \omega \left( N + \frac{1}{2} \right) \]

and the eigenvalues of \( H \) are directly linked to the eigenvalues of \( N \).

Show the preliminary and useful results:

1. \([a, a^\dagger] = I \) (identity operator)

2. \( N^\dagger = N \). What do you conclude about the eigenvalues of \( N \)

3. \([N, a] = -a \)

4. \([N, a^\dagger] = a^\dagger \)

5. Let \( \nu \) and \( |\nu\rangle \) be an eigenvalue and an eigen vector of \( N \) Show that \( a |\nu\rangle \) is also an eigen vector of \( N \) with the eigenvalue \( \nu - 1 \) (use \([N, a] = -a\)\)

6. We can then write \( a |\nu\rangle = \alpha |\nu - 1\rangle \) show that \( |\alpha|^2 = \nu \) using \( \alpha^2 = ||a |\nu\rangle||^2 \)

We deduce that:

- The eigenvalues \( \nu \) of \( N \) are \( \geq 0 \);
- if \( \nu = 0 \), then \( a |\bar{0}\rangle = \bar{0} \) and inversely if \( a |\nu\rangle = \bar{0} \) then \( a^\dagger a |\nu\rangle = \bar{0} = N |\nu\rangle \) and hence each state performing this condition is an eigen vector of \( N \) with eigen value \( \nu = 0 \)
- we can choose \( \alpha \) real and then \( \alpha = \sqrt{\nu} \), or : \( a |\nu\rangle = \sqrt{\nu} |\nu - 1\rangle \),
- it can be similarly shown that \( a^\dagger |\nu\rangle = \sqrt{\nu + 1} |\nu + 1\rangle \)

Being given the eigen vector \( |\nu\rangle \) with eigen value \( \nu \) by applying successively \( a \) we generate successive eigen vector of eigen value \( \nu - 1, \nu - 2, \nu - 3, ... \)

**hyp 1)** \( \nu \notin \mathbb{N} \) then for \( \lambda \) big enough we generate an eigen vector with negative eigen value \( (\nu - \lambda < 0) \) not acceptable

**hyp 2)** \( \nu \in \mathbb{N} \) let's say \( \nu = n \) by applying successively \( a \) we generate eigen values and eigen vector \( n - 1, n - 2, ... \)until operator \( a^n \) for which \( N(a^n |n\rangle) = (n - n) |0\rangle = 0 \) but
\[ \langle 0 | N | 0 \rangle = 0 = |a|_0 |^2 \text{ hence } a^{n+1} |0\rangle = 0 \text{ and } a^p |0\rangle = 0 \text{ for } p \geq n + 1 \text{ we do not create negative eigen value by going on applying } a. \]

Finally

\[ E_n = \hbar \omega (n + 1/2) \quad n \in \mathbb{N} \]

C.

Prove the following results for an eigenstate of the Hamiltonian of a one-dimensional harmonic oscillator.

1. The expectation values of the position and momentum are zero
2. The expectation values of the potential and kinetic energies are equal/
3. \( \Delta x \) and \( \Delta p \), the uncertainties in position and momentum, satisfy the relation \( \Delta x \Delta p = (n + \frac{1}{2}) \hbar \), where \( n \) is the quantum number of the state
4. Show that the ground-state eigenfunction \( u_o \) is a Gaussian, and hence that the parity of the state \( n \) is even for even \( n \), and odd for odd \( n \)
2.1 Hydrogenoid atoms

Spectra of atomic hydrogen, $H$, are of paramount astronomical importance. This is because approximately 90% of atomic matter by number is hydrogen. This occurs in a variety of forms: $H^+$ or protons, $H$ atoms, $H_2$ molecules and indeed the molecular ions $H_2^+$ and $H_3^+$. The spectral lines of hydrogen are prominent in a great variety of astronomical objects and are much studied. All aspects of hydrogen spectroscopy therefore need to be considered in detail.

Any atom comprising a single electron orbiting a nucleus of charge $Z$ can be described as hydrogen-like. The Hamiltonian operator for this system is:

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (2.1)$$

where $Z$ is the number of proton in the nucleus, $r$ the position of the electron and $\mu$ the reduced mass since we deal with a two body problem $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{nucleus}} \simeq \frac{1}{m_e}$

Putting $4\pi\epsilon_0 = 1$ the Hamiltonian written as operator becomes:

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \quad (2.2)$$

This equation can be solved analytically in spherical coordinates $\Psi(r, \theta, \phi)$ in splitting the hamiltonian in radial and angular part.

$$H = -\frac{\hbar^2}{2m} (\nabla_r^2 + \nabla_\perp^2) - \frac{Ze^2}{r} \quad (2.3)$$

Recalling that

$$\nabla_r^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$$

and

$$\nabla_\perp^2 = \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Useful Remark :

Let $L^2$ be the angular momentum operator where $\vec{L} = \vec{r} \times \vec{p}$. $L^2$ can be written in spherical coordinates

$$L^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

The demonstration can be done but a little bit long and not mandatory (don’t forget that the vectorial product ‘$\times$’ has a simple definition in cartesian coordinates and you should...
have to start from it before expressing it in spherical coordinates)

With the previous remark we can also write \( \nabla^2 = \nabla_r^2 - \frac{L^2}{\ell^2 r^2} \) We then look for a solution of the form \( \Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \)

Introduce \( \Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \) in equation (2.3) and write the equality between a differential equation in \( r \) and a differential equation in \( \theta \) and \( \phi \). This equality implies that both differential equations are equal to the same constant \( \lambda \) and leads to two separated differential equations. Write the radial and the angular differential equation as a function of \( \lambda \)

2.1.1 Angular Solution

One again we separate variables (\( \theta \) and \( \phi \) in writing \( Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \) Applying the previous principle saying that 2 functions of different variables are equal only if they are equal to the same constant \( \nu \) show that we obtain the two following equations:

\[
\frac{1}{\Theta(\theta) \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left( \lambda - \frac{\nu}{\sin^2 \theta} \right) \Theta(\theta) = 0 \quad (2.4)
\]

\[
\frac{d^2 \Phi(\phi)}{d\phi^2} + \nu \phi = 0 \quad (2.5)
\]

We know (or should easily demonstrate) that \([H, L^2] = [H, L_z] = [L^2, L_z] = 0 \) (resp. for \( L_x \) and \( L_y \)). Hence these different operators can lead to simultaneous measurements or in other words they posse common set of eigen functions. Equation (2.5) is easily solvable and leads to \( \phi \propto \exp(-im\phi) \) (where \( m^2 = \nu \)). Being given that when \( \phi \) advance by \( 2\pi \) we return to the same point in space so it’s natural to require that \( \Phi(\phi) = \Phi(\phi + 2\pi) \) and hence \( m \) is an integer \( m = 0, \pm 1, \pm 2, \ldots \)

From equation (2.5) show that the operator \( L_z = -i\hbar \frac{\partial}{\partial \phi} \) (in spherical coordinates) has the same eigen functions and hence that the eigen value of \( L_z \) are discrete. Give their value

In equation (2.4) do the variable change \( \omega = \cos \theta \) and show this equation becomes

\[
\frac{\partial}{\partial \omega} \left( (1 - \omega^2) \frac{\partial \Theta(\omega)}{\partial \omega} \right) + \left( \lambda - \frac{m^2}{1 - \omega^2} \right) \Theta(\omega) = 0 \quad (2.6)
\]

Taking into account the ”Usefull remark”, \([L^2, L_z] = 0 \) and the \( m \) eigen values of \( \Phi(\phi) \) (and in introducing two additional operator \( L_+ = L_x + iL_y \) and \( L_- = L_x - iL_y \) which have the same role as creator and annihilator operator in the harmonic oscillator problem) it can be shown that the eigen value of \( L^2 \) are \( l(l+1)\hbar^2 \) where \( l = N/2 \) (\( N \) is an integer) and hence \( l \) can be either integer or half integer. We can the re-write eq (2.6) as follows.

\[
\frac{\partial}{\partial \omega} \left( (1 - \omega^2) \frac{\partial \Theta(\omega)}{\partial \omega} \right) + \left( l(l+1) - \frac{m^2}{1 - \omega^2} \right) \Theta(\omega) = 0 \quad (2.7)
\]

Hence \( \Theta(\theta) = \Theta_{l,m}(\theta) \) We recall \( H \psi = E \psi, L^2 \psi = \hbar^2 l(l+1) \psi \) and \( L_z \psi = m \hbar \psi \) (be aware \( m \) here is NOT the mass). Solutions of equation (2.6) are Legendre function defined by

\[
P_l^m(\omega) = (1 - \omega^2) \frac{d^{|m|}}{d\omega^{|m|}} P_l(\omega) \quad (2.8)
\]
where \( P_l(x) \) is the \( l \)th Legendre polynomial defined by

\[
P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l
\]  

(2.9)

Give expression and plot of the 6 first Legendre polynomials.

Give the expressions of the Legendre functions \( P_2^0(x) \), \( P_2^1(x) \), \( P_2^2(x) \).

Since \( x = \cos \theta \), give the expression and plot (in polar representation):

\( P_0^0(\theta), P_1^0(\theta), P_1^1(\theta), P_2^0(\theta), P_2^1(\theta), P_2^2(\theta), P_2^3(\theta), P_3^0(\theta), P_3^1(\theta), P_3^2(\theta), P_3^3(\theta) \)

Hence \( \Theta(\theta) = AP_l^m(\cos \theta) \) and

\[
Y(\theta, \phi) = Y_l^m(\theta, \phi) = Ae^{im\phi} P_l^m(\cos \theta)
\]  

(2.10)

where \( A \) is obtained by normalisation

\[
\int_0^{2\pi} \int_0^\pi |Y|^2 \sin \theta d\theta d\phi = 1
\]

\[
Y(\theta, \phi) = Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l - 1)(l - |m|)!}{4\pi}} \frac{1}{(l + |m|)!} e^{im\phi} P_l^m(\cos \theta)
\]  

(2.11)

\( \epsilon = 1 \) for \( m < 0 \) and \( \epsilon = (-1)^m \) for \( m > 0 \)

\( Y_l^m \) are the spherical harmonics and we have \( \langle Y_l^m | Y_{l'}^{m'} \rangle = \delta_{ll'} \delta_{mm'} \)

### 2.1.2 Radial Solution

From equation (2.2) and considering \( \nabla^2 = \nabla_r^2 \) and \( \frac{L^2}{\hbar^2 r^2} \), make the change of variable \( u(r) = rR(r) \) and how that leads to the 1D Schrödinger equation for \( u(r) \) with an effective potential

\[
V_{\text{eff}} = V(r) + \frac{\hbar^2 l(1 + l)}{2m r^2}
\]

The additional term is called centripetal term

The normalisation leads to: \( \int_0^\infty |R|^2 r^2 dr = \int_0^\infty |u|^2 dr = 1 \)

Exercise:

Consider \( V(r) = 0 \) if \( r \leq a \) and \( V(r) = \infty \) if \( r > a \). Find the wave function and the allowed energy for the easy case \( l = 0 \)

From the above exercise it appears that the energy depends on two integers \( E_{n,l} \) and the wave function of three integers \( \Psi_{n,l,m}(r, \theta, \phi) \)

For an arbitrary \( l \) things become more difficult and

\[
u(r) = Ar_{jl}(kr) + Br_{nl}(kr)\text{ where } k = \frac{\sqrt{2mE}}{\hbar} \text{ (take care } m \text{ is the mass)}.
\]

\[
j_l(x) = (-x)^l \left( \frac{d}{dx} \right)^l \frac{\sin x}{x} \text{ are the spherical Bessel functions and}
\]

\[
n_l(x) = -(x)^l \left( \frac{d}{dx} \right)^l \frac{\cos x}{x} \text{ are the spherical Neumann functions}
\]

Express \( j_l \) and \( n_l \) for \( l = 0, 1, 2 \). Give their expression for \( x << 1 \).

Since \( n_l \) blow up at the origin \( B = 0 \) and then \( R(r) = Aj_l(kr) \). The condition \( R(a) = 0 \) is still valid. The zeros of \( j_l(kr) \) have to be computed numerically and we can write

\[
E_{nl} = \frac{\hbar^2}{2ma^2} \beta^2_{nl} \text{ where } \beta_{nl} \text{ is the } n^{th} \text{ zero of } l^{th} \text{ spherical Bessel function. Finally the wave function is}
\]
\[ \Psi_{nlm}(r, \theta, \phi) = A_{nl}j_l(\beta_{nl}r/a)Y_l^m(\theta, \phi). \]
\( A_{nl} \) is determined by normalization.

Exercise Hydrogen atom: Consider the case \( Z = 1 \). Let be \( \kappa = \frac{\sqrt{-2mE}}{\hbar} \) (for bound state \( E < 0 \) and \( \kappa \) is real), \( \rho = \kappa r, \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}. \) Show that the differential equation for \( u(r) \) can be written
\[
\frac{d^2u}{d\rho^2} = \left[ 1 - \frac{\rho}{\rho_0} + \frac{l(l+1)}{\rho^2} \right] u. \]
For \( \rho \to \infty \) show that \( u(\rho) \sim Ae^{-\rho} \) and verify that for \( \rho \to 0, u(\rho) = C\rho^{j+1} + D\rho^{-l} \) is solution. Necessarily \( D = 0. \) Justify. Hence \( u(\rho) \sim C\rho^{j+1} \) for small \( \rho. \)

We are so going to search a solution in the form \( u(\rho) = \rho^{j+1}e^{-\rho}v(\rho). \) Show that \( v(\rho) \) verifies:
\[
\rho \frac{d^2v}{d\rho^2} + 2(l + 1 - \rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0
\]
We assume \( v(\rho) \) can be expressed by \( v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j. \) Show that we obtain the following recursive relation:
\[
c_{j+1} = \frac{2(j + l + 1) - \rho_0}{(j + 1)(j + 2l + 2)} c_j
\]
\( c_0 \) can be obtained by normalisation and \( c_1 \) is given by the above relation, the \( c_2... \) etc..

For large values of \( j \) (which means large \( \rho \)) show that the recursive relation can be written
\[
c_{j+1} = \frac{2j}{j+1}c_j \text{ (why do we keep 1 at the numerator and not neglect it compare to } j?)
\] and hence \( c_j = \frac{2^j}{j!}c_0. \) Deduce that (considering this approximation is ok) that \( u(\rho) = c_0\rho^{j+1}e^\rho. \)

This expression blows up for large \( \rho \) except if it exists a \( j_{max} \) so that \( c_{j_{max}+1} = 0. \) Show that \( \rho_0 = 2n \) where \( n = j_{max} + l + 1. \) \( n \) is the principal quantum number. Deduce that
\[
E_n = -\frac{m}{2\hbar^2}\left(\frac{\epsilon^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} \frac{E_1}{n^2}. \]
This is the famous Bohr formula. Give the numerical value of \( E_1. \) Show that \( \kappa = \frac{1}{an} \) where \( a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \) is the so called Bohr radius. Give its numerical value. It follows that \( \rho = \frac{\rho}{an} \) and \( \Psi_{nlm} = R_{nl}Y_l^m(\theta, \phi) = \frac{1}{r}\rho^{j+1}e^{-\rho}v(\rho)Y_l^m(\theta, \phi). \) Give the expression of the fundamental state wave function \( \Psi_{100}. \) How many wave function are associated to the first excited level \( n = 2. \)

For an arbitrary level \( n \) the possible values for \( l \) are \( l = 0, 1, 2, \ldots, n-1 \) and for each \( l \) there are \( 2l + 1 \) possible values for \( m = -l, -l + 1, \ldots, l - 1, l, \)
the degree of degeneracy for each level \( n \) is then \( d(n) = \sum_{l=0}^{n-1} = n^2 \)

The polynomial \( v(\rho) \) can be written \( v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \) where
\[
L_q^p(x) = (-1)^p \frac{d^p}{dx^p}L_q(x) \text{ is the associated Laguerre polynomial of order } p
\]
and
\[
L_q(x) \text{ is the } q^{th} \text{ Laguerre polynomial: } L_q(x) = e^x \frac{d^q}{dx^q}(e^{-x}x^q)
\]

Finally the normalised wave function for the hydrogen atom are
\[
\Psi_{nlm} = \sqrt{\frac{2}{na}}^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} e^{-r/na} \left( \frac{2r}{na} \right)^l \left[ L_{n-l-1}^{2l+1}(2r/na) \right] Y_l^m(\theta, \phi) \quad (2.12)
\]
Compute $L_0$, $L_1$, $L_2$, and $L_1^0$, $L_1^1$, $L_1^2$

The wave functions are mutually orthogonal:

$$\int \Psi_{nlm}^* \Psi_{n'l'm'} r^2 \sin \theta dr d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

Keep in mind that we have made the approximation $\mu \simeq m_e$ for the reduce mass. If we do not make this approximation we have to consider two equations: one for the center of mass with $M = m_n + m_e$ and one for a fictive particle of mass $\mu$ around the center of mass.

### 2.1.3 Spectrum of Hydrogen

A transition between level $i$ and $f$ leads to: $E_i - E_f = -E_1(\frac{1}{n_i^2} - \frac{1}{n_f^2})$ and occurs by an absorption or the emission of a radiation at a wavelength $\lambda$ with $\frac{1}{\lambda} = R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$ where $R$ is the Rydberg Constant. Give the expression and the value of $R$

- $n_f = 1$ is the Lyman (Ly) series and occurs in ultraviolet
- $n_f = 2$ is the Balmer (H) series in visible
- $n_f = 3$ is the Paschen (P) series in infra red
- $n_f = 3$ is the Bracket (Br) series in infra red
- $n_f = 3$ is the Pfund (Pf) series in infra red

if $\Delta n = 1$ we use the greek letter $\alpha$
if $\Delta n = 2$ we use the greek letter $\beta$
if $\Delta n = 3$ we use the greek letter $\gamma$
if $\Delta n = 4$ we use the greek letter $\delta$ ... All hydrogen series transitions between bound states are described as boundbound transitions

For hydrogenoid ($Z > 1$) determine the Bohr radius $a(Z)$, binding energy $E_1(Z)$, Rydberg constant $R(Z)$ What is the spectral domain of the Lyman series for $Z = 2$ and $Z = 3$

Note if we do not make the $\mu \simeq m_e$ approximation we should make $R \rightarrow R_H = \frac{\mu}{m_e} R$

and for Deuterium for example $R \rightarrow R_D = \frac{\mu_D}{\mu_H} R$

## 2.2 L-S coupling: Atomic Notation

In classical mechanics we define an orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ (rotation around the center of mass) and a spin $\vec{S} = I\omega$ (proper rotation). In Q mechs we have seen the angular momentum operator and we know that particle have an intrinsic spin. Describe the Stern-Gelarch experiment qualitatively and quantitatively. In the frame of mathematical
formulation the intrinsic spin $S$ is a carbon copy of the extrinsic angular momentum $L$ BUT the eigen state of the spin are NOT described by function of $\theta$, $\phi$ (as the $Y_l^m(\theta, \phi)$ for the orbital angular momentum). Nevertheless the eigen state as for $L$ is described by two quantum numbers $s$ and $m_s$ and we have the known algebra (as for $L$): $[S_x, S_y] = i\hbar S_z$, $[S_y, S_z] = i\hbar S_x$, $[S_z, S_x] = i\hbar S_y$ and the eigen values for the eigen states $|s m_s\rangle$ are:

$$S^2 |s m_s\rangle = \hbar^2 s(s + 1) |s m_s\rangle \quad \text{and} \quad S_z |s m_s\rangle = \hbar m_s |s m_s\rangle$$

$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ and $m_s = -s, -s + 1, \ldots s - 1, s$

pi meson have spin $s = 0$, proton, electron, neutron, quarks, (leptons) $s = 1/2$, photon $s = 1$, graviton $s = 2$.

Exercise Pauli spin matrices

Let’s consider $s = 1/2$. There a two eigen states $|\frac{1}{2}, \frac{1}{2}\rangle$ corresponding to spin up $\uparrow$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ i.e spin down $\downarrow$. The general state $\chi$ of a particle of spin $\frac{1}{2}$ can be expressed as a two column matrix (spinor): $\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-$ where $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Show that the spin operator $S^2$ is a 2x2 matrix and $S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $S_z$ is a 2x2 matrix $S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. Introducing the operators $S_+$ and $S_-$ by $S_\pm |s m_s\rangle = \hbar \sqrt{s(s + 1) - m(m \pm 1)} |s (m_s \pm 1)\rangle$ (analog to the operator creator and annihilator already seen) show that $S_x = \frac{\hbar}{2}\sigma_x, S_y = \frac{\hbar}{2}\sigma_y$ and $S_z = \frac{\hbar}{2}\sigma_z$ where $\sigma_x, \sigma_y, \sigma_z$ are the Pauli spin matrices $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ and $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

2.2.1 Notation L-S

In Q mechs, a particle is characterized by four parameters : the four quantum numbers $n, l, m$ and $s$.

- $n$ is the principal quantum number and represents the number of the electronic layer.

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>layer</td>
<td>K</td>
<td>L</td>
<td>M</td>
<td>N</td>
<td>O</td>
<td>P</td>
<td>Q</td>
</tr>
</tbody>
</table>

- $l$ the secondary quantum number represents the orbital angular momentum varies from 0 to $n - 1$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbital</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
<td>g</td>
</tr>
</tbody>
</table>

if we deal with serval particles the total angular momentum is $L = \sum_{i=1}^{N} l_i$ (orbit-orbit coupling)

- $m$ is the magnetic quantum number $m = -l, -l + 1, \ldots, l - 1, l$ givesinfo on the orbital shape.
if we deal with serval particles the total magnetic number is

\[ M = \sum_{i=1}^{N} m_i \]

\* s is the spin

if we deal with serval particles the total spin is

\[ S = \sum_{i=1}^{N} s_i \] (spin-spin coupling).

The LS notation or Russel Saunders notation is \( ^{2S+1}L^\Pi \) (L-S coupling), \( L \) is the total angular momentum and represented by a letter

\[ L = 0 \rightarrow S, L = 1 \rightarrow P, L = 2 \rightarrow D \ldots \]

and \( S \) is the total spin. \( \Pi \) is the parity : if \((-1)^L = 1\) then \( \Pi \) can be omitted if \((-1)^L = -1\) then \( \Pi = 0 \)

Exemple: Fluor : \( 1s^22s^22p^5 \): \( L = 1 \rightarrow P, S = \frac{1}{2} \) (dont forget the Pauli exclusion hence electron on the same orbital have opposite spins \( 2S + 1 = 2 \), \( \Pi = 0 \) hence the ground state of Fluor in L-S notation is \( ^2P \).

Show by direct evaluation that the configurations \( np^2 \) and \( np^4 \) give the same L-S term

List all possible combinations of \((m,s)\) for three equivalent electrons in a \( d \) open subshell

In heavier atoms, \( Z > 18 \), the electron nucleus force becomes strong enough to cause the breakdown of the LS coupling scheme. The velocity of an electron increases to relativistic level, its electrostatic interaction with other electrons weakens, and the total angular momentum of individual electrons needs to be considered. \( j \) is the sum of the individual total electron angular and spin momenta \( j_i = l_i + s_i \).

The LSJ notation \( ^{2S+1}L^\Pi J \).

\[ J = \sum_{i=1}^{N} j_i \] is the total angular momentum of all electrons in the atom with multiplicity or degeneracy \( 2J + 1 \). For two electrons, the values of \( J \) range from \(|j_1 + j_2|\) to \(|j_1 - j_2|\).

Express the Hund’s rules
Three Perturbations

Seen in classroom

3.1 Independent Time Perturbations
3.2 Dependant Time Perturbations
3.3 Fine Structure of H-like atoms
3.4 Variational Methods
4.1 Maxwell equations

We recall
\[ \vec{E} = -\nabla \phi - \frac{\partial \vec{A}}{\partial t} \]  
\[ \vec{B} = \nabla \times \vec{A} \]  
\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \]  
\[ \nabla \cdot \vec{B} = 0 \]  
\[ \nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0} \]  
\[ \nabla \cdot \vec{A} + \frac{1}{c^2} \frac{\partial \phi}{\partial t} = 0 \]

or
\[ \nabla \cdot \vec{A} = 0 \]

The two last equations are respectively the Lorentz and Coulomb gauges. It comes from the fact that \( \vec{A} \) and \( \phi \) can be replaced by \( \vec{A}' = \vec{A} + \nabla \chi \) and \( \phi' = \phi - \frac{\partial \chi}{\partial t} \) without changing Maxwell equations so there is a degree of freedom for the choice of \( \vec{A} \) and \( \phi \). The Lorentz gauge leads to \( \vec{A} \) and \( \phi \) follow the d'ALEMBERT equation and the Coulomb gauge to the Poisson equation. Show that \( \vec{A} \) and \( \phi \) should be solutions of d’ALEMBERT equation. Solve it.

Let consider the plane wave solution of the d Alembert equation
\[ \vec{A}(\vec{r}, t) = A_0(\omega) \hat{\epsilon} \cos (\vec{k}.\vec{r} - \omega t + \delta_\omega) \]

Show \( \vec{E}(\vec{r}, t) = E_0(\omega) \sin (\vec{k}.\vec{r} - \omega t + \delta_\omega) \hat{\epsilon} \) and
\( \vec{B}(\vec{r}, t) = B_0(\omega) \cos (\vec{k}.\vec{r} - \omega t + \delta_\omega) \hat{\epsilon} \times \vec{k} \). Express \( E_0 \) and \( B_0 \) as a function of \( A_0 \). \( \hat{\epsilon} \) give the direction of the linear polarisation. An arbitrary polarisation can be seen as superimposition of linear polarisations so we limit our study to linear polarisation.

The density energy is \( \epsilon_0 |E|^2 + \frac{1}{\mu_0} |B|^2 = \epsilon_0 E_0^2 \sin^2 (\vec{k}.\vec{r} - \omega t + \delta_\omega) \).

Averaging over a period \( T \) the energy density becomes \( \rho(\omega) = \frac{1}{2} \epsilon_0 E_0^2 \).
If \( N(\omega) \) is the number of photon at angular frequency \( \omega \) we can connect the classical
electric field and the Q mechs: $E_0 = \sqrt{2N(\omega)\hbar\omega/(\epsilon_0 V)}$ where $V$ is a given volume. The intensity is $I(\omega) = \rho(\omega)c$ (energy by unit of time crossing a unit surface).

Keep in mind that a radiation is never monochromatic (wave packet on a spectral band $\Delta\omega$) hence

$$\vec{A}(\vec{r}, t) = \hat{e} \int_{\Delta\omega} [A_0(\omega)e^{i\vec{k}\cdot\vec{r}-\omega t+\delta\omega} + cc]d\omega$$

$$\rho = \int_{\Delta\omega} \rho(\omega)d\omega$$

$$I = \int_{\Delta\omega} I(\omega)d\omega$$

### 4.2 Charged particle and radiation

The Hamiltonian is for a spinless particle of mass $m$ charge $q$ moving in an electromagnetic field described by a vector potential $\vec{A}(\vec{r}, t)$ and a scalar potential $\phi$:

$$H = \frac{1}{2m}(\vec{p}-q\vec{A})^2 + q\phi$$

Using Coulomb Gauge, show that the Schrödinger equation is:

$$i\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + i\hbar\frac{q}{m}\vec{A}\cdot\nabla + \frac{e^2}{\mu}\vec{A}^2\right]\Psi(\vec{r}, t).$$

Let’s consider the interaction of an electromagnetic field with 1 electron atom with a nucleus of charge $Ze$ nd mass $M$ and 1 electron of charge $-e$ and mass $m$. Since $M \gg m$ we can neglect the interaction nucleus electromagnetic field. We must consider the Coulombian field $-\frac{Ze^2}{4\pi\epsilon_0 r}$

$$i\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \left[H_0 - i\hbar\frac{e}{\mu}\vec{A}\cdot\nabla + \frac{e^2}{2\mu}\vec{A}^2\right]\Psi(\vec{r}, t)$$

where $H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$ and $\mu = \frac{Mm}{m+M}$ is the reduced mass. We consider the weak field approximation hence the term $\vec{A}^2$ is neglected. Thus we will treat the linear term as a small perturbation. That means that in term of photon we will consider only absorption and spontaneous emission of one photon at a time. The simultaneous emission or absorption of two or more photons is negligible for weak field. This is not the case for strong field (simulated emission). Hence in the approximation of weak field the Hamiltonian becomes:

$$H = H_0 + H'$$

with $H' = -i\frac{\hbar e}{\mu}\vec{A}\cdot\nabla$ (note that we can also approximate $\mu = m$) and the Schrödinger equation becomes $i\frac{\partial}{\partial t}\Psi(\vec{r}, t) = [H_0 + H']\Psi(\vec{r}, t)$

### 4.3 Rayleigh Schrödinger perturbation Theory

This is an application of the time dependent perturbation applied to the interaction with radiation
4.3.1 Time dependent perturbation

Let’s consider an Hamiltonian of the form \( H = H_0 + \lambda H'(t) \) \( H_0 \) is the unperturbed Hamiltonian and \( H' \) is a time dependent perturbation, \( \lambda \) can be taken equal 1 and is here for convenience to identify the different order of perturbation. Let’s put \( E_k^{(0)} \) the eigen values of \( H_0 \) with the corresponding eigen function \( \Psi_k^{(0)} \). \( H_0 \Psi_k^{(0)} = E_k^{(0)} \Psi_k^{(0)} \). The general solution of the time dependent unperturbed Schrödinger equation \( i \frac{\partial}{\partial t} \Psi_0 = H_0 \Psi_0 \) is given by:

\[
\Psi_0 = \sum_k c_k^{(0)} \Psi_k^{(0)} e^{-iE_k^{(0)} t/\hbar}. \]

Since \( H(t) \) it is meaningless to look for correction to the energy eigen values (the energy is not conserved). We rather seek for \( \Psi = \sum_k c_k(t) \Psi_k^{(0)} e^{-iE_k^{(0)} t/\hbar} \) where \( c_k(t) \) are the unknown coefficients. We recall that \( |c_k(t)|^2 = |\langle \Psi_k^{(0)} | \Psi(t) \rangle|^2 \) is the probability to find the system in the unperturbed state \( \Psi_k^{(0)} \) at time \( t \). Then

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \Psi = H \Psi \quad (4.8)
\]

Replace \( \Psi \) in eq. (4.8) in which we will note \( \frac{\partial c_k}{\partial t} = \dot{c}_k \). Let’s consider the scalar product of each member of this equation with \( \Psi_b^{(0)} \in \{ \Psi_k \} \). Show that :

\[
\dot{c}_b = \frac{1}{i\hbar} \lambda \sum_k H'_{bk}(t) e^{i\omega_{bk} t} c_k(t) \quad (4.9)
\]

where \( H'_{bk}(t) = \langle \Psi_b^{(0)} | H'(t) | \Psi_k^{(0)} \rangle \) is a matrix element and \( \omega_{bk} = \frac{E_b^{(0)} - E_k^{(0)}}{\hbar} \) is the Bohr angular frequency.

The set of eq (4.9) for all \( b \) is a set of coupled first order differential equations strictly equivalent to eq (4.8). Now make the assumption \( \lambda H' \) is weak we can the expand the coefficient \( c_k \) in power of \( \lambda : c_k = c_k^{(0)} + \lambda c_k^{(1)} + \lambda^2 c_k^{(2)} + \ldots \). \( c_k^{(0)} \) is the stationary term and \( c_k^{(n)} \) is the correction of order \( n \). Show that \( \dot{c}_b^{(0)} = 0 \) and \( \dot{c}_b^{(s+1)} = \frac{1}{i\hbar} \sum_k H'_{bk}(t) e^{i\omega_{bk} t} c_k^{(s)} \) for \( s = 0, 1, 2 \ldots \)

If we assume that before the perturbation is applied \( t \leq t_0 \) the system is in a particular unperturbed state \( \Psi_a^{(0)} \) with energy \( E_a^{(0)} \). Hence \( c_k^{(0)} = \delta_{ka} \) then

\[
\dot{c}_b^{(1)} = \frac{1}{i\hbar} H'_{ba}(t) e^{i\omega_{ba} t} \quad \text{where} \quad \omega_{ba} = \frac{E_b^{(0)} - E_a^{(0)}}{\hbar}. \]

It comes easily that

\[
\dot{c}_a^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} H'_{aa}(t') dt' \quad \text{and}
\]

\[
\dot{c}_b^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} H'_{ba}(t') e^{i\omega_{ba} t'} dt' \quad \text{(the integration constant is chosen so that} \ c_a^{(1)}(t) \text{) and} \ c_b^{(1)}(t) \text{) vanish when} \ t \rightarrow t_0). \]

At the first order the probability of transition \( a \rightarrow b \) (from state \( a \) to state \( b \) at time \( t \)) is:

\[
P_{ab}^{(1)}(t) = |c_b^{(1)}(t)|^2 = \frac{1}{\hbar^2} \left| \int_{t_0}^{t} H'_{ba}(t') e^{i\omega_{ba} t'} dt' \right|^2. \]
Note that at the first order for \( t > t_0 \):
\[
c_a(t) \simeq c_a^{(0)}(t) + c_a^{(1)}(t) \simeq 1 + \frac{1}{\hbar} \int_{t_0}^{t} H'_{aa}(t')dt' \simeq \exp \left[ -\frac{i}{\hbar} \int_{t_0}^{t} H'_{aa}(t')dt' \right]
\]
\[|c_a(t)|^2 \simeq 1 \] and the principal effect of the perturbation on the initial state is a phase change.

4.3.2 Application to the interaction with radiation

Let’s apply the previous time dependent perturbation to weak field interaction. We consider \( \lambda = 1 \) and \( H' = -\frac{\hbar c}{\mu} \vec{A} \vec{\nabla} \). Let’s consider for sake of simplicity in the writing a monochromatic radiation
\[
\vec{A}(\vec{r}, t) = \hat{\varepsilon}[A_0(\omega)e^{i(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega)} + cc]
\]
and let be \( t_0 = 0 \) and \( \mu \approx m \). Applying the above results it comes :
\[
H'_{ba}(t) = -\frac{i\hbar c}{m} \langle \Psi_b | \vec{A} \vec{\nabla} | \Psi_a \rangle
\]
\[
c_b^{(1)} = -\frac{e}{m} A_0(\omega)e^{i\delta_\omega} \left[ \langle \Psi_b | e^{i\vec{k}\cdot\vec{r}'} \vec{\nabla} | \Psi_a \rangle \int_{0}^{t} e^{i(w_{ba} - \omega)t'} dt' + \langle \Psi_b | e^{-i\vec{k}\cdot\vec{r}'} \vec{\nabla} | \Psi_a \rangle \int_{0}^{t} e^{i(w_{ba} + \omega)t'} dt' \right]
\]

In this expression let’s consider the two integrals \( I_1 = \int_{0}^{t} e^{i(w_{ba} - \omega)t'} dt' \) and \( I_2 = \int_{0}^{t} e^{i(w_{ba} + \omega)t'} dt' \).

Typically \( |w_{ba}| \) is of order \( 10^{12} \) to \( 10^{14} \ s^{-1} \) for transition in IR and even larger in visible.

Hence \( I_1 \) and \( I_2 \) are negligible except if \( w_{ba} \approx \omega \) for \( I_1 \) or \( w_{ba} \approx -\omega \) for \( I_2 \). Since both condition cannot fulfilled simultaneously we can deal with the two terms separately. \( I_1 \) leads to \( E_b = E_a + \hbar \omega \) and corresponds to absorption and \( I_2 \) leads to \( E_b = E_a - \hbar \omega \) and corresponds to emission.

Let’s come back to the fact that a radiation is never monochromatic and is rather a wave packet defined on bandwidth \( \Delta \omega \). This leads to modify :
\[
\vec{A} \to \vec{A} = \hat{\varepsilon} \int_{-\Delta \omega}^{+\Delta \omega} [A_0(\omega)e^{i(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega)} + cc] d\omega
\]

we will then rewrite
\[
c_b^{(1)} = -\frac{e}{m} \int_{-\Delta \omega}^{+\Delta \omega} d\omega A_0(\omega)e^{i\delta_\omega} \left[ \langle \Psi_b | e^{i\vec{k}\cdot\vec{r}'} \vec{\nabla} | \Psi_a \rangle \int_{0}^{t} e^{i(w_{ba} - \omega)t'} dt' + \langle \Psi_b | e^{-i\vec{k}\cdot\vec{r}'} \vec{\nabla} | \Psi_a \rangle \int_{0}^{t} e^{i(w_{ba} + \omega)t'} dt' \right]
\]

4.3.2.1 Absorption

Show that in the case of Absorption we can write the probability to jump from the state \( a \) to the state \( b \) as follows:
\[
|c_b^{(1)}|^2 = 2 \left( \frac{e}{m} \right)^2 |M_{ba}|^2 \int_{-\Delta \omega}^{+\Delta \omega} A_0(\omega) F(t, \overline{\omega}) d\omega
\]

where \( M_{ba} = \langle \Psi_b | e^{i\vec{k}\cdot\vec{r}'} \vec{\nabla} | \Psi_a \rangle \), \( \overline{\omega} = \omega_{ab} - \omega \) and \( F(t, \overline{\omega}) = \frac{1 - \cos \overline{\omega}t}{\overline{\omega}^2} \). Plot this function for different smaller and smaller value of \( \overline{\omega} \). From this plots deduce that when \( \overline{\omega} \to 0 \) (i.e
\( \omega_{ab} \sim \omega \) then \( \int_{\Delta \omega} F(t, \omega) d\omega \to \pi t \delta(\omega) \). Here \( \delta(\omega) \) is the Dirac distribution.

Deduce that \( |c_b^{(1)}|^2 = 2\pi \left( \frac{eA_0(\omega_{ab})}{m} \right)^2 |M_{ba}|^2 t \)

Express the transition rate \( W_{ba} \) defined by \( W_{ba} = \frac{d}{dt} |c_b^{(1)}|^2 \). Introducing the intensity \( I(\omega) = \frac{1}{2} \epsilon_0 c \omega^2 A_0^2(\omega) \) then \( W_{ba} = 4\pi \left( \frac{e}{m} \right)^2 I(\omega_{ab}) |M_{ba}|^2 \)

We can write \( W_{ba} = \sigma_{ab} I(\omega_{ab}) \) where \( \sigma_{ab} \) is the absorption cross section. Compute the dimension of \( \sigma_{ab} \).

### 4.3.2.2 Stimulated Emission

The term stimulated is to be understood as due to the interaction with a radiation.

Let \( \dot{W}_{ba} \) be the rate of the transition rate for emission (you will exchange the states \( a \) and \( b \) in order to keep the same notation) and \( \sigma_{ab} \)

Show \( \dot{W}_{ba} = W_{ba} \) and \( \sigma_{ba} = \sigma_{ba} \)

### 4.3.2.3 Spontaneous Emission

see section Einstein Coefficients

### 4.3.3 Dipole Approximation

When the wavelength of the electric field is large compare to atom size we can consider it as constant over the atom. In this framework we can put \( e^{i\hat{\epsilon}\vec{r}} \simeq 1 \). Moreover we can introduce \( \vec{D} = e\vec{r} \) the electric dipole of one electron of the atom. We can rewrite the above expression as :

\[
c_b^{(1)} = \frac{1}{m} A_0(\omega) e^{i\omega_0} \left[ \langle \Psi_b | \hat{\epsilon} \vec{\nabla} | \Psi_a \rangle \int_0^t e^{i(w_{ba} - \omega)t'} dt' + \langle \Psi_b | \hat{\epsilon} \vec{\nabla} | \Psi_a \rangle \int_0^t e^{i(w_{ba} + \omega)t'} dt' \right]
\]

Show that \( M_{ba} = \frac{im}{\hbar} \langle \Psi_b | \hat{\epsilon} \vec{r} | \Psi_a \rangle \hat{\epsilon} \). Being given the Schrödinger equation \( H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \) show that for a given operator \( X \) we have :

\[
\frac{dX}{dt} = \frac{\partial X}{\partial t} + \frac{1}{i\hbar} [X, H].
\]

Use this general result to show :

\( M_{ba} = -\frac{m \omega_{ba}}{\hbar} \langle \Psi_b | \vec{r} | \Psi_a \rangle \hat{\epsilon} \)

Writing \( \vec{r}_{ab} = \langle \Psi_b | \vec{r} | \Psi_a \rangle \), show that we can write \( W_{ba} = \frac{\pi}{\epsilon \hbar^2 \epsilon_0} I(\omega_{ba}) |\hat{\epsilon} \vec{D}_{ba}|^2 \)

where \( \vec{D}_{ba} = -e\vec{r}_{ba} \) is the electric dipole momentum

Note :

- If \( \hat{\epsilon} \vec{D}_{ba} = 0 \) (\( \hat{\epsilon} \perp \vec{r}_{ab} \)) the transition is prohibited

- We have \( |\hat{\epsilon} \vec{D}_{ba}|^2 = \cos^2 \theta |\vec{D}_{ba}|^2 \) where \( \theta \) is the angle between \( \hat{\epsilon} \) and \( \vec{D}_{ba} \). If the radiation is unpolarized and isotropic the direction of \( \hat{\epsilon} \) is at random and we can
replace $\cos^2 \theta$ by its mean value in the space i.e. by $\int \cos^2 \theta \frac{d\Omega}{4\pi} = \frac{1}{3}$ and hence

$$W_{ba} = \frac{\pi}{3 \epsilon_0 c} I(\omega_{ba}) |\vec{D}_{ba}|^2$$

- If we consider some higher order in the expansion of $e^{i\vec{k}.\vec{r}}$ we can consider the term $i\vec{k}.\vec{r}$ which corresponds to the so-called magnetic moment dipole term and the term $-\frac{(\vec{k}.\vec{r})^2}{2}$ called the electric quadrupole.

### 4.4 Einstein Coefficients

Let’s consider a finite volume $V$ containing single kind atoms and radiations in thermal equilibrium a temperature $T$. Let $a$ and $b$ be two non degenerated atomic states of energy $E_a < E_b$, $N_a$ the number of atoms in state $a$. The number of atoms making the transition from state $a$ to $b$ ($a \rightarrow b$) by unit of time, $\dot{N}_{ba}$, by absorbing a photon of energy $\hbar \omega_{ab}$ is proportional to $N_a$ and to the energy density of the radiation:

$$\dot{N}_{ba} = B_{ba} N_a \rho(\omega_{ab})$$

where $B_{ba}$ is the absorption Einstein coefficient. In the other hand the transition rate for absorption by atom we have

$$\dot{N}_{ba} = W_{ba} N_a$$

knowing that $I(\omega) = \rho(\omega)c = \frac{N(\omega)}{V} \hbar \omega c$

it comes :$B_{ba} = c \frac{W_{ba}}{I(\omega_{ba})}$

which becomes in the dipolar approximation: $B_{ba} = c \frac{\pi}{3 \hbar \epsilon_0} |\vec{D}_{ba}|^2$.

Let’s now consider the transition from state $b$ to $a$ ($b \rightarrow a$) per unit of time $\dot{N}_{ab}$ is the sum of the number spontaneous emission per unit of time which is independent of the radiation energy density and of the number of the stimulated transitions per unit of time which is proportional to $\rho$:

$$\dot{N}_{ab} = A_{ab} N_b + B_{ab} \dot{N}_{ba} \rho(\omega_{ba})$$

since at equilibrium $\dot{N}_{ba} = \dot{N}_{ab}$ then $\frac{N_a}{N_b} = \frac{A_{ab} + B_{ab} \rho(\omega_{ba})}{B_{ba} \rho(\omega_{ba})}$.

In the thermal equilibrium the thermodynamics gives us

$$\frac{N_a}{N_b} = \exp\left(-\frac{E_a - E_b}{k_B T}\right) = \exp\left(-\frac{\hbar \omega_{ba}}{k_B T}\right)$$

We deduce :

$$\rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba} \exp\left(\frac{\hbar \omega_{ba}}{k_B T}\right)} - B_{ab}$$

Being given the Planck formula for the spectral energy density deduce that:

$$B_{ba} = -B_{ab}$$ and $\frac{A_{ab}}{B_{ba}} = \frac{\hbar \omega_{ba}^3}{\pi \epsilon_0 c^3}$ Note that if the state $a$ and $b$ are degenerated with respec-
4.5. Line Intensity and Lifetime of an Excited State

In the dipole approximation we deduce the transition rate for spontaneous emission

\[ W_{ab}^s = A_{ab} = \frac{\omega_{ba}^3}{3\pi c_\epsilon_0 |D_{ba}|^2} \]

(3) if the averaging in all direction is not considered then we have to write

\[ W_{ab}^s \propto |\hat{\epsilon} \cdot D_{ba}|^2 \]

4.5 Line Intensity and Lifetime of an Excited State

The decay law:

In the previous sections we have considered the function \( F(t, \omega) = \delta(\omega) \) but in fact even if this function is very sharp around \( \omega = 0 \) (i.e for \( \omega = \omega_{ba} \)) there exist a non zero probability (very small but not zero) that an atom starting from an excited state \( b \) will be after a spontaneous emission in state \( a \) plus a photon of energy \( \hbar \omega \). Hence the state \( b \) is not coupled to state \( a \) uniquely but rather to a continuum and it s not a two level system (when spontaneous emission is taken into account) since the final state is of energy \( E_a + \hbar \omega \) (note that the different photon are incoherent and cannot act cooperatively to insure a reverse transition so that the probability of finding the atom in state \( b \) decrease with time)

4.5.1 Lifetime

Suppose the transition rate of spontaneous emission from state \( b \) to state \( a \) is \( W_{ba}^s \) is independent of time. Then the probability \( P_b(t + dt) \) to find the atom in state \( b \) at \( t + dt \) is the probability \( P_b(t) \) to find it in state \( b \) at \( t \) multiplied by the probability that no transition has been taken place in time \( dt \). So :

\[ P_b(t + dt) = P_b(t)(1 - W_{ba}^s dt) \]

Considering \( c_b(t) \) as real and that initially the atom is in state \( b \) (i.e \( P_b(0) = 1 \)) show that we can write :

\[ \Psi_b(\vec{r}, t) = \Psi_b(\vec{r}) \exp(-i(E_b - i\hbar/2\tau)/\hbar) \]

where \( \Psi_b(\vec{r}) \) si the time independant wave function

express \( \tau \) in function of \( W_{ba}^s \)

4.5.2 Line Shape

Let’s set \( P_b(t < 0) = 0 \) (since we are not interested by state \( b \) for \( t < 0 \)).

In absence of coupling radiation field an excited state \( b \) would be stable and the function would be \( \Phi_b(\vec{r}, t) = \Psi_b(\vec{r}) \exp(-iE_b t/\hbar) \)

\( \Phi_b(\vec{r}, t) \) being solution of \( i\hbar \frac{\partial}{\partial t} \Phi_b(\vec{r}, t) = E_b \Phi_b(\vec{r}, t) \)

In presence of radiative field the equation is modified by
\[ i\hbar \frac{\partial}{\partial t} \Psi_b(\vec{r}, t) = \left( E_b - i\hbar/2\tau \right) \Psi_b(\vec{r}, t) \]

and

\[ \Psi_b(\vec{r}, t) = \Psi_b(\vec{r}) \exp(-i(E_b - i\hbar/2\tau)/\hbar) = \Psi_b(\vec{r}) f(t) \]

The energy of state \( b \) is no more real. Anyway we can always decompose a wave function in term of eigen function i.e

\[ \exp(-\frac{i}{\hbar}(E_b - i\hbar/2\tau)) = \int_{-\infty}^{+\infty} a(E') e^{-i\hbar E'/\hbar} dE' \]

or another way to say it we can describe \( f(t) \) from its Fourier transform:

\[ f(t) = \int_{-\infty}^{+\infty} g(\omega) e^{-i\omega t} d\omega \text{ where } g(\omega) \propto \int_{-\infty}^{+\infty} f(t) e^{i\omega t} dt \]

Show that \( |a(E)|^2 \) or \( |g(\omega)|^2 \) \( \propto \frac{1}{((E_b - E)^2 + \hbar^2/4 \tau^2)} \)

Hence, recalling that \( E = E_a + \hbar \omega \), the line profile \( (I(\omega)) \) can be written as

\[ I(\omega) = I_0 \frac{1}{\hbar \omega + E_a - E_b)^2 + \Gamma^2/4} \]

Express \( \Gamma \). Plot \( I(\omega) \). And superimpose the plot of a Gaussian function of the same width at half maximum Note: if the state \( a \) is also unstable we will have to consider

\[ \frac{1}{\tau} = \frac{1}{\tau_a} + \frac{1}{\tau_b} \]

4.5.3 Broadening

4.5.3.1 Pressure broadening

If other processes than spontaneous emission allow transition form state \( b \) to \( a \) we must replace \( W_{ab} \) by \( W_{tot} \) which include (sum of ) all the possible processes. Then the lifetime of the level becomes \( \tau = \frac{1}{W_{tot}} \) leading to a broadening of the line (verify it).

One process that can be considered is the collision between atoms. For each collision it exists a probability to an atom initially in state \( b \) to make a radiationless transition to some other states. The transition rate is \( W_c \) and proportional to the density of the concerned atoms and the relative velocity between two pairs of atoms \( v \). So that \( W_c = n v \sigma \). Where \( \sigma \) is a surface and is called the collision cross section (it depends on the species of the atom and \( v \)). \( n \) depends on the pressure and \( v \) on the temperature, hence information on pressure and temperature can be deduced from the study of the line profile.

4.5.3.2 Doppler broadening

The wavelength of the radiation emitted from a moving object is shifted by Doppler effect \( \lambda = \lambda_0(1 \pm \frac{v}{c}) \), \( \lambda_0 \) the wavelength emitted by the stationary atom. Show that \( \omega = \omega_0(1 \mp \frac{v}{c}) \)
If the light is emitted by a gas at temperature $T$ the number of atom with velocities between $v$ and $v + dv$ is given by Maxwell’s distribution

$$dN = N_0 \exp(-Mv^2/(k_BT))dv$$

where $M$ is the atomic mass. Hence the intensity emitted between $\omega$ and $\omega + d\omega$ is proportional to the number of atoms with a velocity between $v$ and $v + dv$. Show that we obtain a Gaussian distribution for an $i$:

$$I(\omega) = I(\omega_0) \exp\left(-\frac{Mc^2}{2k_BT}\left(\frac{\omega - \omega_0}{\omega_0}\right)^2\right).$$

Compute the fwhm of the line. Discuss.

Combining the pressure broadening which conserve the Lorentzian profile and the Doppler broadening which leads to a Gaussian profile, the observed profile is a Voigt profile. Look for other processes of line broadening.

### 4.6 Selection Rules in the dipole approximation

Let’s come back to the dipole approximation which as led us to conclude that absorption, stimulated emission and spontaneous emission between to states $\alpha$ and $\beta$ depends on the quantity $|\hat{\epsilon} \cdot \vec{D}_{ba}|$ where $\hat{\epsilon}$ is the polarisation vector and $\vec{D}_{ba}$ the matrix element of the dipole electric moment. In the case of one electron atom states $\alpha$ and $\beta$ are associated to the wave functions $\Psi_\alpha$ and $\Psi_\beta$ with the quantum number $n, l$ and $n', l'$ respectively.

$$\Psi_\alpha = R_{nl}(r)Y_{lm}(\theta, \phi) \quad \text{and} \quad \Psi_\beta = R_{n'l'}(r)Y_{l'm'}(\theta, \phi)$$

In cartesian system of coordinate we have the $x$ component of $\vec{D}_{ba}$ is $(D_{ba})_x = -e \int \Psi_\beta^*(\vec{r})x\Psi_\alpha(\vec{r})d\vec{r}$ (resp. for $y$ and $z$ coordinates). Expressing $x, y$ and $z$ in spherical coordinates we can write

$$(D_{ba})_j = \int_0^\infty R_{n'l'}r^3R_{nl}d\!r \int_0^{2\pi}d\phi Y_{l'm'}^*(\theta, \phi) \int_0^{\pi}d\theta \sin\theta \cos\theta Y_{lm}(\theta, \phi)$$

Show that

$$I_x(l'm', lm) = \int_0^\pi d\theta \sin\theta \int_0^{2\pi}d\phi Y_{l'm'}^*(\theta, \phi)$$

Give the expression of $I_y(l'm', lm)$ and $I_z(l'm', lm)$

The radial part is always non-zero but the $I_j(l'm', lm)$ integrals are not zero only for some given values of $(lm)$ and $(l'm')$ which leads to the selection rules.

#### 4.6.0.1 Parity

The parity operation consist in changing $\vec{r}$ in $-\vec{r}$ i.e $x$ in $-x$, $y$ in $-y$ and $z$ in $-z$ which in spherical coordinate correspond to the changes of $r, \theta, \phi$ in $r, \pi - \theta, \phi + \pi$. It can be shown that $Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^lY_{lm}(\theta, \phi)$ hence $I_j(l'm', lm) = (-1)^lI_j(l'm', lm)$ and all $I_j(l'm', lm)$ vanish except if $l + l'$ is odd.

#### 4.6.0.2 Magnetic quantum number

Using eq (2.11) we show that the integral over $\phi$ contained in $I_x(l'm', lm)$ is proportional to the quantity

$$K(m', m) = \int_0^{2\pi} \exp[i(m - m')\phi] \cos\phi d\phi$$

which vanishes except if $m - m' = \pm 1$. $I_y$ vanishes except of $m - m' = \pm 1$ and $I_z$ vanishes except if $m = m'$. During a transition
between state \( a \) and state \( b \) only one of these condition can be fulfilled so either \((D_{ba})_z = 0\) or \((D_{ba})_x \) and \((D_{ba})_y \) are zero

### 4.6.0.3 Orbital angular momentum

Using eq (2.11) again we see that both \( I_x \) and \( I_y \) contain the integrals:

\[
L^{\pm}(l, l', m, m') = \int_0^\infty d\theta \sin^2(\theta) P_{l'}^{m \pm 1}(\cos \theta) P_{l}^{m}(\cos \theta)
\]

The recurrence relation of the functions \( P_{l}^{m} \) and the orthogonality relation of these function it can be shown that these integrals subsist only for \( l' = l + 1 \) or \( l' = l - 1 \). The remaining \( I_z \) contains the term

\[
M(l', l, m) = \int_0^\pi d\theta \sin(\theta) \cos(\theta) P_{l'}^{m}(\cos \theta) P_{l}^{m}(\cos \theta)
\]

which from the recurrence relation vanishes except if \( l' = l \pm 1 \)

### 4.6.0.4 Summary of the selection rules

The electric dipole transition can take place if:

\[
\Delta l = \pm 1 \quad (\text{state } a \text{ and } b \text{ differ in parity})
\]

\[
\Delta m = 0 \text{ or } \Delta m = \pm 1
\]

Under these conditions the transitions are said allowed if both condition are not fulfilled the transition is said forbidden.

We can observe some forbidden lines. Why? (several arguments)
5.1 He-like atom

Let’s consider a nucleus of charge $Ze$ and mass $m_N$ that will be taken as the origin of coordinates and two electrons of charge $e$ and mass $m$.

Write the Hamiltonian of the system on the form $H = H_0 + V_{12}$ where $H_0$ represents the interactions between nucleus an electrons and $V_{12}$ represents the interaction between the two electrons. this later interaction have been neglected in this Hamiltonian ? Show that the corresponding Schrödinger equation is a differential equation of 6 not separable variables (neither in cartesian nor in spherical coordinates)
The $H_0$ part is treated in classroom and corresponds to the electron independent approximation and leads to singulet states ($S = 0$) for para Helium and triplet states ($S = 1$) for ortho Helium.
The Schrödinger equation $H\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$ is particularly hard to solve and the analytic solution is still unknown. Nevertheless sophisticated functions are built from different techniques and the proper values of the equations are computed with high precision. In fact it is not really proper values strictly speaking but mean energies $<H> = \langle \phi(\vec{r}_1, \vec{r}_2) \rvert H \rvert \phi(\vec{r}_1, \vec{r}_2) \rangle$ computed from trial functions $\phi(\vec{r}_1, \vec{r}_2)$. The integrals in the computation of $<H>$ are on the six variables with element of volume $d^3r_1d^3r_2$. Note that $V_{12}$ being positive its mean value leads to an increase of the energy.

### 5.1.1 Hyllerass Equation

For both $S$ states the situation is simpler. In this state $\psi(\vec{r}_1, \vec{r}_2)$ does not depend on the orientation of the triangle formed by the 3 particles but only on its form and dimensions and $\psi(\vec{r}_1, \vec{r}_2) = \psi(r_1, r_2, r_{12})$. $H\psi(r_1, r_2, r_{12}) = E\psi(r_1, r_2, r_{12})$ (Hyllerass equation)

Show that in this case we can write $H = T_1 + V_1 + T_2 + V_2 + V_{12} + T'_{12}$.

with

$T_i = -\frac{\hbar^2}{2m} \frac{1}{r_i} \left( \frac{\partial}{\partial r_i} \left( \frac{r_i^2}{2m} \frac{\partial}{\partial r_i} \right) \right)$ and $V_i = -\frac{Ze^2}{r_i}$ where $i=1, 2$

$T_{12} = -\frac{\hbar^2}{2m} \frac{1}{r_{12}} \left( \frac{\partial}{\partial r_{12}} \left( \frac{r_{12}^2}{2m} \frac{\partial}{\partial r_{12}} \right) \right)$ and $V_{12} = \frac{e^2}{r_{12}}$
\[ T'_1 = -\frac{\hbar^2}{2m} \left( \frac{r_1^2 - r_2^2 + r_1^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \right) \]

In order to compute mean energy the elementary volume will be \( 8\pi r_1 r_2 r_{12} dr_1 dr_2 dr_{12} \) and the domain : \( 0 \leq r_1 < \infty, 0 \leq r_2 < \infty, |r_1 - r_2| \leq r_{12} \leq r_1 + r_2 \).

Apart from the \( T' \) term we have terms of type \( T_i + V_i \) in Hylerraas equation. So in neglecting the \( T' \) term we have separable variables and the equation admit a solution of type \( f(r_1)g(r_2)h(r_{12}) \) Each factor being a solution of an H-like Schrödinger equation. This solution discard the 3 singularities (the 3 body problem becomes 3 two body problems.). The \( T' \) term avoids this separation.

### 5.1.2 Singularities : Kato conditions

In order to study the behavior of the wave function in the vicinity of the singularities we introduce a "mean trial function" \( \bar{\psi}(\vec{r}_1, \vec{r}_2) \). It is computed from a trial function \( \psi(\vec{r}_1, \vec{r}_2) \) integrated on a small spherical surface centered on the singular point. From the expression of \( \Delta_i \) in spherical coordinates we deal with two terms \( -\frac{1}{r_i^2} L^2_i \) and \( \frac{2}{r_i} \frac{\partial}{\partial r_i} \) both singular in \( r_i = 0 \). The first term is not to be considered since \( L_i^2(\theta_i, \phi_i)\psi(\vec{r}_1, \vec{r}_2) = 0 \). The second term has to be compensated by \( -\frac{Ze^2}{r_i} \) to eliminate the singularity. Hence we should have

\[
\left[ \frac{\partial \bar{\psi}(\vec{r}_1, \vec{r}_2)}{\partial r_i} \right]_{r_i=0} = -\frac{mZe^2}{\hbar^2} \left[ \bar{\psi}(\vec{r}_1, \vec{r}_2) \right]_{r_i=0} \text{ for } i = 1, 2
\]

and

\[
\left[ \frac{\partial \bar{\psi}(\vec{r}_1, \vec{r}_2)}{\partial r_{12}} \right]_{r_{12}=0} = -\frac{me^2}{\hbar^2} \left[ \bar{\psi}(\vec{r}_1, \vec{r}_2) \right]_{r_{12}=0}
\]

These are the Kato conditions that can be generalized for two particles of mass \( m_i, m_j \) and charge \( q_i, q_j \):

\[
\left[ \frac{\partial \bar{\psi}}{\partial r_{ij}} \right]_{r_{ij}=0} = -\frac{\mu_{ij} q_i q_j}{\hbar^2} \left[ \bar{\psi} \right]_{r_{ij}=0}
\]

where \( \mu_{ij} = m_i m_j / (m_i + m_j) \) Using Kato’s conditions we can deduce the wave function near the singularities:

\[ \bar{\psi} = 1 + \frac{\mu_{ij} q_i q_j}{\hbar^2} r_{ij} \]

Write \( \bar{\psi} \) for \( r_i = 0 \) and \( r_{12} = 0 \) in the case of He-like atom. Verify that Kato’s conditions are fulfilled for H atom. Even if the notion of mean trial function is no more meaningful. Why?

### 5.1.3 Asymptotic Behavior

Two asymptotic behaviors are to be considered (1) \( r_1, r_2, r_{12} \to \infty \) all together (2) only one of the electron \( \to \infty \) the other one staying at a finite distance from the nucleus. The first case is difficult and still debated. The second one leads to the screening behavior. Let’s consider \( r_2 \to \infty, r_1 \) remains finite and we can consider \( r_{12} \approx r_2 \). We can then write \( V_2 + V_{12} = -\frac{(Z_1)e^2}{r_2} \). The external electron feels the nucleus screened by the inner electron \( (Q = (Z - 1)e) \). Schrödinger equation becomes:
Many Electrons

\[ -\frac{\hbar^2}{2m}(\Delta_1 + \Delta_2) - \frac{Ze^2}{r_1} - \frac{(Z - 1)e^2}{r_2} \] \psi(r_1, r_2) = E\psi(r_1, r_2)

Since the variables are separable we have \( \psi(r_1, r_2) = \phi(r_1)\phi(r_2) \) where \( \phi(r_1) = \phi_{n_1,l_1,m_1}(\tilde{r}_1) \) solution of the hydrogen-like atom with energy \( E_{n_1} = -(n_{He}/2)(Z^2/2n_1^2) \). After substitution in Schrödinger equation we have:

\[ -\frac{\hbar^2}{2m} \frac{\Delta_2 - (Z - 1)e^2}{r_2} \phi(r_2) = (E - E_{n_1})\phi(r_2) \]

which leads when \( r_2 \to \infty \) to \( \psi(r_1, r_2) \approx \phi_{n_1,l_1,m_1}(\tilde{r}_1)r_2^\beta e^{-ar_2} \) with \( \beta = \frac{me^2(Z - 1)}{\hbar^2} \alpha \) and \( \alpha = \sqrt{\frac{2m}{\hbar^2}(E_{n_1} - E)} \). \( E_{n_1} - E \) is the ionization potential (He \( \to \) He\(^+\)).

This result can be generalized to \( N \) electrons (when only one electron goes to infinity). For this electron (i) the behavior of the radial function is \( r_i^\beta e^{-ar_i} \) with \( \beta = \frac{me^2(Z - N + 1)}{\hbar^2} \alpha \)

and \( \alpha = \sqrt{\frac{2m}{\hbar^2}I_p} \). The nucleus is screened by the \( N - 1 \) internal electrons and \( I_p \) is the ionization potential of the atom (energy needed to extract one electron). x

5.2 Hartree Fock Approximation

5.2.1 \( N \) electron atoms

Considering an atom with \( N \) electrons in its fundamental states, we have seen in classroom, the physical wave function is given under the form of a Slater determinant of orthonormal spin-orbitals \( u_{\alpha}(q_i) \) where \( i, \alpha, q_i \) represent respectively the considered electron, the quantum numbers \( (n, l, m_s) \), and the set of spatial and spin coordinates:

\( u_{\alpha}(q_i) = u_{\alpha}(\tilde{r}_i)\chi_{\pm} (\chi_{\pm} \text{ spin function}) \). Being given the orthogonality of \( \chi_{\pm} \), the orthonormality of the spin orbitals \( u_{\alpha}(q_i) \) is \( \int u_{\alpha}^*(\tilde{r}_i)u_{\beta}(\tilde{r}_i)dr_i = \delta_{\alpha\beta} (i = 1, \cdots N) \). The goal is to built the optimal Slater determinant: the one for which \( u_{\alpha}^*(q_i) \) are solutions of the Hartree Fock equation that we are going to derive.

Each electron move in an effective potential which takes into account the attraction of the nucleus and the effects of the average repulsive interactions of the other electrons. Each electron is described by its own wave function. In atomic units \( H = H_1 + H_2 \)

with \( H_1 = \sum_{i=1}^{N} h_i \),

\[ h_i = -\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i} \] and \( H_2 = \sum_{i,j=1}^{N} \frac{1}{r_{ij}} \) \( r_{ij} = |r_i - r_j| \);

Let’s denote \( E_0 \) the energy of the ground state of the system. According to the variational method seen in classroom \( E_0 \leq E[\phi] = \langle \phi | H | \phi \rangle \) with \( \langle \phi | \phi \rangle = 1 \), and \( \phi \) is the trial function. In HF method \( \phi \) is the Slater determinant (classroom).

\[ \phi(q_1, q_2, \cdots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{\alpha}(q_1) & u_{\beta}(q_1) & \cdots & u_\nu(q_1) \\ u_{\alpha}(q_2) & u_{\beta}(q_2) & \cdots & u_\nu(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_{\alpha}(q_N) & u_{\beta}(q_N) & \cdots & u_\nu(q_N) \end{vmatrix} \]

each \( \alpha, \beta, \cdots, \nu \) represent a set of quantum numbers \( (n, l, m_s) \) and \( \langle u_\lambda | u_\mu \rangle = \delta_{\lambda\mu} \)

We can rewrite the Slater determinant in more compact form:
\[ \phi(q_1, q_2, \ldots, q_N) = \frac{1}{\sqrt{N!}} \sum_N (-1)^P P u_\alpha(q_1) u_\beta(q_2) \cdots u_\nu(q_N) = \sqrt{N!} A \phi_H \] where
\[ \phi_H = u_\alpha(q_1) u_\beta(q_2) \cdots u_\nu(q_N) \] is the Hartree wave function, \( A = \frac{1}{N!} \sum_N (-1)^P \) is the antisymmetrisation operator. \( P \) is a permutation of electron coordinates : \( (-1)^P = -1 \) if \( P \) is an even permutation and \( 1 \) if \( P \) is an odd permutation (\( P \) is said even or odd if the number of interchange leading to it is even or odd).

Check the compact form of the Slater determinant on 3x3 determinant and show that \( A^2 = A \)

We have the properties : \( A^2 = A \) (\( A \) is Hermitic and is a projector), \( [H_1, A] = 0 \) and \( [H_2, A] = 0 \)

Let’s calculate \( E[\phi] = \langle \phi | H_1 | \phi \rangle + \langle \phi | H_2 | \phi \rangle \)

Show that \( \langle \phi | H_1 | \phi \rangle = \sum_i \sum_P (-1)^P \langle \phi_H | h_i | \phi_H \rangle \)

We can show that \( \sum_\lambda \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle = \sum_\lambda I_\lambda \) where \( \lambda = \alpha, \beta, \cdots, \nu \) and \( I_\lambda = \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle \)

Make a try with two electrons to verify the previous expression

The second expectation value \( \langle \phi | H_2 | \phi \rangle \) leads to:

\[ \langle \phi | H_2 | \phi \rangle = \sum_i \sum_j (-1)^P \langle \phi_H | \frac{1}{r_{ij}} P | \phi_H \rangle = \sum_i \sum_{ij} \langle \phi_H | \frac{1}{r_{ij}} (1 - P_{ij}) | \phi_H \rangle \]

where \( P_{ij} \) is an operator that interchanges the coordinates (spatial and spin) of electrons \( i \) and \( j \).

Show that \( \langle \phi | H_2 | \phi \rangle = \sum_{\lambda, \mu} \left[ \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_i) u_\mu(q_j) \rangle - \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\mu(q_i) u_\lambda(q_j) \rangle \right] \)

We can also write:

\[ \langle \phi | H_2 | \phi \rangle = \frac{1}{2} \sum_\lambda \sum_\mu \left[ \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_i) u_\mu(q_j) \rangle - \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\mu(q_i) u_\lambda(q_j) \rangle \right] \]

\( J_{\lambda, \mu} \) is the direct term which is the average value of \( \frac{1}{r_{ij}} \) relative to the state \( u_\lambda(q_i) u_\mu(q_j) \)

(the electron \( i \) is in the spin orbital \( u_\lambda \) and electron \( j \) in the spin orbital \( u_\mu \)). \( K_{\lambda, \mu} \) is the exchange term which is the matrix element of the interaction \( \frac{1}{r_{ij}} \) between the two states \( u_\lambda(q_i) u_\mu(q_j) \) and \( u_\mu(q_i) u_\lambda(q_j) \) obtained by interchanging electron \( i \) and \( j \)

Finally we can write the energy functional:

\[ E[\phi] = \sum_\lambda I_\lambda + \frac{1}{2} \sum_\lambda \sum_\mu \left[ J_{\lambda, \mu} - K_{\lambda, \mu} \right] \]

We the need to express that \( E[\phi] \) is stationary with respect to the variation of spin orbitals \( u_\lambda \) taking into account the \( N^2 \) constraints \( \langle u_\lambda | u_\mu \rangle = \delta_{\lambda, \mu} \). Using the Lagrange multiplier techniques the variational equation becomes:

\[ \delta E = - \sum_\lambda \sum_\mu \epsilon_{\lambda, \mu} \delta \langle u_\lambda | u_\mu \rangle = 0 \]

where \( \epsilon_{\lambda, \mu} \) are the Lagrange multipliers. After having made a diagonalisation of the matrix \( \epsilon_{\lambda, \mu} \) we can rewrite \( \delta E - \sum_\lambda E_\lambda \delta \langle u_\lambda | u_\lambda \rangle = 0 \)

This leads to the HF integro differential equations:

\[ \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] u_\lambda(q_i) + \left[ \sum_\mu \int u_\mu^*(q_j) \frac{1}{r_{ij}} u_\mu(q_j) dq_j \right] u_\lambda(q_i) - \sum_\mu \left[ \int u_\mu^*(q_j) \frac{1}{r_{ij}} u_\lambda(q_j) dq_j \right] u_\mu(q_i) = E_\lambda u_\lambda(q_i) \]

The summation is made on the \( N \) occupied state and the integrations are made both
on spatial and spin coordinates. Being given that \( u_\lambda(q_i) = u_\lambda(\vec{r}_i) \chi_{1/2,m_\mu} \) and that 
\( \langle \chi_{1/2,m_\mu} | \chi_{1/2,m_\mu'} \rangle = \delta_{m_\lambda,m_\mu'} \), we can rewrite the HF equation uniquely for the spatial coordinates. Just Do it

Let s call \( V_d(\vec{r}_i) = \sum_\mu \int u_\mu^*(\vec{r}_j) \frac{1}{r_{ij}} u_\mu(\vec{r}_j) d\vec{r}_j \)

and

\[ V_{ex}(\vec{r}_i) = \sum_\mu v_{ex}^\mu(\vec{r}_i) \]

where

\[ v_{ex}^\mu(\vec{r}_i) = \left[ \int u_\mu^*(\vec{r}_j) \frac{1}{r_{ij}} u_\lambda(r_i) d\vec{r}_j \right] u_\mu(\vec{r}_i) \]

Finally writing \( V(q_i) = -\frac{Z}{r_i} + V_d(\vec{r}_i) + V_{ex}(q_i) \) the HF equation takes a very common form:

\[ \left[ -\frac{1}{2} \nabla_\vec{r}_i^2 + V(q_i) \right] u_\lambda(q_i) = E_\lambda u_\lambda(q_i) \]

5.2.2 Go back to He

Exercise: Consider the states \( 1^1S \) and \( 2^3S \) of He. Give the Slater determinants for each state and give the expression of the HF equation for the orbital \( u_{1s}(\vec{r}) \)

Let \( \psi(\vec{r}_1,\vec{r}_2) \) be the spatial part of a parahelium state. We suppose \( \psi(\vec{r}_1,\vec{r}_2) = u(\vec{r}_1)u(\vec{r}_2) \) where \( u(\vec{r}) \) is a normalized function (note that in parahelium state \( \psi \) is symmetrical when interchanging the two electrons). The Schrödinger equation becomes:

\( (H_1 + H_2 + V_{12})u(\vec{r}_1)u(\vec{r}_2) = E\ u(\vec{r}_1)u(\vec{r}_2) \)

In multiplying this equation by \( u^*(r_1) \) and integrating over \( d^3 r_1 \) (resp \( u^*(r_2) \) and integrating over \( d^3 r_2 \) show that

\[ \begin{bmatrix} H_2 + \langle u(\vec{r}_1) | H_1 | u(\vec{r}_1) \rangle + \langle u(\vec{r}_1) | V_{12} | u(\vec{r}_1) \rangle \end{bmatrix} u(\vec{r}_2) = Eu(\vec{r}_2) \]

resp.

\[ \begin{bmatrix} H_1 + \langle u(\vec{r}_2) | H_2 | u(\vec{r}_2) \rangle + \langle u(\vec{r}_2) | V_{12} | u(\vec{r}_2) \rangle \end{bmatrix} u(\vec{r}_1) = Eu(\vec{r}_1) . \]

The term \( \langle u(\vec{r}_1) | H_1 | u(\vec{r}_1) \rangle \)

is a constant and \( \langle u(\vec{r}_1) | V_{12} | u(\vec{r}_1) \rangle \) is a function of \( \vec{r}_2 \) (resp. for the second expression). These two equation are coupled integro-differential equations since the searched function appear in both equations. There are not equation to eigen values since the operator change when the coordinates vary. In order to solve these two equations we first choose a function \( u(\vec{r}_1) \) then we solve the second equation which leads to \( u(\vec{r}_2) \) which is then used in te first equation. This allows to define a new function \( u(\vec{r}_1) \). The process converge by iterations. The HF solution is the best one we can obtain under the format of product of two functions.
Make a theoretical presentation and astrophysical applications of the following peculiar effects.

6.1 Zeeman and Starck Effect
6.2 Scattering and cross section
6.3 $e^-$ ion collision
6.4 Photoionization
6.5 $e^-$ ion recombination
6.6 Multi wavelength emission spectra
6.7 Emission line and radiative transfert
6.8 Opacity and radiative forces
6.9 Gaseous nebulae and H II regions
6.10 AGN and Quasars
6.11 Cosmology
Bibliography

Griffith: Introduction to Quantum Mechanics
Atkins: Molecular Quantum Mechanics
Atkins: Physical Chemistry
Mc Quarrie: Quantum Chemistry
O Levine: Quantum Chemistry
Tennyson: Astronomical Spectroscopy
Kitchin: Astronomical Spectroscopy