

One electron atoms

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19 de mayo de 2025

1 General situation

We describe the hydrogen atom as a motionless Z positive charge situated in the center of the system and an electron attracted by the electric force. The radial equation is:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2mr^2} \right] u(r) = Eu(r) . \quad (1.1)$$

We confine our attention to the case $E < 0$. Dividing this equation by E , and introducing the following quantities:

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} = \frac{\sqrt{-2(mc^2)E}}{\hbar c} , \quad \rho \equiv \kappa r , \quad \rho_0 \equiv \frac{Zme^2}{2\pi\epsilon_0 \hbar^2 \kappa} \quad (1.2)$$

We have the following equation:

$$\frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u(r) \quad (1.3)$$

In the asymptotic regions ($\rho \rightarrow \infty$) it is:

$$\frac{d^2 u}{d\rho^2} = u(r) \quad (1.4)$$

The general solution is:

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \quad (1.5)$$

In order to be finite it is necessary that $B = 0$.

For $\rho \rightarrow 0$ the centrifugal terms dominates so we have:

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u \quad (1.6)$$

The general solution is:

$$u(\rho) = C\rho^{l+1} + D\rho^{-l} \quad (1.7)$$

but it assumed $\rho \rightarrow 0$ so $D = 0$ is needed. So:

$$u(\rho) \rightarrow_{\rho \rightarrow 0} C\rho^{l+1} \quad (1.8)$$

Then we propose $u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$ as a solution. Inserting it in the radial equation we get:

$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0 \quad (1.9)$$

Assuming v can have the form of a power series:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad (1.10)$$

Inserting this in the radial equation we get the following relation for the coefficients c_j :

$$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right] c_j \quad (1.11)$$

If the series don't terminate the function blows up for large ρ . Therefore that's the condition we must impose, there's always a value j_{max} for which c_{j+1} gets zero, that's it:

$$2(j_{max} + l + 1) = \rho_0 \quad (1.12)$$

Now we define the principal quantum number n as:

$$2n = \rho_0 \quad (1.13)$$

And this is what gives us the values for energies:

$$E_n = -\frac{1}{n^2} \left[\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \right] = -\frac{1}{n^2} \left[\frac{mc^2}{2(\hbar c)^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \right] \quad (1.14)$$

So the relation for the coefficients for any given pair of (n, l) is:

$$c_{j+1} = \left[\frac{2(j+l+1-n)}{(j+1)(j+2l+2)} \right] c_j \quad (1.15)$$

being the maximum value of j :

$$j_{max} = n - l - 1 \quad (1.16)$$

and by definition $j_{max} \geq 0$, otherwise wavefunction turns zero. Therefore we have the following relation for possible values of quantum numbers:

$$n \geq l + 1 \quad l \leq n - 1 \quad l = 0, 1, \dots, n - 1 \quad (1.17)$$

Here we define a constant a called the Bohr radius:

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad (1.18)$$

And the energy can be expressed as:

$$E_n = -\frac{e^2}{4\pi\epsilon_0} \frac{Z^2}{2an^2} = -\frac{Z^2\hbar^2}{2ma^2n^2} \quad (1.19)$$

Sustituting the energy in eq.[1.2]:

$$\rho = \frac{Zr}{na} \quad (1.20)$$

1.1 General form to obtain c_0

Given a pair of quantum numbers we have a vale for the last coefficient j_{max} . Now let's denote as $f_{nl}(j+1)$ to the factor that multiplies c_j to obtain c_{j+1} :

$$f_{nl}(j+1) = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} \quad (1.21)$$

and we define $f_{nl}(0) = 1 \forall n, l$. So we have:

$$c_{j+1} = f_{nl}(j+1)c_j = f_{nl}(j+1)f_{nl}(j)c_{j-1} = \left[\prod_{j'=j+1}^{j'=0} f_{nl}(j') \right] c_0 \quad (1.22)$$

So the radial eigenfunction has the following form:

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} c_0 \left[\sum_{j=0}^{j_{max}} \left(\prod_{j'=0}^{j'=j} f_{nl}(j') \right) \rho^j \right] \quad (1.23)$$

The normalization condition lead us to:

$$c_0^2 \int_{r=0}^{\infty} \rho^{2(l+1)} e^{-2\rho} \left[\sum_{j=0}^{j_{max}} \left(\prod_{j'=0}^{j'=j} f_{nl}(j') \right) \rho^j \right]^2 dr = 1 \quad (1.24)$$

if we denote β_j as:

$$\beta_j = \prod_{j'=0}^{j'=j} f_{nl}(j') \quad (1.25)$$

then we have:

$$c_0^2 \int_{r=0}^{\infty} \rho^{2(l+1)} e^{-2\rho} \left[\sum_{j=0}^{j_{max}} \beta_j \rho^j \right]^2 dr = 1 \quad (1.26)$$

using that $dr = \frac{d\rho}{\kappa}$. Therefore we have:

$$c_0^2 \int_{r=0}^{\infty} \rho^{2(l+1)} e^{-2\rho} \left[\sum_{j=0}^{j_{max}} \beta_j \rho^j \right]^2 d\rho = \kappa \quad (1.27)$$

From here we obtain c_0 , and using the relation formula we obtain all the coefficients.

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} \left[\sum_{j=0}^{j_{max}} c_j \rho^j \right] \quad (1.28)$$

1.2 Laguerre polynomials

Associated Laguerre polynomials $L_q^p(\rho)$ follow the following equation:

$$\left[\rho \frac{d^2}{d\rho^2} + (p+1-\rho) \frac{d}{d\rho} + (q-p) \right] L_q^p(\rho) = 0 \quad (1.29)$$

We compare with eq.[1.9] and we have that:

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \quad (1.30)$$

In total we have that:

$$R_{nl}(r) = \left[\left(\frac{2Z}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]} \right]^{1/2} e^{-\rho} (2\rho)^l \left[L_{n-l-1}^{2l+1}(2\rho) \right] \quad (1.31)$$

where $\rho = \rho(r)$ is described in eq. [1.20]. Defining N_{nl} as:

$$N_{nl} = \left[\left(\frac{2Z}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]} \right]^{1/2} \quad (1.32)$$

we have:

$$R_{nl}(r) = N_{nl} e^{-\rho} (2\rho)^l \left[L_{n-l-1}^{2l+1}(2\rho) \right] \quad (1.33)$$

Some examples:

$$R_{10}(r) = 2 \left(\frac{Z}{a} \right)^{3/2} e^{-\frac{Zr}{a}} \quad (1.34)$$

$$R_{21}(r) = \frac{1}{\sqrt{24}} \left(\frac{Z}{a} \right)^{3/2} \left(\frac{Zr}{a} \right) e^{-\frac{Zr}{2a}} \quad (1.35)$$

$$R_{41}(r) = \frac{Z^{3/2}}{a^{3/2}} \frac{\sqrt{5}}{16\sqrt{3}} e^{-\frac{Zr}{4a}} \frac{Zr}{a} \left[\frac{1}{80} \left(\frac{Zr}{a} \right)^2 - \frac{1}{4} \left(\frac{Zr}{a} \right) + 1 \right] \quad (1.36)$$

Whenever we have to use these radial functions as integrands it is advantageous to not use any constant such as a inside the integrand for numerical reasons. For that reason let's define H_{nl} and $N_{nl}^{a=1}$ as:

$$H_{nl}(\rho) = e^{-\rho} (2\rho)^l \left[L_{n-l-1}^{2l+1}(2\rho) \right] \quad (1.37)$$

and:

$$N_{nl}^{a=1} = \left[\left(\frac{2Z}{n} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]} \right]^{1/2} \quad (1.38)$$

then we have:

$$R_{nl}(r) = \frac{1}{a^{3/2}} N_{nl}^{a=1} H_{nl}(r) \quad (1.39)$$

therefore, for any expected value or matrix elements of an operator depending only on r we have:

$$\langle R_{n'l'} | O(r) | R_{nl} \rangle = \frac{1}{a^3} N_{nl}^{a=1} N_{n'l'}^{a=1} \int H_{n'l'}(r) O(r) H_{nl}(r) r^2 dr \quad (1.40)$$

still the dependence on a is in the eigenfunctions through ρ . But we can make the change of variable $r' = \frac{r}{a}$, then ρ has no dependence on a :

$$\langle R_{n'l'} | O(r) | R_{nl} \rangle = N_{nl}^{a=1} N_{n'l'}^{a=1} \int H_{n'l'}(r') O(r', a) H_{nl}(r') r'^2 dr' \quad (1.41)$$

and sometimes you might extract the dependence on a from the operator out of the integral.

Using these definitions we obtain the radial functions that can be observed in figure[1].

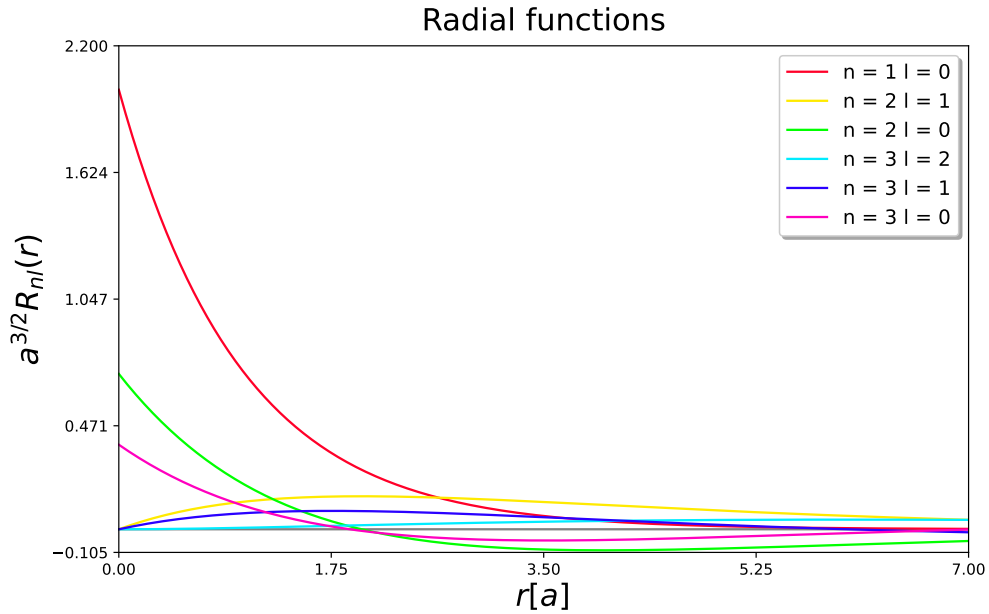


Figure 1: Radial functions for different values of n and l for $Z = 1$. The dimension of r is the Bohr radius.

As we can see only the states with $l = 0$ has a radial function different from zero in $r = 0$. The centrifugal term prevent the electron to get close to $r = 0$. Take into account these function are the density probability per fm^2 , that's it, per point in circumference r . To take into account all the circumference we need to multiply with r^2 . We can observe those quantities in figure [2]

There you can observe the actual density probability for every circumference r . What it's the correct quantity to measure where it's most probable to find the electron. For example, for $n = 1$ the maximum is found near $r = a$ and almost all the probability is contained in $r < 4a$.

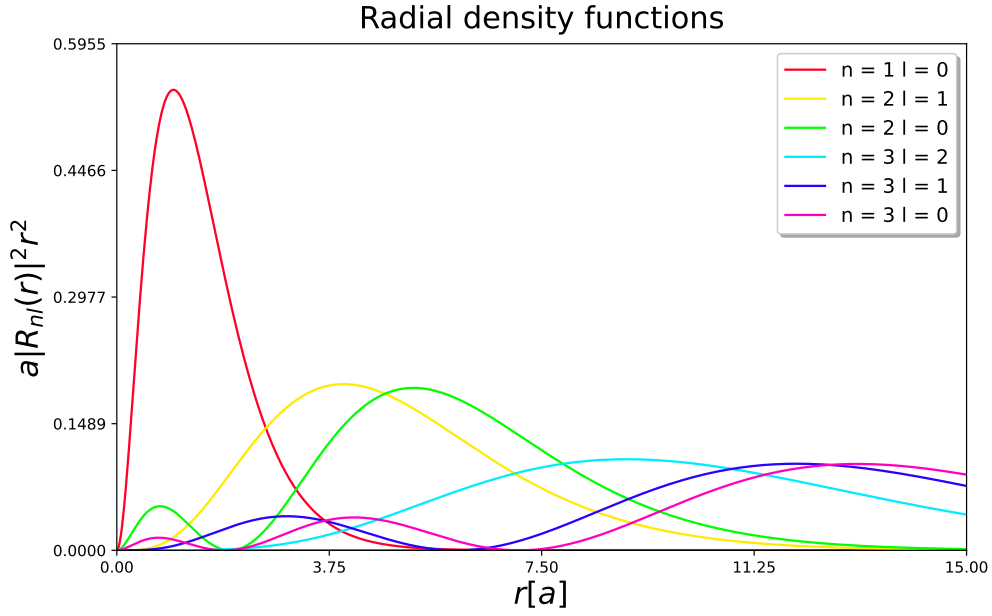


Figura 2: Radial density functions for different values of n and l for $Z = 1$. The dimension of r is the Bohr radius.

1.2.1 Checking the normalization

For the case of just computing the normalization the operator O is just the identity so there's no dependence at all on a . We have that:

$$\langle R_{nl} | R_{nl} \rangle = [N_{nl}^{a=1}]^2 \int_0^\infty [H_{nl}(r')]^2 r'^2 dr' = 1 \quad (1.42)$$

1.2.2 Probability of finding inside a volume

The probability of finding the electron inside two spherical surfaces defined by r_a and r_b is:

$$\int_{r_a}^{r_b} |R_{nl}(r)|^2 r^2 dr = [N_{nl}^{a=1}]^2 \int_{r_a/a}^{r_b/a} [H_{nl}(r')]^2 r'^2 dr' \quad (1.43)$$

with $r' = r/a$

If we talk about any region giving freedom to the angles we have that the probability is:

$$\begin{aligned}
& \int_{r_a}^{r_b} |R_{nl}(r)|^2 r^2 dr \int_{\theta_1}^{\theta_2} \int_{\varphi_1}^{\varphi_2} |Y_{lm}(\theta, \varphi)|^2 \sin(\theta) d\theta d\varphi \\
&= [N_{nl}^{a=1}]^2 \int_{r_a/a}^{r_b/a} [H_{nl}(r')]^2 r'^2 dr' \int_{\theta_1}^{\theta_2} \int_{\varphi_1}^{\varphi_2} |Y_{lm}(\theta, \varphi)|^2 \sin(\theta) d\theta d\varphi \\
&= p_{lm}^2 [N_{nl}^{a=1}]^2 \int_{r_a/a}^{r_b/a} [H_{nl}(r')]^2 r'^2 dr' \int_{\theta_1}^{\theta_2} (P_{lm}(\cos\theta))^2 \sin(\theta) d\theta \int_{\varphi_1}^{\varphi_2} e^{i(m\varphi-m\varphi)} d\varphi \\
&= (\varphi_2 - \varphi_1) p_{lm}^2 [N_{nl}^{a=1}]^2 \int_{r_a/a}^{r_b/a} [H_{nl}(r')]^2 r'^2 dr' \int_{\theta_1}^{\theta_2} (P_{lm}(\cos\theta))^2 \sin(\theta) d\theta \quad (1.44)
\end{aligned}$$

Using this development we calculate different probabilities for different states (n, l) from $r = 0$ to $r = R$, for different values of R and for $Z = 1$. We show this results in table[1].

state(n,l)	$R = 1[a]$	$R = 3[a]$	$R = 6[a]$	$R = 9[a]$	$R = 12[a]$
(1,0)	0.323	0.938	0.999	1	1
(2,0)	0.034	0.073	0.536	0.893	0.984
(2,1)	0.004	0.185	0.715	0.945	0.992
(3,0)	0.01	0.023	0.111	0.135	0.337
(3,1)	0.001	0.053	0.111	0.180	0.442
(3,2)	0	0.005	0.111	0.394	0.687
(4,0)	0.004	0.010	0.041	0.059	0.135

Tabla 1

What we can extract from the table and from the graphics we saw earlier is that states for greater values of n are farther from the nucleus, while $l = 0$ is the state which has more probabilities near the nucleus is a state more spread for greater values of r . That's a rule for lower values of l .

1.2.3 Probability density function

The radial probability density function is:

$$|R_{nl}(r)|^2 r^2 = \frac{1}{a} \left(N_{nl}^{a=1} \right)^2 [H_{nl}(r')]^2 r'^2 \quad (1.45)$$

where $r' = r/a$.

The total pdf is:

$$|\Psi(\vec{r})|^2 = |R_{nl}(r)|^2 |Y_{lm}(\theta, \varphi)|^2 = \frac{1}{a} p_{lm}^2 \left(N_{nl}^{a=1} \right)^2 [H_{nl}(r')]^2 (P_{lm}(\cos\theta))^2 \quad (1.46)$$

1.3 Degeneracy

Energy levels only depends on the quantum number n , for each of this levels we have some possible states, all of the different possibilities for the rest of the quantum numbers

l , m_l and m_s for a fixed n . We have $l_{max} + 1$ different l values and $2l_{max} + 1$ different values of m_l . Moreover, the two possible states of spin m_s . So:

$$d(n) = 2(l_{max} + 1)(2l_{max} + 1) = 2n(2n - 1) = 4n^2 - 2n \quad (1.47)$$

1.4 Observing the states

1.4.1 Fixing a direction φ

We are going to study the probability density functions given by eq. [1.46] for different states fixing a direction φ in the spherical coordinates. Because the pdf does not depend on φ the value we choose has no importance. For convenience we choose this value as $\varphi = 0$.

In cartesian coordinates that implies $y = 0$, letting freedom to x and z . So we are gonna move through that spherical surface defined by:

$$r = \sqrt{x^2 + z^2} \quad (1.48)$$

To define the point through every circumference defined by a fixed r we move through θ . θ is defined from 0rads to πrads . To have the whole circumference and the spherical surface we need to combine the results with those using $\varphi = \pi$.

The axis are gonna be specified by z and x . In the programs the inputs are r and θ so we need to transform them into the cartesian coordinates. For $\varphi = 0$ we have:

$$\varphi = 0 \Rightarrow x = r\sin\theta \quad y = 0 \quad z = r\cos\theta \quad (1.49)$$

For $\varphi = \pi$ we have:

$$\varphi = \pi \Rightarrow x = -r\sin\theta \quad y = 0 \quad z = r\cos\theta \quad (1.50)$$

In fig. [3] we observe the state $n = 1, l = 0$. It has the spherical symmetric shape of the $l = 0$ states. Most of the probability is contained inside the radius a .

In fig. [4] we observe the state $n = 2, l = 1$ and $m_l = 0$. We can observe the effect of the centrifugal force which prevent the electron gets close around $r = 0$. Because $m_l = 0$ we find the lobules symmetric to $x = 0$. While in fig [5] we observe the state $n = 2, l = 1$ and $|m_l| = 1$ where the lobules are symmetric to $z = 0$. Because of the section we chose from this perspective the states for $m_l = 1$ and $m_l = -1$ are equal.

For states $l = 2$ we have four lobules as we can see from the fig.[6] where we plot the state $n = 3, l = 2$ and $m_l = 1$.

2 Corrections

2.1 Fine structure

Relativistic kinetic energy can be expressed as:

$$T = mc^2 \left[\sqrt{1 + \left(\frac{p}{mc} \right)^2} - 1 \right] = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots \quad (2.1)$$

where we have developed the expression in powers of $p/(mc)$ in the non-relativistic limit $p \ll mc$. So our hamiltonian now is:

$$H = H_0 + H' \quad (2.2)$$

where:

$$H_0 = \frac{p^2}{2m} + V(r) \quad (2.3)$$

$$H' = -\frac{1}{8m^3c^2} p^4 \quad (2.4)$$

2.1.1 Applying perturbation theory

The eigenfunctions of H_0 can be represented as $\Psi(\vec{r}, \sigma)_{nlm_l m_s}$. That's it, the non-perturbative hamiltonian commutes with L^2 , L_z , S^2 and S_z , without two eigenfunctions with same set of eigenvalues. H_0 is direct sum of subspaces of E_n with dimension $d(n)$. Now, if H' commutes with that set of operators, then $\langle nl m_l m_s | H' | n' l' m'_l m'_s \rangle = W_{lm_l m_s}^{(n)} \delta_{ll'} \delta_{m_l m'_l} \delta_{m_s m'_s}$. H' will couple eigenfunctions with different n values but diagonal with the same n .

In this case the expected value does not depend on s , m_l and m_s so $W_{lm_l m_s}^{(n)} \equiv W_l^{(n)}$. And one can get that the correction is:

$$W_l^{(n)} \equiv E_r^{(1)} = -\frac{(E_n^2)}{2mc^2} \left[\frac{4n}{l+1/2} - 3 \right] \quad (2.5)$$

We note that this formula is valid for all Z .

2.1.2 Spin-orbit-coupling

This component comes from the interaction between the magnetic dipole of the electron and the magnetic field generated by the central charge. (Electron at rest and the central charge looping around it). The term is:

$$H_{so} = -\vec{\mu} \cdot \vec{B} = \left(\frac{Ze^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} \quad (2.6)$$

but because:

$$\vec{S} \cdot \vec{L} = S_x L_x + S_y L_y + S_z L_z = \frac{1}{2} (J^2 - L^2 - S^2) \quad (2.7)$$

obviously now $|nlsm_l m_s\rangle$ are not eigenfunctions anymore, but $|njls m_j\rangle$ they are, therefore we work on these eigenfunctions of H^0 . Let's span angular and spin part of these eigenfunctions in the old eigenfunction for the electron case ($s = 1/2$):

$$|l1/2jm_j\rangle = \sum_{m_l=m_j-1/2}^{m_l=m_j+1/2} \langle lsm_l m_s | jm_j \rangle |l1/2m_l m_s\rangle \quad (2.8)$$

Let's define the eigenfunctions associated with these states on the coordinates space:

$$\langle \theta \varphi \sigma | njlsm_j \rangle \equiv Y_{ls}^{jm_j}(\theta, \varphi, \sigma) = \sum_{m_s, m_l} \langle lsm_l m_s | jm_j \rangle Y_{lm_l}(\theta, \varphi) \chi_{sm_s}(\sigma) \quad (2.9)$$

We have to use the following results:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a^3 n^3 l(l+1/2)(l+1)} \quad (2.10)$$

Now the coefficients $W_{jls m_l m_s}^{(n)}$ they indeed depend on l, j and $s = 1/2$ and we can get that the first order correction is:

$$W_{jl}^{(n)} \equiv E_{so}^{(1)} = \frac{(E_n)^2}{mc^2} \left[\frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right] \quad (2.11)$$

We note that this formula is valid for all Z .

2.1.3 Fine structure correction

Adding the relativistic correction and the spin orbit correction we get:

$$E_{fs} = E_r^{(1)} + E_{so}^{(1)} = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right) \quad (2.12)$$

They are put together because they are of the same order. In table [2] we show the corrections for relativistic energy E_r and spin-orbit E_{so} for different values of n, l and j .

n	l	j	$E_r[eV]$	$E_{so}[eV]$
1	0	1/2	$-9.1e^{-4}$	0
2	1	3/2	$-2.6e^{-5}$	$8.3e^{-5}$
		1/2	$-2.6e^{-5}$	$3.8e^{-5}$
		0	$-1.5e^{-4}$	0
3	2	5/2	$-4.0e^{-6}$	$1.5e^{-5}$
		3/2	$-4.0e^{-6}$	$1.1e^{-5}$
		1/2	$-1.1e^{-5}$	$1.8e^{-5}$
	1	3/2	$-1.1e^{-5}$	$4.5e^{-6}$
		1/2	$-1.1e^{-5}$	$4.5e^{-6}$
		0	$-4.7e^{-5}$	0

Tabla 2: sssssss.

3 External fields

3.1 Zeeman effect

Let's study the case in which we apply an external magnetic field $\vec{B} = B\hat{k}$ to our hydrogenoid atom. With this external field in the medium we a torque appears in the system and provides a new term in the hamiltonian:

$$H_Z = -(\mu_l + \mu_s) \cdot \vec{B} = \frac{e}{2m} (\vec{l} + 2\vec{s}) \cdot \vec{B} = \frac{eB}{2m} (l_z + 2s_z) = \frac{eB}{2m} (j_z + s_z) \quad (3.1)$$

We could study the effect of this term using perturbation theory but we did it already with the spin-orbit term so we have to decide what will be treated as the perturbation: the Zeeman hamiltonian, the spin-orbit hamiltonian or both.

$$H_{so} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{s} \cdot \vec{l} \quad (3.2)$$

3.1.1 Weak field

In this case we take the unperturbed hamiltonian H_0 as:

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} - \frac{1}{8m^3 c^2} p^4 + H_{so} \quad (3.3)$$

We don't know the real eigenfunctions of this hamiltonian nor the eigenvalues but we take them as:

$$E_{nlj} = E_n + W_{jl}^{(n)} \quad (3.4)$$

These are the considered unperturbed states which are degenerated in the values of m_j . Therefore we need to use degenerate perturbation theory where it is always an advantage to find an operator A which conmmutes with both H_0 and H' , where the eigenfunctions of that A are degenerate for H_0 and not for A . In that case we know H' does not couple states from different subspaces of H_0 . So those are the 'right' eigenfunctions of H_0 to use like in non-degenerate theory.

The operator j_z conmmutes with H_Z so we could think about using the eigenstates $\langle nlm_j \rangle$ but j^2 does not conmmute with s_z it is not demonstrated s_z is diagonal in that basis but it can be shown that it is in blocks with fixed n, l and j :

$$\langle nlm'_j | H_Z | nlm_j \rangle = 0 \quad \text{for} \quad m'_j \neq m_j \quad (3.5)$$

The diagonal terms of these blocks are:

$$\langle nlm_j | j_z | nlm_j \rangle = m_j \hbar \quad (3.6)$$

$$\langle nlm_j | s_z | nlm_j \rangle = \frac{\hbar}{2} [\langle lm_l 1/2 | ljm_j \rangle^2 - \langle lm_l - 1/2 | ljm_j \rangle^2] \quad (3.7)$$

So the diagonal elements of the perturbed hamiltonian are:

$$\Delta E^1 = \langle nlm_j | H_Z | nlm_j \rangle = \frac{eB}{2m} \left[m_j \hbar + \frac{\hbar}{2} [\langle lm_l 1/2 | ljm_j \rangle^2 - \langle lm_l - 1/2 | ljm_j \rangle^2] \right] \quad (3.8)$$

Therefore the total energy till first-order perturbation energy is:

$$E_{nlj} = E_n + W_{jl}^{(n)} + \Delta E^1 \quad (3.9)$$

You can get this value as the form:

$$\Delta E^1 = \mu_B g_J B m_j \quad (3.10)$$

where:

$$g_J = 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \quad (3.11)$$

3.1.2 Strong field

Now we suppose the external magnetic field is much greater than the internal magnetic field so we take as the unperturbed hamiltonian H_0 as:

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} + \frac{e}{2m} B(l_z + s_z) \quad (3.12)$$

In this case the old basis $|nlm_l m_s\rangle$ are the exact eigenfunctions of this unperturbed hamiltonian. The basis $|nljm_j\rangle$ could not be eigenfunctions of this hamiltonian because j^2 does not commute with s_z . While the eigenvalues now are:

$$E_{nlm_l m_s}^0 = E_n + \mu_B B(m_l + 2m_s) \quad (3.13)$$

Here it is important to note that this states are not degenerate so we can apply non perturbed perturbation theory. And the perturbed hamiltonian is:

$$H' = -\frac{1}{8m^3 c^2} p^4 + H_{so} \quad (3.14)$$

We already calculated the first order correction energy for the first part of this hamiltonian in eq.[]. Now let's calculate the term H_{so} in the basis $nlm_l m_s$:

$$\langle \vec{S} \cdot \vec{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle L_y \rangle \langle S_y \rangle + \langle L_z \rangle \langle S_z \rangle = \hbar^2 m_l m_s \quad (3.15)$$

because $\langle S_i \rangle = 0$ and $\langle L_i \rangle = 0$ for $i = x, y$.

Then the first correction energy is:

$$E^1 = E_r^{(1)} + \hbar^2 m_l m_s \quad (3.16)$$

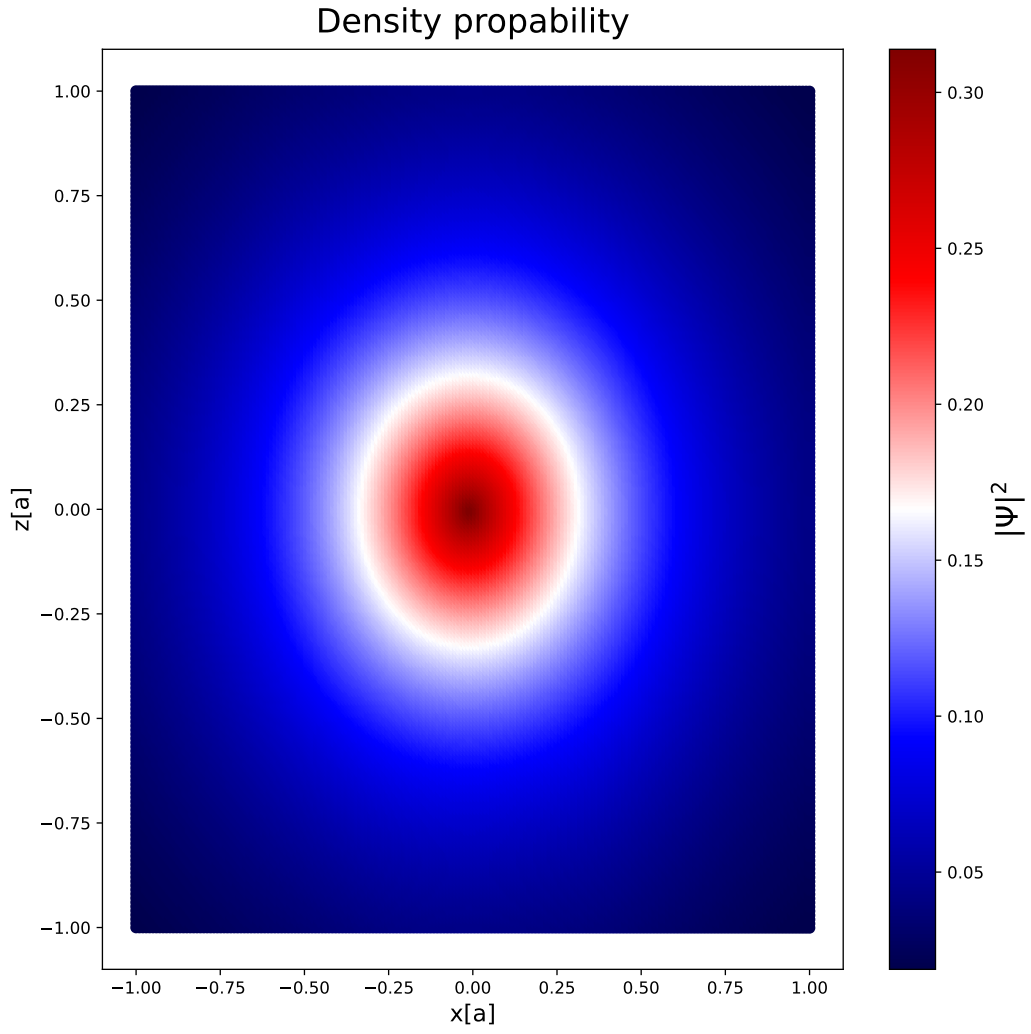


Figure 3: Density probability function for $n = 1$ and $l = 0$ in the section $\varphi = 0$ and $\varphi = \pi$. The dimension of z and x is the Bohr radius.

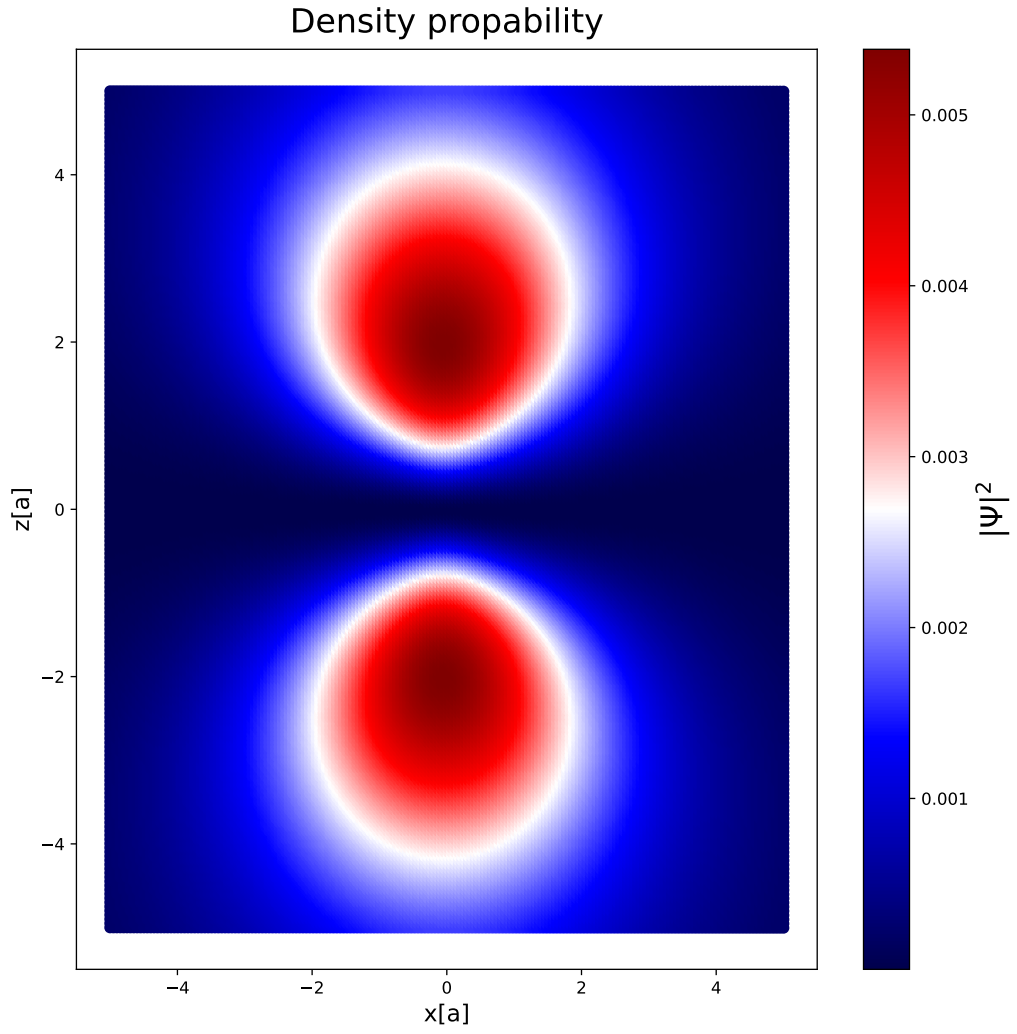


Figura 4: Density probability function for $n = 2$, $l = 1$ and $m_l = 0$ in the section $\varphi = 0$ and $\varphi = \pi$. The dimension of z and x is the Bohr radius.

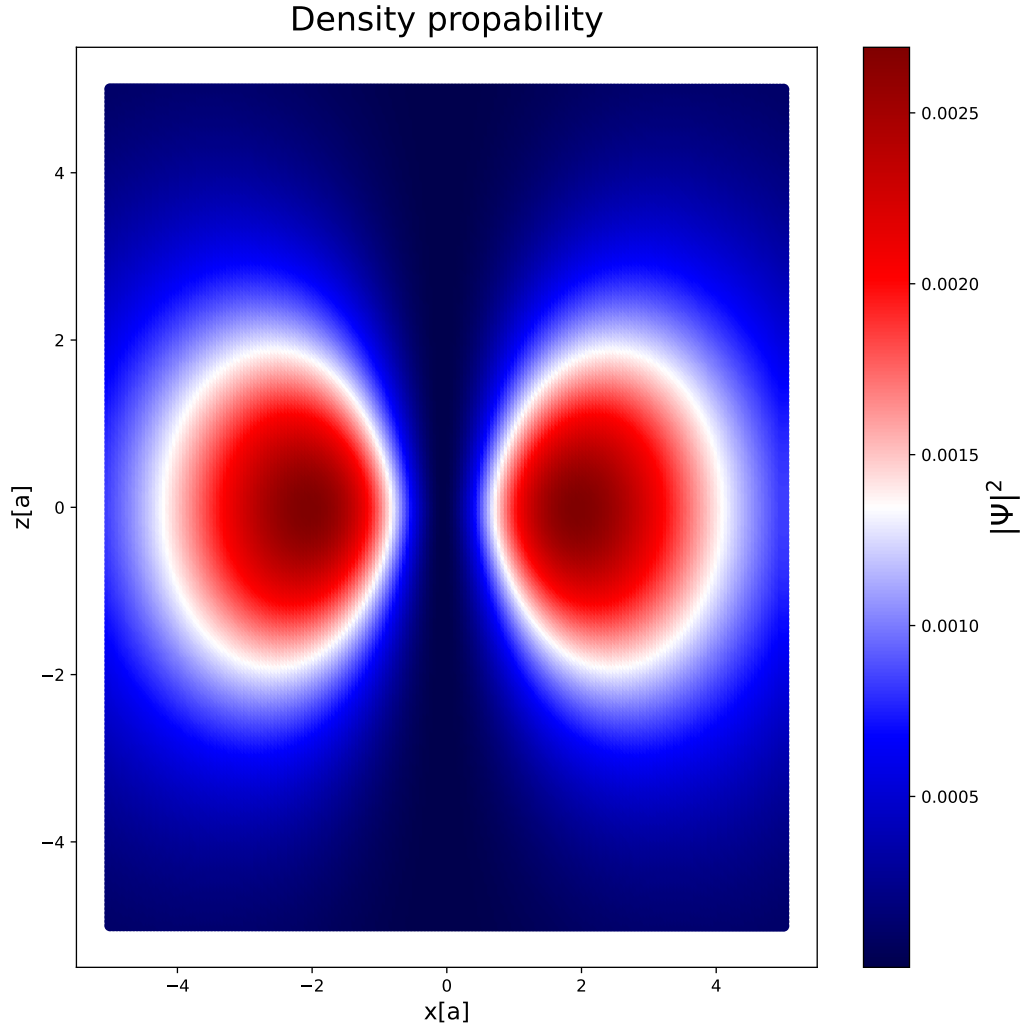


Figure 5: Density probability function for $n = 2$, $l = 1$ and $|m_l| = 1$ in the section $\varphi = 0$ and $\varphi = \pi$. The dimension of z and x is the Bohr radius.

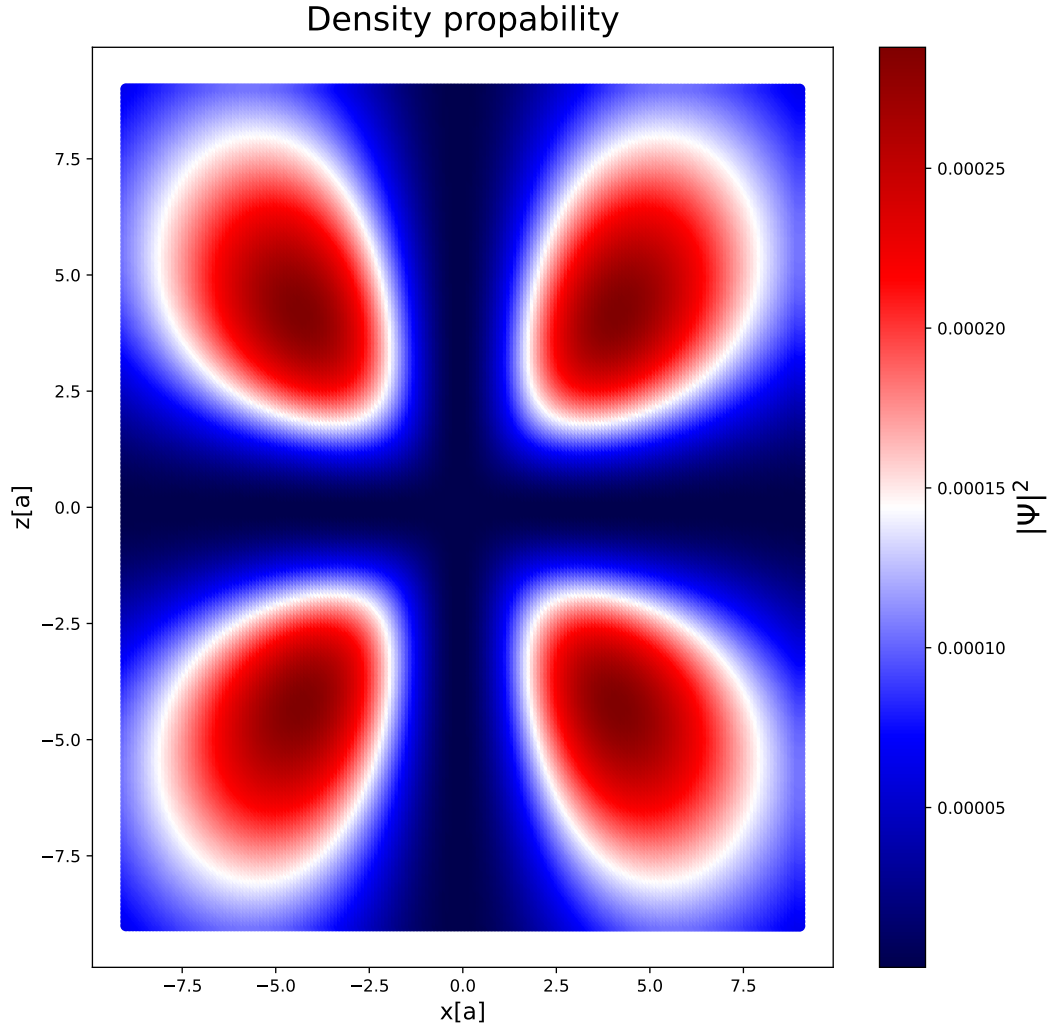


Figure 6: Density probability function for $n = 2$, $l = 1$ and $|m_l| = 1$ in the section $\varphi = 0$ and $\varphi = \pi$. The dimension of z and x is the Bohr radius.