L3 SdM, ENS Lyon – UCBL Atomes et molécules Ann ? universitaire 2022/2023 Davis Amans, Clara Montagnon, Thomas Niehaus, Andrew Pell

TD1 : Rydberg atoms

Rydberg atoms are atoms whose outermost electron is in a highly excited state, $n \gg 1$. In this exercise we will imagine to have an hydrogen atom, although many of the properties we find here carry on with minor corrections to the case of *N*-electron atoms.

1 Radius of the excited orbitals

We would like to calculate the average radius of the (*nlm*) orbital of the hydrogen atom, $\langle r \rangle_{nlm} = \langle nlm | r | nlm \rangle$.

1.1

Write down the expression of $\langle r \rangle_{nlm}$, normalizing explicitly the hydrogen wavefunction $\psi_{nlm}(r,\theta,\phi)$. Show that it can be cast in the form

$$\langle r \rangle_{nlm} = n a_0 \frac{\int_0^\infty dy \, y \, A(y) \, e^{-2y}}{\int_0^\infty dy \, A(y) \, e^{-2y}} \tag{1}$$

where

$$A(y) = \sum_{k=0}^{2(n-l-1)} c_k y^{k+2l+2}$$
(2)

1.2

Assuming that for $n \gg 1$ the polynomial expressing A(y) is dominated by the highest order term, justify that the ratio of integrals takes the value $\approx (n + 1/2)$.

(Suggestion : integration by part can help.).

Conclude about the dependence of $\langle r \rangle$ on *n*.

The exact result is $\langle r \rangle_{nlm} = n^2 a_0 \left[\frac{3}{2} - l(l+1)/(2n^2) \right]$. Is the scaling of $\langle r \rangle$ with *n* surprising? (think about the energy scaling with *n*, $E_n = -\text{Ry}/n^2$).

2 Circular Rydberg states

Circular Rydberg states are states with $n \gg 1$ which maximize the angular moment *l* and its projection along the quantization axis m, $|n; C\rangle = |n, l = n - 1, m = l\rangle$. These states have a particularly simple wavefunction.

2.1

Using the fact that the raising operator of angular momentum vanishes on the state maximizing the *m* projection of the angular momentum, $L^+|l, m = l\rangle = 0$, show that

$$\mathscr{Y}_{ll}(\theta,\phi) \sim (\sin\theta)^l e^{il\phi} \tag{3}$$

where $\mathscr{Y}_{lm}(\theta,\phi) = P_l^{(m)}(\theta)e^{im\phi}$ are the spherical harmonics (seen in class).

2.2

Using the definition of the Laguerre polynomials, calculate the radial part of the wavefunction (up to a normalization constant).

The exact expression is

$$\psi_{n,n-1,n-1}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} \frac{1}{n^n n!} \left(\frac{r}{a_0} \sin\theta \ e^{i\phi}\right)^{n-1} e^{-r/(na_0)} \tag{4}$$

Write down the probability density function $P_r(r)$ (up to a normalization constant) to find the electron at a distance *r* from the nucleus. Calculate the maximum value of the radial probability. Assuming that $r_{\text{max}} \approx \langle r \rangle$, show that the result found here is consistent with the one of the previous section.

2.4

Estimate the variance of the radial distribution $\sigma_r^2 = \langle (r - r_{\text{max}})^2 \rangle$. To do so, you can write $P_r(r) = \exp[\Phi(r)]$ and expand $\Phi(r)$ around its maximum. Show that $\sigma_r/r_{\text{max}} \approx 1/\sqrt{2n}$.

2.5

Write down the probability $P_{\theta}(\theta)$ (up to a normalization constant) for the polar angle θ . Show that $\sigma_{\theta} \approx 1/\sqrt{2n}$.

2.6

Conclude that, for $n \gg 1$, the orbital of the circular Rydberg states is close to a circular orbit of radius $\approx n^2 a_0$.

2.7

Write down the classical energy of an electron describing a circular orbit of radius $R = n^2 a_0$ with squared angular momentum $L^2 = \hbar^2 n(n-1)$, and compare to the exact energy coming from the solution of the quantum problem.

2.8

Consider the transition between two consecutive circular Rydberg states, $|n; C\rangle$ and $|n + 1; C\rangle$. Show that, for $n \gg 1$, $\Delta E = E_{n+1} - E_n \approx 2\text{Ry}/n^3$. As we will see in the following of the course, this transition can be obtained via the absorption of a photon : calculate the photon wavelength for n = 50. What is the width of a cavity whose lowest frequency mode matches this wavelength ?

Note : cavities which are suited to study the interaction between photons and Rydberg atoms are realized in famous experiments of so-called "cavity QED", e.g. in S. Haroche's group at the ENS in Paris.

Appendix

Hydrogen atom wavefunctions :

$$\psi_{nlm}(r,\theta,\phi) = N_{nl} \left(\frac{r}{a_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) e^{-r/(na_0)} \mathscr{Y}_{lm}(\theta,\phi)$$
(5)

 $L_{n+l}^{2l+1}(\rho)$: associated Laguerre polynomial; polynomial of order n-l-1 N_{nl} : normalization constant $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$: Bohr radius

 (θ, ϕ) -representation of the raising operator for the angular momentum : $L^+ \rightarrow \hbar e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right)$

Photon dispersion relation : $\omega = ck = 2\pi c/\lambda$.

TD2: Sum of angular momenta - isotope effect

1 Sum of angular momenta : spin of the nucleus

The knowledge of the spin *I* of the nucleus is of crucial importance to understand the electronic energy levels of the atom (through the hyperfine coupling, that we will explore later in the course); as well as to know whether the nucleus of an atom can be used to probe its surrounding environment via nuclear magnetic resonance (NMR), which only works with non-zero nuclear spins.

1.1

The constituents of the nucleus, protons and neutrons, have spin a *S* with quantum number S = 1/2 defining $|S^2| = \hbar^2 S(S+1)$. The nuclear spin is defined then as $I = \sum_i S_i$ where the sum runs over all nucleons (protons/neutrons)¹. Write the possible values of the quantum number *I* defining $I^2 = \hbar^2 I(I+1)$ for a system of 2 protons and 2 neutrons.

1.2

Suppose that an experiment measures the projection of the nuclear spin along the *z* axis, I^z , to be $2\hbar$. Can you deduce with certainty the value of I?

1.3

The shell model of the nucleus gives the following rules for the nuclear spin :

- *Even/even* : if the nucleus contains an even number of neutrons and protons, then I = 0;
- *Odd/odd* : if the nucleus contains an odd number of $N_n = 2n + 1$ neutrons and $N_p = 2m + 1$ protons (with *n* and *m* integers), then *I* is an integer;
- Odd/even : if the nucleus contains and odd number of protons and an even number of neutrons (or vice-versa), then *I* is half integer.

Write the possible values of the nuclear spin *I* in the odd/odd case; and do the same in the odd/even case when $N_n = 2n$ and $N_p = 2m + 1$.

1.4

Predict the nuclear spin *I* of ¹H, ¹²C, ¹⁴C, ¹⁶O. Which one(s) of these nuclei would be useful for NMR?

1.5

Let us now consider the so called *hyperfine spin*, given by the sum of the nuclear spin I and the total angular momentum of the electron J, namely F = J + I. In the case of deuterium ²H we have that I = 1. We suppose that the electronic angular momentum has J = 1/2 (valid *e.g.* for the ground state of the atom). We shall call $\hbar m_F$, $\hbar m_J$ and $\hbar m_I$ the eigenvalues of the operators F^z , J^z and I^z respectively. If we measure the state of the hyperfine spin to be |F = 3/2, $m_F = 1/2$), write the probability that $m_I = 0$, $m_j = 1/2$. (*Suggestion* : use the table of Clebsch-Gordan coefficients).

^{1.} In fact the nuclear spin can also take a contribution from the orbital angular momentum of the nucleons moving inside the nucleus, but for simplicity we shall neglect this aspect in the following.

2 Recursive formula for Clebsch-Gordan coefficients

We remind of the definition of the Clebsch-Gordan CG coefficients $\langle j_1 j_2; JM | j_1 m_1; j_2 m_2 \rangle$ when summing two arbitrary (orbital or spin) angular momenta $J = J_1 + J_2$ with lengths j_1 and j_2 :

$$|j_1 m_1; j_2 m_2\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} \langle j_1 j_2; JM | j_1 m_1; j_2 m_2\rangle | j_1 j_2; JM\rangle .$$
(6)

where $\langle j_1 j_2; JM | j_1 m_1; j_2 m_2 \rangle \sim \delta_{M=m_1+m_2}$. Inverting this relationship, one obtains

$$|j_1 j_2; JM\rangle = \sum_{m_1 + m_2 = M} \langle j_1 m_1; j_2 m_2 | j_1 j_2; JM\rangle \ |j_1 m_1; j_2 m_2\rangle .$$
⁽⁷⁾

Please notice that CG coefficients are real, so that $\langle j_1 m_1; j_2 m_2 | j_1 j_2; JM \rangle = \langle j_1 j_2; JM | j_1 m_1; j_2 m_2 \rangle$.

2.1

Considering the operator $J^{\pm} = J_1^{\pm} + J_2^{\pm}$, show that

$$J^{\pm}|j_{1}j_{2};JM\rangle = \hbar\sqrt{J(J+1) - M(M\pm 1)} \sum_{m_{1}=-j_{1}}^{j_{1}} \sum_{m_{2}=-j_{2}}^{j_{2}} |j_{1}m_{1};j_{2}m_{2}\rangle \langle j_{1}m_{1};j_{2}m_{2}|j_{1}j_{2};J(M\pm 1)\rangle$$
(8)

2.2

Using the definition of Clebsch-Gordan coefficients, deduce the recursive formula

$$\sqrt{J(J+1) - M(M\pm 1)} \ \langle m_1 m_2 | J(M\pm 1) \rangle = \sqrt{j_1(j_1+1) - m_1(m_1\mp 1)} \ \langle (m_1\mp 1) m_2 | JM \rangle + \sqrt{j_2(j_2+1) - m_2(m_2\mp 1)} \ \langle m_1(m_2\mp 1) | JM \rangle$$
(9)

where we have introduced the short-hand notation

$$|j_1m_1; j_2m_2\rangle \rightarrow |m_1m_2\rangle |j_1j_2; JM\rangle \rightarrow |JM\rangle.$$
 (10)

2.3

Let us now consider the case $j_1 = 1/2$, $j_2 = 1/2$, with the notation $|m = 1/2 > = |\uparrow\rangle$, $|m = -1/2 > = |\downarrow\rangle$. Using the two cases : 1) equation for J^- , J = 1, M = 1; and 2) equation for J^+ , J = 1, M = -1, show that

Knowing that $|11\rangle = |\uparrow\uparrow\rangle$ and $|1, -1\rangle = |\downarrow\downarrow\rangle$ reconstruct the form of $|10\rangle$. Can you also deduce the form of $|00\rangle$?

3 Isotope effect in He⁺

Helium exists in two isotopes ³He et ⁴He. We consider the He⁺ ion and we aim at studying the influence of the mass of the isotopes on the absorption spectrum of this ion.

3.1

Write the Hamiltonian (without the spin) for He⁺.

3.2

Give the general formula for the energy spectrum of the electronic excitations of the He⁺ ion.

We now focus on the isotopes ${}^{3}\text{He}^{+}$ and ${}^{4}\text{He}^{+}$. How do the energies of the ions depend on the nuclear mass?

3.4

We aim at distinguishing the two isotopes of He⁺ via absorption spectroscopy. Determine the different wavelengths λ exciting each of the two isotopes to their first excited state – you can limit yourself to the mathematical formula, without providing the numerical value.

3.5

What is the value $\Delta \lambda / \lambda$, where $\Delta \lambda = \lambda ({}^{3}\text{He}^{+}) - \lambda ({}^{4}\text{He}^{+})$? We shall assume that the electron mass is 2000 times lighter than a nucleon.

TD3: Three-dimensional harmonic oscillator and spin-orbit coupling

In this TD we will explore the physics of a quantum particle in a three-dimensional harmonic oscillator potential and the effect of spin-orbit coupling on the spectrum. The results we shall obtain will allow you to contrast the solution of this problem with that of a particle in a Coulomb potential, that we have explored in the lectures. Moreover these results are directly relevant in the context of the so-called *shell model* for the atomic nucleus.

4 Three-dimensional harmonic oscillator

We shortly recall the quantization of the one-dimensional harmonic oscillator Hamiltonian

$$\mathcal{H}_{1dHO} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \,. \tag{12}$$

Solving the Schrödinger's equation $\mathcal{H}|\psi_n\rangle = E_n|\psi_n\rangle$ one finds eigenvalues $E_n = \hbar\omega(n+1/2)$ (n = 0, 1, ...) and corresponding eigenfunctions

$$\psi_n(x) = \langle x | \psi_n \rangle = \frac{1}{\sqrt{2^n n!}} \left(\frac{1}{\pi a^2} \right)^{1/4} H_n(x/a) \ e^{-x^2/(2a^2)} \tag{13}$$

where $a = \sqrt{\hbar/(m\omega)}$ is the so-called harmonic oscillator length, and $H_n(y)$ is Hermite polynomial of order *n*. We shall consider in the following the three-dimensional harmonic oscillator

$$\mathcal{H} = \frac{\boldsymbol{p}^2}{2m} + \frac{1}{2}m\omega^2 \boldsymbol{r}^2 \tag{14}$$

with $p^2 = p_x^2 + p_y^2 + p_z^2$ and $r^2 = x^2 + y^2 + z^z$.

4.1

Using the separation of variables, show that the eigenvectors of the three-dimensional problem in Cartesian coordinates can be written as

$$\Psi_{n_x,n_y,n_z}(x,y,z) = \psi_{n_x}(x)\,\psi_{n_y}(y)\,\psi_{n_z}(z) \tag{15}$$

with $n_x = 0, 1, ..., n_y = 0, 1, ..., n_z = 0, 1, ...;$ and with corresponding eigenvalues

$$E_N = \hbar\omega(N+3/2)$$
 $N = n_x + n_y + n_z$. (16)

4.2

Show that the degeneracy the *N*-th eigenvalue is $D_N = (N+1)(N+2)/2$.

5 Three-dimensional harmonic oscillator in spherical coordinates

Moving from Cartesian coordinates (x, y, z) to spherical coordinates (r, θ , ϕ), one realizes that the Hamiltonian of the three-dimensional harmonic oscillator is one example of a particle in a central potential $V(r) = (1/2)m\omega^2 r^2$. The Hamiltonian in spherical coordinates reads

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{L^2}{2mr^2} + \frac{1}{2}m\omega^2 r^2$$
(17)

where *L* is the angular-momentum operator.

We search for a solution of the Schrödinger's equation with separation of variables

$$\psi_{Nlm}(r,\theta,\phi) = R_{Nl}(r)Y_{lm}(\theta,\phi),\tag{18}$$

with Y_{lm} the spherical harmonics. Show that the radial wavefunction satisfies the equation

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + \frac{1}{2}m\omega^2 r^2\right]R_{Nl}(r) = E_N R_{Nl}(r) .$$
(19)

5.2

Introducing the dimensionless variable $\rho = r/a$, show that

$$\left[-\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho}\right) + \frac{l(l+1)}{\rho^2} + \rho^2 \right] R_{Nl}(a\rho) = (2N+3) R_{Nl}(a\rho) .$$
⁽²⁰⁾

5.3

In the limit $\rho \rightarrow \infty$ show that

$$\frac{d^2}{d\rho^2} e^{-\rho^2/2} \approx \rho^2 e^{-\rho^2/2} \,. \tag{21}$$

Conclude that, in the same limit, $R_{Nl}(a\rho) \sim e^{-\rho^2/2}$ is a solution to the radial Schrödinger's equation.

5.4

In the limit $\rho \to 0$ search for a solution in the form $R_{Nl}(a\rho) \sim \rho^s$, and determine *s*.

5.5

Using the information of the asymptotic limits, one can search for a radial wavefunction in the form

$$R_{Nl}(a\rho) = \rho^l e^{-\rho^2/2} \sum_{k=0} a_k \rho^k \qquad (a_0 \neq 0) .$$
(22)

Plugging this form into the radial Schrödinger's equation, one obtains the recursion relation for the a_k coefficients

$$a_{k+2} = -\frac{2E_N/(\hbar\omega) - (2l+2k+3)}{(k+2)(2l+k+3)} a_k.$$
⁽²³⁾

From this relation (which you do not need to prove!), conclude that, starting from k = 0, the series terminates at $k = 2n_r$ such that $N = 2n_r + l$.

5.6

Show that the possible values for *l* are :

$$- N$$
 even : $l = 0, 2, ..., N$

- N odd: l = 1, 3, ..., N

Calculate the degeneracy of the N-th energy level in the two cases; how does it compare with that found at question 4.2?

5.7

Using the spectroscopic notation Nl (with l = s, p, d, f,... etc. for l = 0, 1, 2, 3, ... - e.g. 2d for N = 2, l = 2) complete the following table for the energy levels and their degeneracy.



6 Spin-orbit coupling

In this final section we consider that the particle immersed in the harmonic potential possesses a spin S = 1/2, and that it is also subject to the spin-orbit interaction – namely its Hamiltonian is $\mathcal{H}' = \mathcal{H} + \mathcal{H}_{SO}$, where

$$\mathscr{H}_{\rm SO} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \boldsymbol{L} \cdot \boldsymbol{S} \,. \tag{24}$$

6.1

Show that $\mathcal{H}_{SO} = AL \cdot S$, and specify the value of the *A* constant.

6.2

We recall that the eigenvalues of the $L \cdot S$ operator are $(\hbar^2/2) [j(j+1) - l(l+1) - S(S+1)]$, where *j* is associated with the eigenvalues of $J^2 = (L + S)^2$. Calculate the spin-orbit corrected eigenvalues

$$E'_{Nlj} = E_N + \Delta E_{lj}^{(SO)} . (25)$$

6.3

Using the spectroscopic notation NL_j (with L=S, P, D, F ... for l = 0, 1, 2, 3, ...) complete the following diagram (with the splittings and the residual level degeneracies) for the spin-orbit-split energy levels of the 3d harmonic oscillator.



Note : the inclusion of spin-orbit coupling in the description of the nucleus is essential to understand the stability of nuclei with special numbers of nucleons, called *magic numbers*.

TD4: Atom-light interaction; Rabi oscillations vs. Fermi's golden rule

We consider an atom immersed in an oscillating electric field in the so-called dipole approximation, with Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{atom}} - \boldsymbol{d} \cdot \boldsymbol{E}(t) \,. \tag{26}$$

Here \mathcal{H}_{atom} is the Hamiltonian of the unperturbed atom, *d* is the electric dipole moment of the atom (d = -er for an hydrogen atom, with *r* is the relative variable), and *E*(*t*) is given by

$$\boldsymbol{E}(t) = \frac{1}{2} \left(\boldsymbol{E}_0 \boldsymbol{e}^{-i\omega t} + \text{c.c.} \right) \,. \tag{27}$$

In this TD we will two different ways of solving for the dynamics of this system.

7 Two-level approximation

L3 SdM, ENS Lyon – UCBL

Atomes et molécules

Out of the complex spectrum of eigenstates of the atom we select only two, the ground state $|g\rangle$ and an excited state $|e\rangle$, and we imagine that the dynamics induced by the external field remains restricted to the Hilbert subspace $H = \{|g\rangle, |e\rangle\}$ (this hypothesis is well verified in many situations). We have that

$$\mathcal{H}_{\text{atom}}|g\rangle = E_g|g\rangle \qquad \mathcal{H}_{\text{atom}}|e\rangle = E_e|e\rangle$$
(28)

7.1

When restricting ourselves to the *H* subspace, we have that $|g\rangle\langle g| + |e\rangle\langle e| = 1$. Therefore, by writing $\mathcal{H} = \mathbb{I}\mathcal{H}\mathbb{I}$ show that

$$\mathcal{H} = E_e |e\rangle \langle e| + E_g |g\rangle \langle g| + \frac{1}{2} \left[\left(\hbar \Omega_{eg} e^{-i\omega t} + \hbar \Omega_{eg}^* e^{i\omega t} \right) |e\rangle \langle g| + \text{h.c.} \right]$$
(29)

where we have introduced the Rabi frequency

$$\Omega_{eg} = -\frac{\boldsymbol{d}_{eg} \cdot \boldsymbol{E}_0}{\hbar} \tag{30}$$

with $d_{eg} = \langle e|d|g \rangle$ the matrix element of the dipole operator – which we assume to be real, namely $d_{eg} = d_{ge}$. h.c. stands for "hermitian conjugate".

7.2

Consider an electric field $E_0 = 1$ V/m. Estimate the Rabi frequency for a transition between two low-energy eigenstates of the hydrogen atom (suggestion : $r \sim a_0$!). How does such a frequency compare to that (ω) of a visible laser?

7.3

Show that the atom Hamiltonian can be rewritten as

$$\mathcal{H}_{\text{atom}} = \frac{E_e - E_g}{2} (|e\rangle \langle e| - |g\rangle \langle g|) + \frac{E_e + E_g}{2} \mathbb{1}.$$
(31)

Introducing the S = 1/2 spin operator

$$S^{z} = \frac{\hbar}{2} \left(|e\rangle \langle e| - |g\rangle \langle g| \right)$$
(32)

rewrite the atom Hamiltonian as

$$\mathcal{H}_{\text{atom}} = \omega_{eg} S^{z} + \text{const.}$$
(33)

where $\omega_{eg} = (E_e - E_g)/\hbar$.

Show that

$$\left[S^{z}, \, \hbar | e \rangle \langle g |\right] = \hbar^{2} | e \rangle \langle g | \,. \tag{34}$$

Therefore we can conclude that $S^+ = \hbar |e\rangle \langle g|$, since we found that it has the same commutation rule with S^z as the spin raising operator, $[S^z, S^+] = \hbar S^+$.

In the following we shall therefore map our two-level atom onto a spin-1/2 spin, with the identification $|\uparrow_z\rangle = |e\rangle$, $|\downarrow_z\rangle = |g\rangle$.

8 Rabi oscillations

The two-level-atom Hamiltonian in the presence of the external field takes therefore the form

$$\mathcal{H} = \omega_{eg}S^{z} + \frac{1}{2}\left[\left(\Omega_{eg}e^{-i\omega t} + \Omega_{eg}^{*}e^{i\omega t}\right)S^{+} + \text{h.c.}\right] + \text{const.}$$
(35)

In the following we shall neglect the constant term, which is irrelevant.

8.1

We want to solve for the dynamics generated by this Hamiltonian. To do so, we move to the rotating frame, which rotates at frequency ω around the *z* axis. This means that, if $|\psi(t)\rangle$ is the solution of the Schrödinger's equation in the "laboratory frame"

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \mathcal{H}|\psi(t)\rangle$$
(36)

the solution in the rotating frame will be

$$|\tilde{\psi}(t)\rangle = U^{\dagger}|\psi(t)\rangle = e^{i\omega S^{z}t/\hbar}|\psi(t)\rangle.$$
(37)

Show that $|\tilde{\psi}(t)\rangle$ is a solution of the Schrödinger's equation

$$i\hbar\frac{d}{dt}|\tilde{\psi}(t)\rangle = \tilde{\mathscr{H}}|\tilde{\psi}(t)\rangle \tag{38}$$

where

$$\tilde{\mathcal{H}} = U^{\dagger} \mathcal{H} U - \omega S^{z} \,. \tag{39}$$

8.2

Justify that $U^{\dagger}S^{z}U = S^{z}$. On the other hand we need to calculate

$$S^{+}(\phi) = e^{iS^{z}\phi/\hbar}S^{+}e^{-iS^{z}\phi/\hbar}.$$
(40)

with $\phi = \omega t$. Show that

$$\frac{dS^+(\phi)}{d\phi} = iS^+(\phi) \tag{41}$$

and then conclude that $U^{\dagger}S^{+}U = S^{+}e^{i\omega t}$.

8.3

Conclude that

$$\tilde{\mathscr{H}} = \Delta S^{z} + \frac{1}{2} \left[\left(\Omega_{eg} + \Omega_{eg}^{*} e^{i2\omega t} \right) S^{+} + \text{h.c.} \right]$$
(42)

where $\Delta = \omega_{eg} - \omega$ is the detuning between the atomic frequency ω_{eg} and the electric-field frequency ω .

In the following we shall apply the so-called "rotating wave approximation" (RWA), which assumes that the rotating term ~ $e^{i2\omega t}$ can be neglected if $\omega \gg \Omega_{eg}$, Δ , because the oscillating term averages to zero during the characteristic time scale of the dynamics induced by the time-independent part of the Hamiltonian.

As a consequence we end up with the time-independent Hamiltonian

$$\tilde{\mathcal{H}}_{\text{RWA}} = \Delta S^{z} + \frac{1}{2} \left(\Omega_{eg} S^{+} + \text{h.c.} \right) .$$
(43)

Assuming for simplicity that $\Omega_{eg} \in \mathbb{R}$, conclude that

$$\tilde{\mathscr{H}}_{\mathrm{RWA}} = \boldsymbol{B} \cdot \boldsymbol{S} \tag{44}$$

where we have introduced the effective "magnetic field" $\boldsymbol{B} = (B_x, B_y, B_z) = (\Omega_{eg}, 0, \Delta)$.

8.4

To diagonalize the Hamiltonian $\tilde{\mathcal{H}}_{RWA}$, we just need to consider that it is the Hamiltonian of a S = 1/2 spin in a magnetic field *B* forming an angle θ with the *z* axis, such that

$$\tan\theta = \frac{|\Omega_{eg}|}{\Delta} \,. \tag{45}$$

The eigenvalues of $\tilde{\mathscr{H}}_{\text{RWA}}$ are $E^{\pm} = \pm \frac{\hbar}{2} \sqrt{\Delta^2 + \Omega_{eg}^2}$ with corresponding eigenstates

$$|+\rangle = \cos(\theta/2)|\uparrow\rangle + \sin(\theta/2)|\downarrow\rangle |-\rangle = \sin(\theta/2)|\uparrow\rangle - \cos(\theta/2)|\downarrow\rangle.$$
(46)

Invert the above relation to express $|\uparrow\rangle$ and $|\downarrow\rangle$ as a function of $|+\rangle$ and $|-\rangle$.

8.5

Let us now consider the initial state $|\psi(0)\rangle = |\tilde{\psi}(0)\rangle = |g\rangle = |\downarrow\rangle$. Show that

$$\langle \uparrow | \tilde{\psi}(t) \rangle = i \sin \theta \sin(E^+ t/\hbar) \tag{47}$$

8.6

Conclude that the probability to excite the atom at time *t* reads

$$P_e(t) = \frac{\Omega_{eg}^2}{\Omega_{eg}^2 + \Delta^2} \sin^2 \left(\frac{\sqrt{\Omega_{eg}^2 + \Delta^2} t}{2} \right).$$
(48)

This is an important formula, describing the so-called Rabi oscillations of the excitation probability.

9 Rabi oscillations vs. Fermi's golden rule

In the lectures we have seen that, if a system is exposed to a time-dependent perturbation

$$\mathscr{H}'(t) = V e^{-i\omega t} + \text{h.c.}$$
(49)

then a transition $|g\rangle \rightarrow |e\rangle$ occurs at a rate

$$\Gamma_{g \to e} = \frac{2\pi}{\hbar^2} \left| \langle e|V|g \rangle \right|^2 \delta(\omega - \omega_{eg}) \,. \tag{50}$$

(the so-called Fermi's golden rule).

We would like to relate this prediction to the above result on Rabi oscillations.

Show that, for the Hamiltonian in Eq. (35), the Fermi's golden rule predicts

$$\Gamma_{e \to g} = \frac{\pi \Omega_{eg}^2}{2} \delta(\omega - \omega_{eg}) \tag{51}$$

9.2

Using the property

$$\frac{\sin^2(\alpha t/2)}{\alpha^2/4} \to 2\pi t \,\delta(\alpha) \qquad (t \to \infty)$$
(52)

show that Eq. (48) leads to Eq. (51) under the assumption $\Delta \gg \Omega_{eg}$ (or, alternatively, to lowest order in a power-series expansion in Ω_{eg}).

TD5: Spontaneous emission; Doppler broadening and fine structure

Useful formulae

Hydrogen radial wavefunctions

$$\mathscr{R}_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$
(53)

$$\mathscr{R}_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{2}{\sqrt{3}} \frac{r}{2a_0} e^{-r/(2a_0)}$$
(54)

Useful integral

$$\int_{0}^{\infty} dy \, y^{n} e^{-ay} = \frac{n!}{a^{n+1}} \tag{55}$$

Spherical harmonics

$$\mathscr{Y}_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}} \qquad \int d\Omega \, \mathscr{Y}_{lm}^* \mathscr{Y}_{l'm'} = \delta_{l,l'} \delta_{m,m'} \tag{56}$$

Useful relations

$$\frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{ma_0} = 2a_0 \text{Ry} \qquad \frac{\text{Ry}}{mc^2} = \frac{\alpha^2}{2}$$
(57)

Fine structure of the hydrogen atom

$$E'_{nj} = E_n \left[1 - \frac{\alpha^2}{n^2} \left(\frac{3}{4} - \frac{n}{j+1/2} \right) \right] \qquad E_n = -\frac{\text{Ry}}{n^2}$$
(58)

10 Decay of $2p \rightarrow 1s$ in hydrogen due to spontaneous emission

The decay rate of the excited 2p level of the hydrogen atom to the 1s ground state by emission of a photon of polarization $\boldsymbol{\epsilon}$ with a frequency ω , a specific wavevector $\boldsymbol{k} = (\omega/c)\hat{k}$, is given within the dipole approximation by the expression

$$\tilde{\Gamma}_{2p\to 1s}(\omega,\hat{\epsilon}) = \frac{2\pi}{\hbar^2} \left(\frac{e\mathscr{E}_0(\omega)}{2}\right)^2 |\langle 21m|(\boldsymbol{\epsilon}\cdot\boldsymbol{r})|100\rangle|^2 \,\delta(\omega-\omega_{2p,1s}) \tag{59}$$

Here $\omega_{2p,1s} = (E_{2p} - E_{1s})/\hbar$ (neglecting fine-structure corrections) and $\mathcal{E}_0(\omega)$ is the amplitude of the ω -frequency component of the electric field.

10.1

When considering the emission process of a photon inside a box of volume V we have that

$$\mathscr{E}_0^2(\omega) = \frac{2\hbar\omega[n(\omega)+1]}{\epsilon_0 V} \,. \tag{60}$$

Justify this expression with the fact that the volume energy density of the e.m. field is $\rho(\omega) = \epsilon_0 \mathcal{E}_0^2/2$, and justify the appearance of the +1 term with the necessity to account for spontaneous emission.

Using a spherical decomposition of the position vector

$$\mathbf{r} = \sqrt{\frac{4\pi}{3}} r \left(\mathscr{Y}_{10} \mathbf{u}_0 + \mathscr{Y}_{11} \mathbf{u}_1 + \mathscr{Y}_{1,-1} \mathbf{u}_{-1} \right)$$
(61)

where $\boldsymbol{u}_0 = \boldsymbol{e}_z$, $\boldsymbol{u}_{\pm 1} = (\boldsymbol{e}_x \pm i \boldsymbol{e}_y)/\sqrt{2}$, show that

$$\langle 21m|\boldsymbol{r}|100\rangle = \frac{24}{3\sqrt{2}} \left(\frac{2}{3}\right)^5 a_0 \boldsymbol{u}_m \,. \tag{62}$$

10.3

Averaging over all possible polarization orientations (or, alternatively, over all possible quantization axes for the hydrogen atom), show that

$$\overline{|\langle 21m|\boldsymbol{r}|100\rangle \cdot \boldsymbol{\epsilon}|^2} = \frac{2^{15}}{3^{11}} a_0^2$$
(63)

10.4

We now study the emission process. Justify that the photon emission rate into any of the electromagnetic field modes is

$$\Gamma_{2p \to 1s} = V \int_0^\infty d\omega \ g(\omega) \ \overline{\tilde{\Gamma}_{2p \to 1s}(\omega, \hat{\epsilon})}$$
(64)

where $g(\omega) = \omega^2 / (\pi^2 c^3)$ is the mode density per unit frequency and volume of the radiation, and $\overline{(...)}$ denotes the average over the polarization orientations.

10.5

Focusing on the spontaneous emission, after a lengthy rearrangement of all the prefactors show that

$$\Gamma_{2p \to 1s} = \left(\frac{2}{3}\right)^8 \alpha^5 \, \frac{mc^2}{\hbar} \tag{65}$$

where $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ is the fine structure constant. Calculate the numerical value and show that it lies in the GHz range.

11 Doppler broadening and spectroscopy of the fine structure

One of the main limitations to the resolution of conventional spectroscopy is represented by the *Doppler broadening* of the transition lines. In this exercise we will examine the impact of such a broadening on the measurement of the fine structure of hydrogen.

We consider a dipole-allowed transition from a lower-energy state $|g\rangle$ with energy E_g to a higher-energy state $|e\rangle$ with energy E_e . The atom can make a $g \rightarrow e$ transition by absorbing a photon with energy $\hbar \omega$ and momentum $\hbar \mathbf{k}$, or a $e \rightarrow g$ transition by emitting the photon. Be \mathbf{p}_i the initial momentum of the atom and \mathbf{p}_f the final one.

11.1

Write down the momentum and energy conservation relations for the absorption and for the emission of the photon.

Deduce that the absorbed/emitted photon has energy

$$\hbar\omega = \hbar\omega_0 + \hbar \boldsymbol{v}_{\rm i} \cdot \boldsymbol{k} \pm E_{\rm rec} \tag{66}$$

where the + sign applies to absorption and – to emission, $\hbar\omega_0 = E_e - E_g$, \boldsymbol{v}_i is the initial velocity of the atom, and $E_{\text{rec}} = \hbar^2 k^2 / (2M)$ is the so-called recoil energy (*M* is the atom mass). What does E_{rec} correspond to physically?

11.3

The $v_i \cdot k$ term is the so-called Doppler shift. Discuss the sign of the shift if the absorbing atom is moving towards/away from the source of the photons.

11.4

Justify that, if $v_i \ll c$, we can write

$$\hbar\omega \approx \hbar\omega_0 \left(1 + \frac{\nu_k}{c}\right) \pm E_{\text{rec}} \left(1 + \frac{\nu_k}{c}\right) + \mathcal{O}((\nu/c)^2) \tag{67}$$

where $v_k = \boldsymbol{v} \cdot \boldsymbol{k} / k$.

11.5

Considering an hydrogen atom, for what frequency is $E_{\text{rec}} \sim \hbar \omega$?

(In the following we will always work under the condition $E_{\rm rec} \ll \hbar \omega$, so that we can neglect the term $E_{\rm rec} v_k / c$).

11.6

We consider a hydrogen cloud, faithfully modeled as a classical ideal gas at room temperature (T = 300 K). The velocity of a single atom in such a cloud follows a Maxwell-Boltzmann distribution

$$P(\boldsymbol{\nu}) = \left(\frac{M}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{M|\boldsymbol{\nu}|^2}{2k_B T}\right]$$
(68)

which is normalized so that $\int d^3 v P(\mathbf{v}) = 1$. Here $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant.

Extract from this distribution the probability $P(v_k)$ for the v_k velocity component, and then the average squared velocity $\sigma_v^2 = \langle v_k^2 \rangle$. Estimate from this a typical order of magnitude for v_k/c .

11.7

Using Eq. (67), calculate the probability $P(\omega)$ for the transition frequency. Why does the absorption / emission line for photons detected along the \mathbf{k} direction reproduce this distribution? Calculate σ_{ω}^2 (the Doppler broadening).

In the following we consider specifically the Doppler broadening of the transitions between the fine-structure multiplets n = 2 and n = 3 of hydrogen.

11.8

Estimate numerically ω_0 , σ_ω and E_{rec} . Comment the results. What kind of radiation can one use to excite this transition?

[*Suggestion* : to compare with the literature values, express (angular) frequencies as $\omega = 2\pi f$, where *f* is the actual frequency].



FIGURE 1 – Doppler-broadened structure of the $(n = 2) \rightarrow (n = 3)$ line. From T. W. Hänsch, A. L. Schawlow and G. W. Series, Scientific American (1979).

Be $E'_{nj} = E_n + \Delta E_{nj}$ the hydrogen energy level with fine-structure corrections. For a transition conserving the *j* quantum number, find the general expression for the transition-line energy $\delta E'_{nj} = E'_{(n+1)j} - E'_{nj}$. Be $\delta E^{(fs)}$ the fine-structure correction to the transition energy $\delta E'_{nj}$. Calculate it explicitly for n = 2, j = 1/2 and for n = 3, j = 3/2. Cite the two transitions with these quantum numbers which are allowed within the dipole approximation.

11.10

Compare the Doppler broadening to the fine-structure splitting between the two above transitions. Is the splitting experimentally observable? Compare with the data in Fig. 1.

TD6: Dipole-allowed transitions; Lamb shift

Useful data

$$\begin{split} & \epsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \\ & m = 9.1 \times 10^{-31} \text{ Kg} \quad (\text{electron mass}) \\ & c = 3 \times 10^8 \text{ m s}^{-1} \\ & h = 6.62 \times 10^{-34} \text{ J s} \quad (\text{Planck's constant}) \\ & a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad (\text{Bohr radius}) \\ & \lambda_c = \frac{\hbar}{mc} \quad (\text{Compton wavelength of the electron}) \\ & \text{Ry} = \frac{e^2}{8\pi\epsilon_0 a_0} \quad (\text{Rydberg energy}) \end{split}$$

12 Transitions between the n = 3 and the n = 4 fine-structure multiplets

We consider the n = 3 and the n = 4 multiplets of the hydrogen atoms.

...

12.1

Organize the fine-structure levels of n = 3 and n = 4 into a table with l on the abscissa and j on the ordinates (below we give the example of the $nS_{1/2}$ level).

$$j = 5/2$$

 $j = 3/2$
 $j = 1/2$ $nS_{1/2}$
 $l = 0$ $l = 1$ $l = 2$

12.2

Draw the allowed transition between the n = 3 and the n = 4 multiplets within the electric-dipole approximation. How many distinct transition lines do you expect to appear?

12.3

CIte at least one transition line which you expect to be split by the Lamb shift.

13 Semiclassical derivation of the Lamb shift

In this exercise we shall explore a semiclassical treatment of the interaction between the electron in the hydrogen atom and the quantum vacuum of the electromagnetic field, leading to a quantitative (albeit approximate) prediction for the Lamb shift. The exercise follows the treatment of T. A. Welton, Phys. Rev. (1948) (following only by

one year the first calculation by H. Bethe) – see also J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics*, McGraw-Hill (1965).

A rigorous treatment of the Lamb shift would require to treat the interaction between a quantized electromagnetic field and the hydrogen atom in its relativistic description (Dirac equation). We will circumvent these technical difficulties by remembering that the model of spontaneous emission we presented in the lectures/TD implied to consider that the *effective* electric field of the blackbody radiation interacting with the atom is $E(\mathbf{r}, t) =$ $\sum_{k,\epsilon} \frac{E_0(\omega_k)}{2} [\epsilon e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_k t)} + \text{c.c.}]$ with

$$E_0(\omega_k) = \sqrt{\frac{2\hbar\omega_k(n(\omega)+1)}{\epsilon_0 V}}$$
(69)

where V is the volume in which the blackbody radiation is contained (in practice, volume of the cell in which the experiment takes place).

Therefore we shall picture (in a very simplistic, yet efficient way) the vacuum of the electromagnetic field, $n(\omega) = 0$, as an electric field

$$\boldsymbol{E}_{\text{vac}}(\boldsymbol{r},t) = \sum_{\boldsymbol{k},\boldsymbol{\epsilon}} \mathscr{E}_0(\omega_{\boldsymbol{k}}) \left[\boldsymbol{\epsilon} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_{\boldsymbol{k}}t)} + \text{c.c.} \right]$$
(70)

with

$$\mathscr{E}_0(\omega_k) = \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}} \,. \tag{71}$$

In principle the above field contains all possible wavevectors \mathbf{k} and corresponding frequencies $\omega_{\mathbf{k}} = c|\mathbf{k}|$, with an amplitude growing as $\sqrt{\omega_{\mathbf{k}}}$. In practice, though, we must remember that in relativistic quantum mechanics the electron is to be thought of as a charge distribution spread over a region of linear size $\sim \lambda_c = \hbar/(mc)$ given by the Compton wavelength. Therefore electric fields with wavelengths smaller than λ_c average to zero over the effective size of the electron. Therefore we can imagine that in practice the sum in Eq. 70 is limited to wavevectors $|\mathbf{k}| \le 2\pi/\lambda_c$.

13.1

Considering the vacuum of the e.m. field in a box volume $V = 1 \text{ m}^3$, estimate the vacuum field amplitude \mathcal{E}_0 for a mode with wavelength $\lambda = \lambda_c$. Compare this electric field with the typical magnitude of that exerted by the proton on the electron at a distance a_0 .

13.2

The Lamb shift results from the agitation of the electron caused by the interaction with the e.m. vacuum. To estimate the spatial amplitude of the motion of the electron under the effect of the e.m. vacuum, we shall treat the motion of the electron within Newton's equations

$$m\frac{d^2\mathbf{r}}{dt^2} = -e\mathbf{E}_{\rm vac}(\mathbf{r},t) .$$
(72)

Writing $\mathbf{r}(t) = \mathbf{r}_0 + \delta \mathbf{r}(t)$, where $\delta \mathbf{r}$ is the displacement caused by the e.m. vacuum field (with $|\delta \mathbf{r}| \ll |\mathbf{r}_0|$), show that, to first order in $\delta \mathbf{r}$

$$m\frac{d^{2}(\delta \boldsymbol{r})}{dt^{2}} = -e\sum_{\boldsymbol{k},\boldsymbol{\epsilon}}\mathscr{E}_{0}(\omega_{\boldsymbol{k}})\left[\boldsymbol{\epsilon}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}_{0}-\omega_{\boldsymbol{k}}t)} + \text{c.c.}\right] + \mathscr{O}(\delta r)^{2}.$$
(73)

13.3

Taking the Fourier decomposition of $\delta r(t)$

$$\delta \boldsymbol{r}(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} \,\delta \boldsymbol{r}_{\omega} \tag{74}$$

and using the fact that

$$\int dt \ e^{i(\omega-\omega')t} = 2\pi\delta(\omega-\omega') \tag{75}$$

show that

$$\int dt \ e^{i\omega t} \ m \frac{d^2(\delta \mathbf{r})}{dt^2} = -m\omega^2 \delta \mathbf{r}_{\omega} \ . \tag{76}$$

Conclude therefore that

$$\delta \boldsymbol{r}_{\omega} = \sum_{\boldsymbol{k},\boldsymbol{\epsilon}} \frac{e\mathscr{E}_{0}(\omega_{\boldsymbol{k}})}{m\omega_{\boldsymbol{k}}^{2}} (2\pi) \left[\boldsymbol{\epsilon} \ e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{0}}\delta(\omega-\omega_{\boldsymbol{k}}) + \boldsymbol{\epsilon}^{*} \ e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_{0}}\delta(\omega+\omega_{\boldsymbol{k}}) \right] \,. \tag{77}$$

13.4

Using the Fourier decomposition of $\delta r(t)$, show that :

$$\delta \boldsymbol{r}(t) \approx \sum_{\boldsymbol{k},\boldsymbol{\epsilon}} \frac{e\mathcal{E}_0(\omega_{\boldsymbol{k}})}{m\omega_{\boldsymbol{k}}^2} \left(\boldsymbol{\epsilon} \ e^{i(\boldsymbol{k}\cdot\boldsymbol{r}_0 - \omega_{\boldsymbol{k}}t)} + \text{c.c.}\right)$$
(78)

We have already commented that $k < k_{\text{max}} = 2\pi/\lambda_c$. On the other hand, if $k < 2\pi/a_0$ with a_0 the Bohr radius, such a field component is essentially uniform over the typical scale of the hydrogen atom. Such a field can only pull the electron and the nucleus in opposite directions, but given that it is so much smaller than the Coulomb field exerted by the nucleus on the electron and viceversa, we shall neglect it. Therefore in the following we consider that $\sum_k \rightarrow \sum_{k:k_{\min} \le k \le k_{\max}}$ with $k_{\min} = 2\pi/a_0$.

Conclude that $\overline{\delta r} \approx 0$, where $\overline{(...)}$ denotes the temporal average.

13.5

Therefore, we shall estimate the electron displacement as $\overline{(\delta r)^2}$. Show that

$$\overline{(\delta \boldsymbol{r})^2} = \sum_{\boldsymbol{k},\boldsymbol{\epsilon}} \frac{e^2 \hbar}{2m^2 \omega_{\boldsymbol{k}}^3 \epsilon_0 V} \sum_{\boldsymbol{k}':\boldsymbol{k}'=\boldsymbol{k};\boldsymbol{\epsilon}'} \left(e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}_0} \boldsymbol{\epsilon} \cdot (\boldsymbol{\epsilon}')^* + \text{h.c.} \right).$$
(79)

We shall assume that in the last sum only the terms with $\mathbf{k}' = \mathbf{k}, \mathbf{\epsilon}' = \mathbf{\epsilon}$ survive. Conclude then on the form of $(\delta \mathbf{r})^2$.

13.6

When V is a macroscopic volume, we can take the integral approximation

$$\frac{1}{V}\sum_{k} \rightarrow \int \frac{d^{3}k}{(2\pi)^{3}} = \int d\Omega \int \frac{dk}{(2\pi)^{3}} k^{2} .$$

$$\tag{80}$$

Conclude that

$$\overline{(\delta \mathbf{r})^2} = \frac{4\alpha}{\pi} \log\left(\frac{1}{\alpha}\right) \lambda_c^2$$
(81)

where $\alpha = \lambda_c / a_0 \approx 1/137$ is the fine structure constant.

13.7

Let us recall for a moment the relativistic correction called the "Darwin term", that we discussed in the lectures. You may remember that it originated phenomenologically from the fact that the electron must be thought of as delocalized over a length scale λ_c . As a consequence, the Coulomb potential between the electron and the nucleus must be rewritten as

$$V_{\rm eff}(r) = V(r) + \Delta V_D(r) \qquad V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \qquad \Delta V_D(r) = \frac{1}{6}\lambda_c^2 \nabla^2 V(r) = \frac{1}{6}\frac{e^2}{\epsilon_0}\lambda_c^2 \delta(r) \tag{82}$$

Within our treatment, the Lamb shift has a similar origin, resulting from a correction to the Coulomb potential $\Delta V_{\text{Lamb}}(r)$. Write $\Delta V_{\text{Lamb}}(r)/\Delta V_D(r)$, which provides an estimate the magnitude of the Lamb shift with respect to the relativistic corrections to the hydrogen atom.

Within a perturbative treatment, justify why the Lamb shift leads to the following shift of the energy levels

$$\Delta E_{nl}^{(\text{Lamb})} \approx \frac{2}{3\pi} \frac{e^2}{\epsilon_0} \lambda_c^2 \alpha \log\left(\frac{1}{\alpha}\right) \left|\psi_{n00}(0)\right|^2 \delta_{l,0}$$
(83)

where $\psi_{nlm}(\mathbf{r})$ are the hydrogen-atom orbitals within Schrödinger's theory.

13.9

Given that $|\psi_{n00}(0)|^2 = (\pi n^3 a_0^3)^{-1}$ show that

$$\Delta E_{nl}^{(\text{Lamb})} \approx \frac{16}{3\pi} \frac{|E_n|}{n} \alpha^3 \log\left(\frac{1}{\alpha}\right) \delta_{l,0}$$
(84)

where $E_n = -\text{Ry}/n^2$.

13.10

Taking n = 2, estimate numerically the Lamb shift $\Delta E_{2s}^{(\text{Lamb})}/h$ of the 2s orbital. Is it comparable with the experimentally measured value $\Delta E_{2s}^{(\text{Lamb})}/h = 1040 \text{ MHz}$?

Note : this calculation contains very crude approximations, but the final result justifies them a posteriori!

TD7: Wigner-Eckart theorem; Zeeman effect in the hydrogen atom (I)

Useful data

$$\langle r^2 \rangle_{nl} \sim n^4 a_0^2 \qquad \left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{1}{n^3 a_0^3 l(l+1)(l+1/2)}$$
 (85)

Spin-orbit correction to the unperturbed hydrogen atom levels

$$\Delta E_{nlj}^{(SO)} / \text{Ry} = \frac{1}{2} \beta_{nl} \left[j(j+1) - l(l+1) - s(s+1) \right]$$

$$\beta_{nl} = \frac{\alpha^2}{n^3} \frac{1}{l(l+1)(l+1/2)}$$
(86)

14 Application of the Wigner-Eckart theorem : the projection theorem

In the lectures we have seen the Wigner-Eckart theorem for vector operators $V = (V_{-1}, V_0, V_1)$, where $V_a = V \cdot e_a$ $(q = 0, \pm 1), e_0 = e_z$ and $e_{\pm 1} = (e_x \pm i e_y)/\sqrt{2}$:

$$\langle \gamma' j' m' | V_q | \gamma j m \rangle = \langle \gamma' j' | | V | | \gamma j \rangle C^{1j}_{am;j'm'}$$
(87)

Here $|\gamma jm\rangle$ are angular momentum eigenstates (joint eigenstates of J^2 and J^z with $J^2 |\gamma jm\rangle = \hbar^2 j(j+1) |\gamma jm\rangle$ and $J^{z}|\gamma jm\rangle = \hbar m |\gamma jm\rangle$, and γ denotes further quantum number; moreover

$$C^{1j}_{qm;j'm'} = \langle jm; 1q | j1; j'm' \rangle \tag{88}$$

is the Clebsch-Gordan coefficient for the basis change from the basis $|jm;1q\rangle$ for two separate angular momenta with length *j* and 1, to the basis $|j1; j'm'\rangle$ for the sum of the two.

In this exercise we would like to apply the Wigner-Eckart theorem to a special case, namely the calculation of the matrix element of the kind $\langle \gamma j m' | V_q | \gamma j m \rangle$ $(j = j', \gamma = \gamma')$. In the following we will denote these matrix elements as $\langle jm'|V_q|jm\rangle$ for brevity.

14.1

Consider the generic vector operator V and the angular momentum operator J. Applying the Wigner-Eckart theorem to both V_q and J_q show that

$$\langle jm'|V_q|jm\rangle = K_V^{(j)}\langle jm'|J_q|jm\rangle \tag{89}$$

where $K_V^{(j)}$ is a proportionality factor to be specified (independent of q, m or m').

14.2

Show that

$$\langle jm|\boldsymbol{J}\cdot\boldsymbol{V}|jm\rangle = K_V^{(j)}\hbar^2 j(j+1)$$
(90)

and deduce therefore an explicit expression for $K_V^{(j)}$ – valid if j > 0. *Suggestion*: use the property that $\sum_m |jm'\rangle\langle jm'| = \mathbb{I}_j$, where \mathbb{I}_j is the identity for the Hilbert subspace spanned by the states at fixed *j*.

The scalar product $J \cdot V$ is invariant under rotations, in particular under the rotations generated by the J^z operator, $U(\phi) = \exp(-i\phi J^z/\hbar)$. Since $U^{\dagger}(\phi)(J \cdot V)U(\phi) = J \cdot V$, justify that $[J \cdot V, J^z] = 0$, and that $\langle jm' | J \cdot V | jm \rangle \sim \delta_{mm'}$. Conclude that

$$\langle jm'|\boldsymbol{J}\cdot\boldsymbol{V}|jm'\rangle\langle jm'|J_q|jm\rangle = \langle jm'|(\boldsymbol{J}\cdot\boldsymbol{V})J_q|jm\rangle$$
(91)

14.4

Justify that

$$\langle jm'|V_q|jm\rangle = \frac{\langle jm'|(\boldsymbol{V}\cdot\boldsymbol{J})J_q|jm\rangle}{\hbar^2 j(j+1)}$$
(92)

or, in vector form

$$\langle jm'|\mathbf{V}|jm\rangle = \frac{\langle jm'|(\mathbf{V}\cdot\mathbf{J})\mathbf{J}|jm\rangle}{\langle jm|\mathbf{J}^2|jm\rangle}$$
(93)

(the so-called projection theorem).

14.5

One can give a semiclassical interpretation of the above result. Consider a classical particle moving along a circular orbit, with orbital angular momentum *L*. Justify that its position vector averaged over its circular motion is

$$\overline{r} = \frac{(r \cdot L)L}{L^2} . \tag{94}$$

15 Coupling of a uniform magnetic field to the hydrogen atom

We investigate the general Hamiltonian for the hydrogen atom in a magnetic field which is uniform over the atomic size :

$$\mathcal{H} = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + \mathcal{H}_{\text{rel}}$$
(95)

where $A = \frac{1}{2}(B \times r)$ is the vector potential associated with the uniform field $B = B u_z$ in the so-called circular gauge, and \mathcal{H}_{rel} contains the relativistic corrections to the Hamiltonian.

15.1

Show that

$$\frac{(\boldsymbol{p}+e\boldsymbol{A})^2}{2m} = \frac{p^2}{2m} + \frac{\mu_B}{\hbar} \boldsymbol{L} \cdot \boldsymbol{B} + \frac{e^2}{8m} (\boldsymbol{B} \times \boldsymbol{r})^2$$
(96)

where *L* is the angular momentum operator and $\mu_B = e\hbar/(2m)$ is the Bohr magneton. Do you understand physically the mechanism that couples the magnetic field to the orbital angular momentum?

15.2

In the following we will only consider the linear term in the magnetic field (*linear* Zeeman effect). Show that the ratio between the quadratic term in *B* and the linear one scales as

$$\frac{E_{\text{quad}}}{E_{\text{lin}}} \sim n^4 \frac{B}{B_0} \tag{97}$$

where $B_0 = \hbar/(ea_0^2)$ is the magnetic field which threads two flux quanta $\Phi_0 = h/e$ through a circumference of radius a_0 . Given that laboratory magnetic fields are typically limited to $B \leq 10$ T, and if one focuses on levels with $n \sim 1$, is it justified to neglect the quadratic term?

The relativistic terms in the Hamiltonian contain a further field-dependent term, which appears naturally in the Dirac equation. It couples the electronic spin to the magnetic field - revealing that there is a magnetic moment associated with the spin, $m = g\mu_B S/\hbar$ with g = -2 (valid in Dirac's theory – in fact $g \approx -2$ when dealing with the full theory including the e.m. field, namely quantum electrodynamics).

The Hamiltonian including all magnetic field terms (up to linear order in B) and spin-dependent terms reads

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{SO}}$$
(98)

$$\mathcal{H}_0 = \frac{p^2}{2m} + V(r) \tag{99}$$

$$\mathcal{H}_{\text{Zeeman}} = \frac{\mu_B B}{\hbar} (L^z + 2S^z)$$
(100)

$$\mathcal{H}_{SO} = \xi(r) \boldsymbol{L} \cdot \boldsymbol{S} \tag{101}$$

Here $\xi(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr}$. The magnetic field term is called the Zeeman coupling. Focusing on the case $n \sim 1$, give an estimate of the spin-orbit correction $\Delta E^{(SO)}$ (*e.g.* using the spin-orbit splitting of the unperturbed energy levels). Find which values of the magnetic field give a Zeeman coupling which is much stronger than the spin-orbit coupling. Justify why the two terms (Zeeman coupling and spin-orbit coupling) cannot be treated simultaneously in a simple way.



FIGURE 2 - Emission from an hydrogen atom in a magnetic field.

Strong field : normal Zeeman effect 16

16.1

We now focus on the situation in which the magnetic field is much stronger than the spin-orbit coupling. Draw a level diagram describing the splitting of the n = 1 and n = 2 levels due to the Zeeman coupling, and specify the residual degeneracy of the energy levels (called Zeeman sublevels). How many transition frequencies between the n = 1 and the n = 2 multiplets do you expect to appear?

16.2

A special feature of the Zeeman effect is that the magnetic field breaks the symmetry of space, and it fixes the quantization axis. One of the consequences is that the emission spectrum varies with the direction of observation (see Fig. 1). Remembering that the polarization of light is completely transverse to the propagation, what is the polarization of the photons which are emitted along the field axis? And what is the polarization of the photons emitted in the equatorial plane transverse to the field?

16.3

Justify the fact that the emission spectrum detected in the equatorial plane has *three* spectral lines, while the emission spectrum detected along the field axis has only *two* lines.

To be continued in TD no. 8 ...

TD8: Zeeman effect in hydrogen and alkali atoms (II)

Useful data

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{1}{n^3 a_0^3 l(l+1)(l+1/2)}$$
 (102)

Spin-orbit correction to the unperturbed hydrogen atom levels

$$\Delta E_{nlj}^{(SO)} / \text{Ry} = \frac{1}{2} \beta_{nl} \left[j(j+1) - l(l+1) - s(s+1) \right]$$

$$\beta_{nl} = \frac{\alpha^2}{n^3} \frac{1}{l(l+1)(l+1/2)}$$
(103)

17 Intermediate field : the Paschen-Back effect

If the field is not too strong compared to the spin-orbit coupling, the latter can be treated as a perturbation to the Hamiltonian $\mathcal{H}_0 + \mathcal{H}_{Zeeman}$.

17.1

Using the fact that

$$\boldsymbol{L} \cdot \boldsymbol{S} = L^{z} S^{z} + \frac{1}{2} \left(L^{+} S^{-} + L^{-} S^{+} \right)$$
(104)

show that \mathcal{H}_{SO} is diagonal on the degenerate states of the Zeeman sublevels.

17.2

Conclude that the spin-orbit correction to the Zeeman sublevels reads

(0.0)

$$\frac{\Delta E_{nlmm_s}^{(SO)}}{\text{Ry}} = \frac{\alpha^2}{n^3 l(l+1)(l+1/2)} \ m \ m_s \,. \tag{105}$$

Is this term splitting the Zeeman sublevels of n = 2?

18 Weak fields : the anomalous Zeeman effect

When the field is weaker that the spin-orbit coupling, we can treat $\mathcal{H}_{\text{Zeeman}}$ as a perturbation of $\mathcal{H}_0 + \mathcal{H}_{\text{SO}}$.

18.1

Introducing the total angular momentum J = L + S, describe shortly why the eigenstates $|nlS; jm_j\rangle$ are appropriate to treat the SO coupling.

Using degenerate perturbation theory to treat $\mathcal{H}_{\text{Zeeman}}$, we need to calculate matrix elements of the form $\langle nlS; jm_j | (L^z + 2S^z) | nlS; jm'_i \rangle$. Writing $L^z + 2S^z = J^z + S^z$, use the Wigner-Eckart theorem to show that

$$\langle nlS; jm_j | (L^z + 2S^z) | nlS; jm'_j \rangle = \left(1 + \frac{j(j+1) + S(S+1) - l(l+1)}{2j(j+1)} \right) \hbar m_j \,\delta_{m_j, m'_j} \tag{106}$$

Conclude that, within each fine-structure sublevel labeled by the quantum numbers *n*, *l*, *S* and *j*, the Zeeman coupling acts in the same way as the Hamiltonian

$$\mathscr{H}_{\rm eff} = \frac{g_{lsj}}{\hbar} \,\mu_B B J^z \tag{107}$$

where

$$g_{lsj} = 1 + \frac{j(j+1) + S(S+1) - l(l+1)}{2j(j+1)}$$
(108)

is the so-called Landé factor.

18.3

Draw a diagram with the Zeeman splitting of the fine-structure multiplet of hydrogen with n = 2. How many Zeeman sublevels does it contain?

19 Landé g-factor and hyperfine structure

This last exercise concerns the splitting of hyperfine levels under the effect of a magnetic field. We shall consider the weak-field case, in which the magnetic field is a perturbation to the hyperfine coupling between electron and nuclear spin.

The coupling between the magnetic field and the electronic and nuclear angular momenta reads

$$\mathcal{H}_{Z} = \frac{\mu_{B}B}{\hbar} (J^{z} + S^{z}) - \frac{g_{p}\mu_{N}B}{\hbar} I^{z}$$
(109)

where $g_p = 5.59$ is the gyromagnetic factor of the proton, $\mu_N = e\hbar/(2m_p)$ is the nuclear Bohr magneton, and I^z is the *z*-component of the nuclear spin.

19.1

In the lectures we have seen that the typical strength of the hyperfine interactions is given by

$$E_{\rm HF}/{\rm Ry} \approx (m_e/m_p)\alpha^2$$
.

Estimating the magnitude of the Zeeman energy as $E_Z \approx \mu_B B$, how small should the magnetic field be to be treated as a perturbation?

Within degenerate perturbation theory, our goal is to calculate the perturbation matrix

$$\langle nlS; jI; Fm'_F | \mathcal{H}_Z | nlS; jI; Fm_F \rangle$$

(for F > 0) and to diagonalize it. We shall treat the three terms (proportional to J^z , S^z and I^z) separately, using over and over the projection theorem for vector operators V

$$\langle \gamma F m'_F | V^Z | \gamma F m_F \rangle = \frac{\langle \gamma F m'_F | (\mathbf{F} \cdot \mathbf{V}) F^Z | \gamma F m_F \rangle}{\hbar^2 F (F+1)} \qquad \langle \gamma j m'_j | V^Z | \gamma j m_j \rangle = \frac{\langle \gamma j m'_j | (\mathbf{J} \cdot \mathbf{V}) J^Z | \gamma j m_j \rangle}{\hbar^2 j (j+1)} \tag{110}$$

Prove the following relationships

$$F \cdot J = \frac{1}{2} (F^2 + J^2 - I^2)$$

$$F \cdot I = \frac{1}{2} (F^2 + I^2 - J^2)$$

$$J \cdot S = \frac{1}{2} (J^2 + S^2 - L^2)$$
(111)

19.3

Prove that

$$\langle nlS; jI; Fm'_F | J^Z | nlS; jI; Fm_F \rangle = \frac{1}{2} \frac{F(F+1) + j(j+1) - I(I+1)}{F(F+1)} \hbar m_F \,\delta_{m_F, m'_F} \,. \tag{112}$$



FIGURE 3 – Zeeman sublevels in ⁸⁷Rb.

20 Zeeman splitting of Rubidium

Rubidium's most common isotope ⁸⁷Rb is an hydrogen-like atom with nuclear spin I = 3/2. We shall regard it in the following as a hydrogen atom with a larger nuclear spin.

20.1

Prove that

$$\langle nlS; jI; Fm'_{F}|S^{Z}|nlS; jI; Fm_{F}\rangle = \frac{1}{2} \frac{j(j+1) + S(S+1) - l(l+1)}{j(j+1)} \langle nlS; jI; Fm'_{F}|J^{Z}|nlS; jI; Fm_{F}\rangle$$
(113)

and conclude therefore that

$$\langle nlS; jI; Fm'_F | J^Z + S^Z | nlS; jI; Fm_F \rangle = \frac{1}{2} g_{ISj} \frac{F(F+1) + j(j+1) - I(I+1)}{F(F+1)} \hbar m_F \,\delta_{m_F,m'_F} \,. \tag{114}$$

Suggestion : use the fact that

$$|nlS; jI; Fm_F\rangle = \sum_{m_j, m_I} C^{jI}_{m_j m_I; Fm_F} |nlS; jm_j\rangle \otimes |Im_I\rangle .$$
(115)

20.2

Prove that

$$\langle nlS; jI; Fm'_F | I^Z | nlS; jI; Fm_F \rangle = \frac{1}{2} \frac{F(F+1) + I(I+1) - j(j+1)}{F(F+1)} \hbar m_F \,\delta_{m_F, m'_F} \,. \tag{116}$$

20.3

The Zeeman splitting of the hyperfine levels reads therefore

$$\Delta E_{lSjFm_F}^Z = g_{lSjIF} \,\mu_B \,B \,m_F \,. \tag{117}$$

Give the expression of the hyperfine Landé factor g_{ISjIF} .

20.4

What are the possible values of *F* in the ground-state multiplet? On the basis of what you have learned in the lectures, can you say which value of *F* corresponds to the hyperfine ground state?

20.5

On the basis of what you have learnt in this TD, try to make sense of the following diagram : what do the low-field regime and high-field regime correspond to?

TD9: N-electron atoms

21 Hartree-Fock equation for the ground-state of Helium

Consider two electrons in an atom with nuclear charge Z, with Hamiltonian

$$\mathscr{H} = -\frac{\hbar^2}{2m} \left(\nabla_1^2 + \nabla_2^2 \right) + \frac{e^2}{4\pi\epsilon_0} \left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right).$$
(118)

During the lecture we have seen that, assigning to a two-electron atom the Slater-determinant wavefunction

$$\Psi(\mathbf{r}_{1},\sigma_{1};\mathbf{r}_{2},\sigma_{2}) = \frac{1}{\sqrt{2}} \begin{bmatrix} \phi_{a}(\mathbf{r}_{1})\chi_{a}(\sigma_{1}) \phi_{b}(\mathbf{r}_{2})\chi_{b}(\sigma_{2}) - \phi_{b}(\mathbf{r}_{1})\chi_{b}(\sigma_{1}) \phi_{a}(\mathbf{r}_{2})\chi_{a}(\sigma_{2}) \end{bmatrix} \\ = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{a}(\mathbf{r}_{1})\chi_{a}(\sigma_{1}) & \phi_{a}(\mathbf{r}_{2})\chi_{a}(\sigma_{2}) \\ \phi_{b}(\mathbf{r}_{1})\chi_{b}(\sigma_{1}) & \phi_{b}(\mathbf{r}_{2})\chi_{b}(\sigma_{2}) \end{vmatrix}$$
(119)

and minimizing the functional

$$E[\phi_{a},\phi_{b}] = \sum_{\sigma_{1},\sigma_{2}} \int d^{3}r_{1}d^{3}r_{2}\Psi^{*}(\mathbf{r}_{1},\sigma_{1};\mathbf{r}_{2},\sigma_{2}) \mathcal{H}\Psi(\mathbf{r}_{1},\sigma_{1};\mathbf{r}_{2},\sigma_{2}) - \lambda_{a} \int d^{3}r|\phi_{a}(\mathbf{r})|^{2} - \lambda_{b} \int d^{3}r|\phi_{b}(\mathbf{r})|^{2}$$
(120)

with respect to the orbitals ϕ_a , ϕ_b (while keeping the spin states χ_a , χ_b fixed), one obtains the Hartree-Fock equations

$$\left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{Z e^2}{4\pi\epsilon_0 r} + \int d^3 r' \frac{e^{2} |\phi_b(\mathbf{r}')|^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}\right) \phi_a(\mathbf{r}) - \delta_{\chi_a,\chi_b} \left(\int d^3 r' \frac{e^2 \phi_b^*(\mathbf{r}') \phi_a(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}\right) \phi_b(\mathbf{r}) = \lambda_a \phi_a(\mathbf{r}) \quad (121)$$

$$\left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{Z e^2}{4\pi\epsilon_0 r} + \int d^3 r' \frac{e^2 |\phi_a(\mathbf{r}')|^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}\right) \phi_b(\mathbf{r}) - \delta_{\chi_a,\chi_b} \left(\int d^3 r' \frac{e^2 \phi_a^*(\mathbf{r}') \phi_b(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}\right) \phi_a(\mathbf{r}) = \lambda_b \phi_b(\mathbf{r}) . \quad (122)$$

In this exercise, we will consider the special case of the ground state of Helium, for which we shall choose $\phi_a(\mathbf{r}) = \phi_b(\mathbf{r}) = \phi(|\mathbf{r}|)$ (*s*-wave).

21.1

We assume that $\int d^3 r |\phi(|\mathbf{r}|)|^2 = 1$. Rewriting the Slater determinant in Eq. (119) for the special choice of orbitals, show that, if χ_a is orthogonal to χ_b – namely if $\sum_{\sigma} \chi_a^*(\sigma) \chi_b(\sigma) = 0$ – then the two-electron state is properly normalized :

$$\sum_{\sigma_1,\sigma_2} \int d^3 r_1 d^3 r_2 |\Psi(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2)|^2 = 1.$$
(123)

21.2

Show that under these assumptions the Hartree-Fock equations reduce to the single (Hartree) equation

$$\left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} + \int d^3 r' \frac{e^2 |\phi(\mathbf{r}')|^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}\right) \phi(\mathbf{r}) = \lambda \phi(\mathbf{r}) .$$
(124)

Can you recognize the appearance a self-consistent screening potential $S(\mathbf{r})$ adding up to the Coulomb potential of the nucleus?

In the following we would like to prove that the screening potential has spherical symmetry. Consider the rotation *R* defining new integration coordinates $\rho' = Rr'$. Given that the Jacobian of a rotation is unity, we have that

$$I(\mathbf{r}) = \int d^3 r' \frac{|\phi(r')|^2}{|\mathbf{r} - \mathbf{r}'|} = \int d^3 \rho' \frac{|\phi(|R^{-1} \boldsymbol{\rho}'|)|^2}{|\mathbf{r} - R^{-1} \boldsymbol{\rho}'|} = \int d^3 \rho' \frac{|\phi(\rho')|^2}{|R^{-1} \boldsymbol{\rho} - R^{-1} \boldsymbol{\rho}'|} \,. \tag{125}$$

Conclude that $I(\mathbf{r}) = I(\mathbf{\rho})$, so that I = I(r) with $r = |\mathbf{r}|$.

21.4

More in detail, one can write $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$ as

$$\frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_{<}^{l}}{r_{>}^{l+1}} \mathscr{Y}_{lm}(\theta, \phi) \mathscr{Y}_{lm}(\theta', \phi')$$
(126)

with $r_{<} = \min(r, r')$ and $r_{>} = \max(r, r')$.

Writing $\phi(\mathbf{r}) = \Re(r)/\sqrt{4\pi}$, with $\int dr r^2 |\Re(r)|^2 = 1$, conclude that

$$I(\mathbf{r}) = \int dr'(r')^2 \frac{|\mathscr{R}(r')|^2}{\max(r,r')} \,. \tag{127}$$

Write the self-consistent Hartree equation for $\mathscr{R}(r)$. Suggestion : $\int \sin\theta d\theta d\phi \mathscr{Y}_{lm}(\theta,\phi) = \sqrt{4\pi} \,\delta_{l,0} \delta_{m,0}$.

21.5

Let us assume that $\Re(r) \approx 0$ for $r > r_0$. Conclude that, for $r > r_0$

$$S(r) = \frac{e^2}{4\pi\epsilon_0} I(r) \approx \frac{e^2}{4\pi\epsilon_0 r} .$$
(128)

Hence conclude on the screening effect of the nucleus at large distance.

Note : the result encountered in this exercise is just a special case of a more general result, valid for *N*-electron atoms with fully filled electronic shells. Indeed, if the outer shell of the electronic structure is fully filled (such as in the case of He), it can be shown that the self-consistent potential terms in the Hartree-Fock equations (those involving integrals of the orbitals ϕ_a , ϕ_b etc.) acquire spherical symmetry. This result offers therefore a mathematical justification for the central-field approximation.

22 Slater determinants vs. eigenstates of S^2

In the lectures the perturbed eigenstates of Helium have been expressed as eigenstates of the total spin operator S^2 with $S = S_1 + S_2$. Here we would like to remark that these states do *not* correspond in general to Slater determinants.

22.1

Consider the two orthogonal orbital and spin eigenstates $\psi_{n_1 l_1 m_1}(\mathbf{r})\chi_{m_{s_1}}(\sigma)$ and $\psi_{n_2 l_2 m_2}(\mathbf{r})\chi_{m_{s_2}}(\sigma)$, out of which we build the Slater determinant

$$\Psi(\mathbf{r}_{1},\sigma_{1};\mathbf{r}_{2},\sigma_{2}) = \frac{1}{\sqrt{2}} \left(\psi_{n_{1}l_{1}m_{1}}(\mathbf{r}_{1})\chi_{m_{s_{1}}}(\sigma_{1})\psi_{n_{2}l_{2}m_{2}}(\mathbf{r}_{2})\chi_{m_{s_{2}}}(\sigma_{2}) - \psi_{n_{2}l_{2}m_{2}}(\mathbf{r}_{1})\chi_{m_{s_{2}}}(\sigma_{1})\psi_{n_{1}l_{1}m_{1}}(\mathbf{r}_{2})\chi_{m_{s_{1}}}(\sigma_{2}) \right).$$
(129)

Justify that this state is an eigenstate of $L^z = L_1^z + L_2^z$ and of $S^z = S_1^z + S_2^z$, and give the corresponding eigenvalues.

On the other hand, justify that eigenstates of S^2 must be of the form

$$\Phi(\mathbf{r}_{1},\sigma_{1};\mathbf{r}_{2},\sigma_{2}) = \mathcal{N}\left(\psi_{n_{1}l_{1}m_{1}}(\mathbf{r}_{1})\psi_{n_{2}l_{2}m_{2}}(\mathbf{r}_{2}) \pm \psi_{n_{2}l_{2}m_{2}}(\mathbf{r}_{1})\psi_{n_{1}l_{1}m_{1}}(\mathbf{r}_{2})\right)\left(\chi_{m_{s1}}(\sigma_{1})\chi_{m_{s2}}(\sigma_{2}) \mp \chi_{m_{s2}}(\sigma_{1})\chi_{m_{s1}}(\sigma_{2})\right)$$
(130)

where $\ensuremath{\mathcal{N}}$ is a normalization factor.

22.3

Considering $(n_1 l_1 m_1) = (100)$ and $(n_2 l_2 m_2) = (21m)$, show that the excited state 2 ¹P of the He atom is written as the sum of *two* Slater determinants.

Reminder : this state is eigenstate of the total spin with quantum number S = 0, so that 2S + 1 = 1.

23 Total angular momentum of Boron in its ground state

Consider the Boron (B) atom (Z = 5), whose ground-state electronic structure is $1s^2 2s^2 2p^1$.

23.1

To the electronic structure above correspond 2(2l+1) degenerate states. Assuming for a moment that the outer electron on the 2p shell is distinguishable from the others, write the possible eigenvalues (m, m_s) of its orbital (L^z) and spin (S^z) angular momentum.

23.2

What are the possible values of the *total* orbital angular momentum $L^z = \sum_i L_i^z$ and *total* spin angular momentum $S^z = \sum_i S_i^z$ of the electrons ?

23.3

Conclude that each of the degenerate ground states, corresponding to different occupied orbitals and spin states of the outer electron, are also eigenstates of L^2 and S^2 with corresponding eigenvalues $\hbar^2 L(L+1)$ and $\hbar^2 S(S+1)$ with L = 1, S = 1/2.



TD10: N-electron atoms (II)

FIGURE 4 – Ionization energy as a function of the atomic number Z.

24 Ionization energy and *e*-*e* interaction effects

24.1

The ionization energy E_i is the minimal energy necessary to extract one electron from an atom. Neglecting the electron-electron interaction in *N*-electron atoms, reconstruct the dependence of E_i on the atomic number *Z*.

24.2

Plot the ionization energy E_i as a function of the atomic number *Z*. Shows that is has peaks for Z = 2, 10, 28, etc.

24.3

The actual plot of the ionization energy of the atoms as a function of the their atomic number is shown in the figure. Comparing with the result of your plot, can you comment on some of the effects of *e*-*e* interaction?

25 Particle-hole symmetry for the *LS* terms

In the lectures we have reconstructed the *LS* terms (possible values of *L* and *S*) for the ground-state electronic configuration of C, namely for the electronic configuration $1s^2 2s^2 2p^2$.

We now consider the ground-state electronic configuration of O, namely 1s² 2s² 2p⁴.

25.1

Focusing on the four outer electrons, draw the possible distributions of the electrons on the 2p orbitals, in the form of diagrams like $\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$, $\uparrow \downarrow \uparrow \uparrow \uparrow \downarrow \uparrow$ etc. How many states do you expect on the basis of the degeneracy of the orbitals and of the Pauli principle? And can you find all the corresponding configurations?

Associate to each *electron* configuration a *hole* configuration, for instance : $\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\downarrow$ \leftrightarrow $\uparrow\downarrow$, etc. Convince yourself that the correspondence between 4-electron configurations and 2-hole configurations is unique.

25.3

Defining the total orbital angular momentum $L = \sum_i L_i$ and total spin $S = \sum_i S_i$ for both the electrons and the holes, show that, for each pair of configurations of electrons and holes as defined above, $S_{\text{electrons}}^z = -S_{\text{holes}}^z$ and $L_{\text{electrons}}^z = -L_{\text{holes}}^z$.

25.4

Conclude that C and O have the same LS terms.

26 Spin-orbit coupling in Titanium

We study the spectroscopy of Titanium (Z = 22), with a ground-state electronic configuration

 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

26.1

Reconstruct the LS spectral terms.

26.2

Applying Hund's rules, order the LS terms in energy (ground-state term, first excited term, etc.).

We now consider the further splitting of the *LS* terms due to spin-orbit coupling. In the lectures we have seen that, when treating the spin-orbit coupling term of *N*-electron atoms $H_{SO} = \sum_i \xi(\mathbf{r}_i) \mathbf{L}_i \cdot \mathbf{S}_i$ as a perturbation with respect to the energy hierarchy imposed by Hund's rules (namely as a perturbation to degenerate states corresponding a given *LS* term), namely as a perturbation within an *LS* term, it is equivalent to the effective spin-orbit Hamiltonian

$$H_{\rm SO}^{\rm (eff)} = \frac{A_{LS}}{\hbar^2} \boldsymbol{L} \cdot \boldsymbol{S},$$

with A a constant depending on all quantum numbers defining the degenerate states expect those associated with L^z , S^z .

We introduce the total electronic angular momentum J = L + S.

26.3

Determine the possible values of J associated with each LS term.

26.4

Justify why $A_{LS} > 0$ for the *LS* terms of Ti. Determine the spin-orbit splitting of each of the energy level corresponding to an *LS* term, and label each split level by its ${}^{2S+1}L_J$ label.

26.5

Imagine that we shine some radiation on the Ti atom. Starting from the ground-state fine-structure term ${}^{3}F_{2}$, and working within the dipole approximation, indicate all the *allowed* transitions to the spin-orbit-split levels reconstructed above.

$TD11: H_2^+$ molecular ion



In this exercise we consider the simplest possible molecule, namely the H_2^+ molecular ion, consisting of two protons (*A* and *B*) at mutual distance $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$, and an electron at distance $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A$ and $\mathbf{r}_B = \mathbf{r} - \mathbf{R}_B$ from proton *A* and *B* respectively.

The *electronic* Hamiltonian of the system (namely the Hamiltonian which contains only the electronic kinetic energy and *all* the potential energy terms) reads

$$\mathcal{H} = -\frac{1}{2}\nabla_r^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$
(131)

where \mathbf{r} is the electron position, $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A$ and $\mathbf{r}_B = \mathbf{r} - \mathbf{R}_B$ represent the electron position with respect to those of the nuclei, and $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$ is the vector connecting the nuclear positions. Here everything is expressed in atomic units – energy units : 1 Hartree = 2 Ry = $\hbar^2 / (ma_0^2)$; length units : Bohr radius a_0 .

In the spirit of the Born-Oppenheimer approximation, we want to reconstruct the eigenstates $\Phi(\mathbf{r}; \mathbf{R})$ of the electronic Hamiltonian :

$$\mathscr{H} \Phi(\boldsymbol{r}; \boldsymbol{R}) = E \,\Phi(\boldsymbol{r}; \boldsymbol{R}) \tag{132}$$

which depend parametrically on the internuclear separation R.

This problem, albeit deceivingly simple, does not admit an exact solution. Yet it can be solved very accurately with approximate methods. Here we will explore two simple methods, based on an *Ansatz* (a specific guess) for the electronic wavefunction : the so-called linear combination of atomic orbitals (LCAO), and a variational improvement thereof, using adjustable orbitals.

27 LCAO treatment

In the LCAO approach we shall search for a solution to the Schrödinger equation in the form

$$\Phi(\mathbf{r};\mathbf{R}) = \langle \mathbf{r} | \Phi \rangle = c_A \phi_A(\mathbf{r}) + c_B \phi_B(\mathbf{r}) = \langle \mathbf{r} | (c_A | \phi_A \rangle + c_B | \phi_B \rangle)$$
(133)

where $\phi_{A(B)}(\mathbf{r}) = \phi_{1s}(\mathbf{r} - \mathbf{R}_{A(B)})$, and $\phi_{1s}(\mathbf{r}) = e^{-r} / \sqrt{\pi}$ is the normalized 1s orbital of the hydrogen atom. In particular we shall recall that

$$\left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^{2}-\frac{1}{r_{A(B)}}\right)\phi_{A(B)}(\boldsymbol{r})=E_{0}\phi_{A(B)}(\boldsymbol{r})$$
(134)

where $E_0 = -1/2$ is the ground-state energy of the H atom (expressed in atomic units).

27.1

Write the Schrödinger equation for $|\Phi\rangle$ and project it onto $|\phi_A\rangle$ and $|\phi_B\rangle$ to get the system of equations

$$\langle \phi_A | \mathcal{H} | \Phi \rangle = E \langle \phi_A | \Phi \rangle$$

$$\langle \phi_B | \mathcal{H} | \Phi \rangle = E \langle \phi_B | \Phi \rangle$$
(135)

Introducing the symbols

$$I = \langle \phi_A | \frac{1}{r_B} | \phi_A \rangle = \langle \phi_B | \frac{1}{r_A} | \phi_B \rangle$$

$$J = \langle \phi_A | \frac{1}{r_A} | \phi_B \rangle = \langle \phi_B | \frac{1}{r_B} | \phi_A \rangle$$

$$S = \langle \phi_A | \phi_B \rangle$$
(136)

write the system of equations Eqs. (135) as a homogeneous linear system for the coefficients c_A , c_B .

27.2

A solution to the above system exists iff the determinant of the matrix defining the linear system vanishes – this condition gives rise to the so-called *secular equation*. Show that this equation admits two solutions

$$E^{\pm} = E_0 + \frac{1}{R} - \frac{I \pm J}{1 \pm S}$$
(137)

27.3

Show that the associated trial states are

$$|\Phi^{\pm}\rangle = \frac{|\phi_A\rangle \pm |\phi_B\rangle}{\sqrt{2(1\pm S)}} \tag{138}$$

27.4

Considering the wavefunction $\Phi^{\pm}(\mathbf{r})$ associated with the above states, sketch its profile for $\mathbf{r} = (x, 0, 0)$, where x is the molecular axis. The associated charge distribution for the electron is $-e|\Phi^{\pm}|^2$. From the point of view of the Coulomb interactions between the electron and the two nuclei, can you guess which configuration has the lowest energy?

27.5

The two electronic states can be given the spectroscopy notation $\Phi^+ \rightarrow \sigma_g^+$; $\Phi^- \rightarrow \sigma_u^+$. Can you justify why? (You actually can not yet, because it has not been discussed in the lecture... For the moment, just take g, u as identical labels to +, -).

27.6

Justify a priori why all three integrals *I*, *J* and *S* are strictly positive. The integrals *I*, *J* and *S* can be calculated exactly, to give the following formulae :

$$I = \frac{1}{R} \left[1 - (1+R)e^{-2R} \right] \qquad J = (1+R)e^{-R} \qquad S = \left(1 + R + \frac{R^2}{3} \right)e^{-R} \tag{139}$$

Show that

$$E^{g/u}(R) = E_0 + \frac{1}{R} \frac{(1+R)e^{-2R} \pm \left(1 - \frac{2}{3}R^2\right)e^{-R}}{1 \pm \left(1 + R + \frac{R^2}{3}\right)e^{-R}}$$
(140)

27.7

Using any computer program for function plotting (Gnuplot, Matlab, Python, Mathematica, etc.) plot the above adiabatic energies. If the energy satisfies the condition $E(R) < E_0$ (for some values of R) one speaks for a *bonding* state for the corresponding orbital, otherwise one has an *anti-bonding* state. Can you justify this terminology?

Show that one of the two states Φ^\pm is bonding while the other is anti-bonding.

Find the minimum energy, and deduce the corresponding *R* value (Answer : $R \approx 2.5$).

28 Variational treatment : optimized LCAO and orbital contraction

The LCAO method provides rather decent results but it can still be improved – *e.g.* the experimental value for the equilibrium distance *R* is $R \approx 2$.

A simple, very effective improvement is to trade the 1s orbitals of hydrogen for adjustable, normalized s-orbitals

$$\phi_{\lambda}(\mathbf{r}) = \sqrt{\frac{\lambda^3}{\pi}} e^{-\lambda r}$$
(141)

which represent the ground state of a hydrogen-like atom with nuclear charge λe . Therefore these orbitals satisfy the property

$$\left(-\frac{1}{2}\boldsymbol{\nabla}_{\boldsymbol{r}}^{2}-\frac{\lambda}{r}\right)\phi_{\lambda}(\boldsymbol{r})=\lambda^{2}E_{0}\,\phi_{\lambda}(\boldsymbol{r})\,.$$
(142)

28.1

Considering the hydrogen Hamiltonian, calculate the variational energy

$$E_{\lambda}^{(H)} = \langle \phi_{\lambda} | \left(-\frac{1}{2} \nabla_{r}^{2} - \frac{1}{r} \right) | \phi_{\lambda} \rangle .$$
(143)

Given that $\langle \phi_{\lambda} | r^{-1} | \phi_{\lambda} \rangle = \lambda$, show that $E_{\lambda=1} = E_0$ is the energy minimum as a function of the variational parameter λ .

28.2

Starting from the adjustable orbitals ϕ_{λ} , we can then build the variational LCAO Ansatz

$$|\Phi_{\lambda}\rangle = \frac{|\phi_{\lambda,A}\rangle + |\phi_{\lambda,B}\rangle}{\sqrt{2(1+S_{\lambda})}}$$
(144)

where $S_{\lambda}(R) = \langle \phi_{\lambda,A} | \phi_{\lambda,B} \rangle$.

Calculate the variational energy $E_{\lambda} = \langle \Phi_{\lambda} | \mathcal{H} | \Phi_{\lambda} \rangle$ as a function of $S_{\lambda}(R)$, $I_{\lambda}(R) = \langle \phi_{\lambda,A} | 1/r_B | \phi_{\lambda,A} \rangle$ and $J_{\lambda}(R) = \langle \phi_{\lambda,B} | 1/r_B | \phi_{\lambda,A} \rangle$. Suggestion : use again the fact that $\langle \phi_{A,\lambda} | r_A^{-1} | \phi_{A,\lambda} \rangle = \lambda$

28.3

One can calculate again the integrals S_{λ} , I_{λ} , S_{λ} , obtaining the expressions

$$I_{\lambda} = \frac{1}{R} \left[1 - (1 + \lambda R)e^{-2\lambda R} \right] \qquad J = \lambda (1 + \lambda R)e^{-\lambda R} \qquad S = \left(1 + \lambda R + \frac{\lambda^2 R^2}{3} \right)e^{-\lambda R} . \tag{145}$$

Give the explicit expression of the adiabatic variational energy $E_{\lambda}(R)$.

28.4

Plot the adiabatic variational energy as a function of λ and R, and identify its minimum. You should find it at $R \approx 2$ and $\lambda \approx 1.24$.

28.5

Finding $\lambda > 1$ corresponds to so-called *orbital contraction*. Why?

Can you justify why orbital contraction can lead to an increase of the kinetic energy with respect to the case of an isolated hydrogen atom?

TD12: H₂ molecule : molecular-orbital vs. valence-bond approach



In this exercise we consider the simplest possible *N*-electron molecule, namely the H₂ molecule, consisting of two protons (*A* and *B*) at mutual distance $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$, and two electrons at distance $\mathbf{r}_{1A} = \mathbf{r}_1 - \mathbf{R}_A$ (resp. $\mathbf{r}_{2A} = \mathbf{r}_2 - \mathbf{R}_A$) and $\mathbf{r}_{1B} = \mathbf{r}_1 - \mathbf{R}_B$ (resp. $\mathbf{r}_{2B} = \mathbf{r}_2 - \mathbf{R}_B$) from protons *A* and *B*.

The electronic Hamiltonian of the system reads

$$\mathcal{H} = h_1 + h_2 + \frac{1}{r_{12}} + \frac{1}{R} \tag{146}$$

where

$$h_1 = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} \qquad h_2 = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{2A}} - \frac{1}{r_{2B}}.$$
(147)

Here $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$ is the vector connecting the nuclear positions, and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ that connecting the two electrons. As usual, everything is expressed in atomic units – energy units : 1 Hartree = 2 Ry = $\hbar^2 / (ma_0^2)$; length units : Bohr radius a_0 .

The experimental values for the equilibrium internuclear distance and the dissociation energies are $R_0 = 1.4$ and $D_e = 0.175$ (in atomic units).

The goal of this sheet is to build constructively the electronic wavefunction $\Phi_s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ for the lowest-energy electronic states, according to two alternative approaches : the (Hund-Mulliken) *molecular-orbital theory*, and the (Heitler-London) *valence-bond* approach.

29 Molecular-orbital approach

The molecular-orbital (MO) approach is based on the LCAO approach (linear combination of atomic orbitals), that we have explored in the TD no. 11. There you have seen that an individual electron in the H_2^+ molecular ion has two low-energy states, given by the bonding(+)/antibonding(-) wavefunctions

$$\psi^{\pm}(\mathbf{r}) = \frac{\phi_A(\mathbf{r}) \pm \phi_B(\mathbf{r})}{\sqrt{2(1\pm S)}}$$
(148)

where $\phi_{A(B)}(\mathbf{r}) = \phi_{1s}(\mathbf{r} - \mathbf{R}_{A(B)})$, and $\phi_{1s}(\mathbf{r}) = e^{-r}/\sqrt{\pi}$ is the normalized 1s orbital of the hydrogen atom; and *S* is the overlap $\langle \phi_A | \phi_B \rangle$.

The MO approach builds electronic states by populating different LCAO orbitals. The two-electron states with definite exchange symmetry (symmetric or anti-symmetric) that can be built our of the ψ^{\pm} LCAO orbitals are

$$\Phi^{(++)}(\mathbf{r}_{1},\mathbf{r}_{2}) = \psi^{+}(\mathbf{r}_{1})\psi^{+}(\mathbf{r}_{2})$$

$$\Phi^{(+-)}_{+}(\mathbf{r}_{1},\mathbf{r}_{2}) = [\psi^{+}(\mathbf{r}_{1})\psi^{-}(\mathbf{r}_{2}) + \psi^{-}(\mathbf{r}_{1})\psi^{+}(\mathbf{r}_{2})]/\sqrt{2}$$

$$\Phi^{(+-)}_{-}(\mathbf{r}_{1},\mathbf{r}_{2}) = [\psi^{+}(\mathbf{r}_{1})\psi^{-}(\mathbf{r}_{2}) - \psi^{-}(\mathbf{r}_{1})\psi^{+}(\mathbf{r}_{2})]/\sqrt{2}$$

$$\Phi^{(--)}_{-}(\mathbf{r}_{1},\mathbf{r}_{2}) = \psi^{-}(\mathbf{r}_{1})\psi^{-}(\mathbf{r}_{2}) \qquad (149)$$

Associate each motional state with one of the eigenstates of the total-spin operators S^2 , S^z

$$\chi_{S=0,M_{S}=0}(\sigma_{1},\sigma_{2}) = \langle \sigma_{1}\sigma_{2}| \left(|\uparrow_{1}\downarrow_{2}\rangle - |\downarrow_{1}\uparrow_{2}\rangle\right)/\sqrt{2}$$

$$\chi_{S=1,M_{S}=0}(\sigma_{1},\sigma_{2}) = \langle \sigma_{1}\sigma_{2}| \left(|\uparrow_{1}\downarrow_{2}\rangle + |\downarrow_{1}\uparrow_{2}\rangle\right)/\sqrt{2}$$

$$\chi_{S=1,M_{S}=1}(\sigma_{1},\sigma_{2}) = \langle \sigma_{1}\sigma_{2}|\uparrow_{1}\uparrow_{2}\rangle$$

$$\chi_{S=1,M_{S}=-1}(\sigma_{1},\sigma_{2}) = \langle \sigma_{1}\sigma_{2}|\downarrow_{1}\downarrow_{2}\rangle$$
(150)

in order to build a fully anti-symmetric 2-electron wavefunction.

29.2

Attach the correct quantum numbers to the above states, namely 1) Λ (angular momentum L^z); 2) +/- parity under reflection with respect to a plane containing the molecular axis; 3) g/u parity under inversion with respect to the midpoint between the nuclei; 4) *S* total spin, using to the spectroscopic notation ${}^{2S+1}\Lambda_{g/u}^{+/-}$. You should find the following combinations : ${}^{1}\Sigma_{g}^{+}$ (two states), and ${}^{1}\Sigma_{u}^{+}$ (one state), ${}^{3}\Sigma_{u}^{+}$ (three states).

29.3

To calculate the energy of the above states, we start by neglecting the electron-electron repulsion, namely by considering the Hamiltonian $\mathcal{H} = h_1 + h_2 + 1/R$.

Considering that $\langle \psi^{\pm} | h_{1(2)} | \psi^{\pm} \rangle = E^{\pm} - 1/R$ (as calculated in the TD no. 11), where

$$E^{\pm} = E_0 - \frac{I \pm J}{1 \pm S} + \frac{1}{R}$$
(151)

calculate $E_{\pm}^{(+-)} = \langle \Phi_{\pm}^{(+-)} | \mathcal{H} | \Phi_{\pm}^{(+-)} \rangle$ and $E^{(++)} = \langle \Phi^{(++)} | \mathcal{H} | \Phi^{(++)} \rangle$ in terms of the *I*, *J*, *S* integrals.

29.4

Remembering that

$$I = \frac{1}{R} \left[1 - (1+R)e^{-2R} \right] \qquad J = (1+R)e^{-R} \qquad S = \left(1 + R + \frac{R^2}{3} \right)e^{-R} \tag{152}$$

plot the adiabatic energies $E_{\pm}^{(+-)}(R)$ and $E^{(++)}(R)$ as a function of R. Which one corresponds to the electronic ground state? Do these electronic trial states correspond to stable molecules, namely do they admit a minimum energy which is lower that the value at $R \to \infty$? And, if so, what is the value of the equilibrium distance R_0 and the dissociation energy $D_e = E(\infty) - E(R_0)$?

29.5

Justify why the addition of the electron-electron interaction is necessarily going to *lower* the dissociation energy D_e .

When doing so on the $\Phi^{(++)}$ state, namely by calculating the integral $\mathscr{I}(R) = \langle \Phi^{(++)} | 1/r_{12} | \Phi^{(++)} \rangle$, one finds an equilibrium position $R_0 = 1.5$ with a dissociation energy of $D_e = 0.098$. Has the result improved with respect to the case without the electron-electron interaction?

29.6

Write the two states $\Phi^{(++)}$, $\Phi^{(--)}$ as

$$\Phi^{(\pm\pm)}(\mathbf{r}_1, \mathbf{r}_2) = \Phi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) \pm \Phi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2)$$
(153)

where Φ_{ion} describes a situation in which *both* electrons are around the same nucleus (*ionic* wavefunction), while Φ_{cov} describes the situation in which each electron is attached to a different nucleus (*covalent* wavefunction).

Justify qualitatively why the ionic wavefunction is not energetically favorable from the point of view of the electron-electron repulsion.

29.7

An improvement of the MO approach is to introduce a trial state which is a superposition of ionic and covalent wavefunctions with *unequal weights*, namely

$$\Phi_{\lambda}(\mathbf{r}_{1},\mathbf{r}_{2}) = \mathcal{N}\left[(1+\lambda)\Phi_{\text{ion}} + (1-\lambda)\Phi_{\text{cov}}\right]$$
(154)

where \mathcal{N} is a normalization factor.

Using λ as a variational parameter to minimize the energy, one finds an optimum value λ_{\min} such that $q = (1 + \lambda_{\min})/(1 - \lambda_{\min}) \approx 0.2$. The corresponding equilibrium distance and dissociation energies are $R_0 = 1.42$ and $D_e = 0.147$ respectively.

Comment on the improvement with respect to the previous results, and on its physical origin.

30 Valence-bond theory

Within the valence-bond theory only covalent wavefunctions are considered as trial states, namely

$$\Phi_{\rm VB}^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) \pm \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)}{\sqrt{2(1\pm S^2)}}$$
(155)

30.1

Associate to the above spatial wavefunctions an appropriate spin state $\chi_{S=0,M_S=0}$ or $\chi_{S=1,M_S}$ ($M_S = 0, \pm 1$) in order to have a fully antisymmetric state. Attach quantum numbers to the resulting states (using spectroscopic notation) : you should find a ${}^{1}\Sigma_{g}^{+}$ and three ${}^{3}\Sigma_{u}^{+}$ states.

30.2

Write the states $\Phi_{VB}^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2)\chi_{S=0,M_S=0}$ as the sum/difference of two Slater determinants. Suggestion : use $\chi_{S=0,M_S=0}(\sigma_1, \sigma_2) = (\delta_{\uparrow,\sigma_1}\delta_{\downarrow,\sigma_2} - \delta_{\downarrow,\sigma_1}\delta_{\uparrow,\sigma_2})/\sqrt{2}$.

30.3

Introducing the direct Coulomb integral

$$\mathscr{J} = \int d^3 r_1 d^3 r_2 |\phi_A(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\phi_B(\mathbf{r}_2)|^2$$
(156)

and the exchange Coulomb integral

$$\mathcal{K} = \int d^3 r_1 d^3 r_2 \phi_A(\mathbf{r}_1) \phi_B(\mathbf{r}_2) \frac{1}{r_{12}} \phi_B(\mathbf{r}_1) \phi_A(\mathbf{r}_2)$$
(157)

that we have already encountered in the theory of the He atom, show that

$$E_{\rm VB}^{(\pm)} = \langle \Phi_{\rm VB}^{(\pm)} | \mathcal{H} | \Phi_{\rm VB}^{(\pm)} \rangle = 2E_0 + \frac{1}{R} - \frac{2(I+SJ)}{1\pm S^2} + \frac{\mathscr{J} \pm \mathscr{K}}{1\pm S^2}$$
(158)

30.4

Since $\mathcal{K} < 0$ (as it can be shown), then one can also show that $E_{VB}^+ < E_{VB}^-$. Are the quantum numbers of the valence-bond ground state (Λ , +/-, g/u, S) the same as for the prediction of the MO theory?

The numerical results for the VB ground state show that $R_0 = 1.6$ and $D_e = 0.115$. Compare with the best variational result of MO theory (upon optimization of the λ parameter) : could you expect this result?



TD13: Rovibrational spectrum of H-Cl and its spectroscopy

FIGURE 5 – Absorption spectrum for the $v = 0 \rightarrow v = 1$ rovibrational transitions in gaseous H-Cl at room temperature.

In this exercise we shall examine how many of the properties of the rovibrational spectrum of diatomic heteronuclear molecules can be extracted from the study of the absorption spectrum of the molecules, using the paradigmatic example of the H-Cl molecule.

The rovibrational spectrum of molecules (as seen in the lectures) is

$$E(s, v, K) = E_s(R_0) + \hbar\omega_0 \left(v + \frac{1}{2}\right) + \frac{\hbar^2}{2\mu_n R_0^2} K(K+1) - aK(K+1) \left(v + \frac{1}{2}\right) - \beta\hbar\omega_0 \left(v + \frac{1}{2}\right)^2 + \dots$$
(159)

where

$$a = \frac{3\hbar^3 \omega_0}{4\mu_n \alpha R_0^3 D_e} \left(1 - \frac{1}{\alpha R_0} \right) \qquad \qquad \beta = \frac{\hbar \omega_0}{4D_e} \,. \tag{160}$$

This prediction assumes the Morse-potential approximation of the adiabatic potential

$$E_s(R) \approx E_s(R_0) + D_e[1 - \exp(-\alpha(R - R_0))]^2$$
 (161)

31 Vibrational transitions

As seen in the lecture, the quantum state of a molecule within the Born-Oppenheimer approximation has the form $\sigma^{(s)}(\mathbf{p} - \mathbf{p})$

$$\Psi_{s,v,K,M_K}(\boldsymbol{r}_i;\boldsymbol{R}) = \frac{\mathscr{F}_{v,K}^{(s)}(\boldsymbol{R}-\boldsymbol{R}_0)}{\boldsymbol{R}} \,^{\Lambda}\mathscr{U}_{K,M_K}(\Theta,\Phi) \,\Phi_s(\boldsymbol{r}_i;\boldsymbol{R}) \,.$$
(162)

The selection rules for molecular transitions $(s, v, K) \rightarrow (s', v', K')$ within the dipole approximation are imposed by the non-vanishing of the matrix element of the dipole operator $\mathbf{D} = \sum_i (-e)\mathbf{r}_i + Z_A e\mathbf{R}_A + Z_B e\mathbf{R}_B$

$$\langle s', v', K', M'_{K} | \boldsymbol{D} | s, v, K, M_{K} \rangle = \int d\Theta \sin\Theta \, d\Phi \left({}^{\Lambda'} \mathscr{U}_{K', M'_{K}}(\Theta, \Phi) \right)^{*} \, {}^{\Lambda} \mathscr{U}_{K, M_{K}}(\Theta, \Phi) \, \frac{\left(\mathscr{F}_{v'}^{(s')}(R - R_{0}) \right)^{*}}{R} \, \frac{\mathscr{F}_{v}^{(s)}(R - R_{0})}{R} \, \boldsymbol{D}_{s', s}(\boldsymbol{R}) \tag{163}$$

where

$$\boldsymbol{D}_{\mathcal{S}',\mathcal{S}}(\boldsymbol{R}) = \int \left(\prod_{i} d^{3} \boldsymbol{r}_{i}\right) \Phi_{\mathcal{S}'}^{*}(\boldsymbol{r}_{i};\boldsymbol{R}) \boldsymbol{D} \Phi_{\mathcal{S}}(\boldsymbol{r}_{i};\boldsymbol{R})$$
(164)

is the reduced matrix element of the dipole operator

31.1

Considering $s \rightarrow s$ transitions, we can expand the reduced dipole matrix element around the molecular equilibrium position

$$\boldsymbol{D}_{s,s}(\boldsymbol{R}) = \boldsymbol{D}(R_0 \boldsymbol{e}_R) + \frac{d\boldsymbol{D}_{s,s}}{dR} \Big|_{R=R_0} (R-R_0) + \dots$$
(165)

Show that the matrix element for the dipole operator takes the form

$$\langle s, v', K', M'_{K} | \boldsymbol{D} | s, v, K, M_{K} \rangle = \int_{0}^{\infty} dR \left(\mathscr{F}_{v'}^{(s')}(R - R_{0}) \right)^{*} (R - R_{0}) \mathscr{F}_{v}^{(s)}(R - R_{0}) \times \text{(angular integral)}$$
(166)

31.2

Introducing the variable $x = R - R_0$, the functions $\mathscr{F}_v^{(s)}(x)$ are (to a good approximation) eigenstates of a harmonic oscillator with eigen-energy $\hbar \omega_0(v + 1/2)$, namely $\mathscr{F}_v^{(s)}(x) = \langle x | v \rangle$ where $a^{\dagger} a | v \rangle = v | v \rangle$. Here a, a^{\dagger} are creation and destruction operators, acting on harmonic oscillator eigenstates as $a | v \rangle = \sqrt{v} | v - 1 \rangle$, $a^{\dagger} | v \rangle = \sqrt{v + 1} | v + 1 \rangle$. Given that for a harmonic oscillator of frequency ω_0

$$x = \sqrt{\frac{\hbar}{2m\omega_0}} (a + a^{\dagger}) \tag{167}$$

show that transitions with $\Delta v = v' - v = \pm 1$ are dipole-allowed.

32 Main features of the rovibrational spectrum

The absorption spectrum of gaseous H-Cl at room temperature is shown in Fig. 5. It exhibits rovibrational transitions of the kind

$$(s, v = 0, K) \to (s, v = 1, K')$$
 (168)

without excitation of the electronic state, which remains the ground state.

32.1

The electronic ground state of H-Cl has $\Lambda = 0$. Recall the selection rule for $\Delta K = K' - K$ in the dipole approximation. Justify why a transition $s \rightarrow s$ is possible in H-Cl.

32.2

Consider the rigid rotor spectrum $e(K) = \hbar^2 K(K+1)/(2\mu R_0^2)$. Show that the transition energies take the form

$$e(K+1) - e(K) = 2hcB(K+1)$$
(169)

(where $h = 2\pi\hbar$ and *c* is the speed of light), and express the rotational constant *B* in terms of the parameters of the rotor. Show that *B* has the dimension of the inverse of a length.

In the spectroscopy community *B* is generally expressed in units of cm⁻¹. Considering that for H-Cl $R_0 = 1.27$ Å, and that the most abundant isotope of Cl is ³⁵Cl, calculate *B* for the H-Cl molecule.



FIGURE 6 – Possible $v = 0 \rightarrow v = 1$ transition.

Neglecting the non-linear terms in Eq. (159) ($a = 0, \beta = 0$) calculate the expression for the two series of transition energies

R-branch:
$$R(K) = E(s, v = 1, K + 1) - E(s, v = 0, K)$$
 (170)

P-branch:
$$P(K) = E(s, v = 1, K) - E(s, v = 0, K + 1)$$
 (171)

Draw the corresponding transitions on a diagram like the one of Fig. 6.

Identify the peaks in the figure with the above two series of transitions. The center of the spectrum is at 2886 cm⁻¹ : estimate $\hbar\omega_0$. Justify the existence of a gap in the center of the spectrum.

32.4

If the H-Cl molecule was prepared in its rovibrational ground state, how many absorption lines would you expect?

32.5

A spectroscopic line corresponding to a $K \rightarrow K \pm 1$ transition with K > 0 appears only if the initial state (s, v = 0, K) is thermally populated. At temperature T, the fraction of molecules in a rotational K state inside a large ensemble of molecules is

$$f(K) = \frac{1}{Z}(2K+1)\exp\left[-x(T)K(K+1)\right] \qquad \left(Z = \sum_{K'}(2K'+1)\exp\left[-x(T)K'(K'+1)\right]\right)$$
(172)

where $x(T) = hcB/k_BT$, and $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. At room temperature (T = 300 K), plot the function f(K)Z, and compare it with the modulation of the peak height in Fig. 5. Can you understand the correspondence?

33 Spectrum asymmetry and double peaks

33.1

We now take into account the rotation-vibration coupling term in Eq. (159), namely we consider $a \neq 0$. Recalculate the transition energies R(K) and P(K). A quadratic dependence on K should now appear.

33.2

Conclude that the quadratic term in *K* explains why the spacing between transition lines in the *R*-branch shrinks with *K*, while the same spacing grows with *K* in the *P*-branch.

33.3

Does the above analysis of the absorption spectrum allow to reconstruct the three parameters of the Morse potential (α , D_e , R_0)?

Another way of reconstructing these parameters is to measure the nonlinear constant β by looking at other transitions $v \rightarrow v \pm 1$. Such a measurement gives the estimate $\beta = 0.0177$. From this and previous information already obtained in the exercise, estimate D_e and α .

33.4

A closer look at the spectral peaks shows that each peak is actually double. This can be explained with the existence of two stable isotopes of Cl, 35 Cl and 37 Cl. Justify why one should consider two corresponding *B* constants, $B(^{35}$ Cl) and $B(^{37}$ Cl), leading in principle to two different transition frequencies.

Note : the isotope effect on the *B* constant is in fact far too small to justify the observed peak doubling; the experimentally observed doubling comes from the existence of two different vibrational frequencies $\omega_0(^{35}\text{Cl})$ and $\omega_0(^{37}\text{Cl})$.