1. Hydrogen atom

   (a) What is the spin-orbit interaction? How does it lead to the observed fine-structure splitting of the spectral lines of the hydrogen atom?

   (b) The $n = 3$ with $l = 2$ level of the hydrogen atom comprises ten states whose energies are equal (spin and $m_l$ degeneracy) if the spin-orbit coupling is ignored and if no external magnetic field is applied. Draw a diagram that shows how the degenerated states split when one takes into account the spin-orbit coupling. For each level, indicate the corresponding $j$ quantum number and the degeneracy of the level.
2. Probability Density

For a hydrogen atom in a state designated by the quantum number \( n \) and \( l \), the probability of finding the electron at any location with radial coordinate between \( r \) and \( r + dr \) is given by

\[
P_{nl}(r) \, dr = R_{nl}^*(r) \, R_{nl}(r) \, 4 \pi r^2 \, dr .
\]

Knowing that the radial part of the wavefunction for the hydrogen atom in the \( n = 2, \ l = 1 \) state is given by

\[
R_{21} = A \frac{r}{\sqrt{6 \pi a_o}} e^{-r/2a_o}
\]

where \( A \) is a constant and \( a_o \) is the Bohr radius,

(a) find the value of \( A \).

(b) Calculate the location at which the radial probability density \( P_{nl} \) is maximum.

(c) Explain why the expectation value \( \langle r_{nl} \rangle \) of the position

\[
\langle r_{nl} \rangle = n^2 a_o \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{l (l+1)}{n^2} \right] \right\}
\]

does not necessarily correspond to the location at which the radial probability density \( P_{nl} \) is maximum.
3. Nuclear Potential

The nuclear potential that binds protons and neutrons in the nucleus of an atom is often approximated by a square well. Imagine one proton confined in a one-dimensional infinite square well of length $R$.

(a) Using the uncertainty principle, show how it is possible to estimate the energy of the ground state.

(b) Using the Schrödinger’s equation or the interference of waves, show that the possible energy levels of the system are given by

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2 m_p R^2}$$

(c) Find the wavelength of the photon which is required to excite the proton from $n = 1$ to $n = 3$.

(d) i. Do a sketch of the wavefunction and the probability density associated with the first excited state ($n = 2$). Use your sketch to justify why, in Quantum Mechanics, we cannot define the path followed by a particle.

![Figure 1: Nuclear Potential](image-url)
4. Hydrogen Atom  
Consider the state with \( n = 2 \) and \( l = 1 \) in which the total wavefunction corresponds to the superposition of two wavefunctions with different \( m_l \) values,

\[
\psi_{21} = A [\psi_{210} + \psi_{21-1}]
\]

(a) Calculate the expectation value of \( L_z \).
(b) Calculate the uncertainty on the value of \( L_z \).

5. Hydrogen Atom  
Calculate the expectation value of the potential energy when the electron’s wavefunction of an hydrogen atom is \( \psi = \psi_{21-1} \). Use the potential

\[
U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}
\]
**Formula Sheet**

- Electron mass: \( m_e = 9.11 \times 10^{-31} \text{ kg} = 0.511 \text{ MeV/c}^2 \)
- Proton mass: \( m_p = 1.673 \times 10^{-27} \text{ kg} = 938.3 \text{ MeV/c}^2 \)
- Neutron mass: \( m_n = 1.675 \times 10^{-27} \text{ kg} = 939.6 \text{ MeV/c}^2 \)
- Planck’s constant: \( \hbar = 1.06 \times 10^{-34} \text{ J s} \)
- Speed of light: \( c = 3 \times 10^8 \text{ m/s} \)
- Electron charge: \( e = 1.602 \times 10^{-19} \text{ C} \)
- Vacuum permittivity: \( \epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{N} \cdot \text{m}^2 \)
- Bohr magneton: \( \mu_B = 9.27 \times 10^{-24} \text{ J/Tesla} \)
- Conversion factor: \( 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \)

**Useful Integrals**

<table>
<thead>
<tr>
<th>Integral</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \int_0^\infty x^n e^{-ax} , dx = \frac{n!}{a^{n+1}} )</td>
<td></td>
</tr>
<tr>
<td>( \int_0^\infty x^{2n} e^{-ax} , dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1}a^n} )</td>
<td></td>
</tr>
<tr>
<td>( \int_0^\infty x^{2n+1} e^{-ax} , dx = \frac{n!}{2a^{n+1}} )</td>
<td></td>
</tr>
<tr>
<td>( \int x \sin^2 ax , dx = \frac{x^2}{4} - \frac{x \sin 2ax}{4a} - \frac{\cos 2ax}{8a^2} )</td>
<td></td>
</tr>
<tr>
<td>( \int x \cos^2 ax , dx = \frac{x^2}{4} + \frac{x \sin 2ax}{4a} + \frac{\cos 2ax}{8a^2} )</td>
<td></td>
</tr>
<tr>
<td>( \int x^2 \sin^2 ax , dx = \frac{x^3}{6} - \left( \frac{x^2}{4a} - \frac{1}{8a^2} \right) \sin 2ax - \frac{x \cos 2ax}{4a^2} )</td>
<td></td>
</tr>
<tr>
<td>( \int x^2 \cos^2 ax , dx = \frac{x^3}{6} + \left( \frac{x^2}{4a} - \frac{1}{8a^2} \right) \sin 2ax + \frac{x \cos 2ax}{4a^2} )</td>
<td></td>
</tr>
</tbody>
</table>

**Trigonometry Formulas**

- \( \cos^2 \alpha = \frac{1}{2} (1 + \cos 2\alpha) \)
- \( \sin^2 \alpha = \frac{1}{2} (1 - \cos 2\alpha) \)
- \( \cos \alpha = \frac{e^{i\alpha} + e^{-i\alpha}}{2} \)
- \( \sin \alpha = \frac{e^{i\alpha} - e^{-i\alpha}}{2i} \)

**Schrödinger’s equation in one dimension**

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + U(x) \, \Psi(x) = E \, \Psi(x)
\]

with the total wavefunction given by

\[
\Psi_n(x, t) = \Psi_n(x) \, \Phi_n(t) = \Psi_n(x) \, e^{-iE_n t/\hbar}
\]

**Uncertainty Principle**

\[
\Delta x \, \Delta p_x \geq \frac{\hbar}{2}
\]
One-Electron Atoms:
\[ H \Psi_{n,l,m}(r, \theta, \phi) = E_n \Psi_{n,l,m}(r, \theta, \phi) \]

\[ \Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi) \]

These wavefunctions are orthogonal and normalized, hence

<table>
<thead>
<tr>
<th>( m_l )</th>
<th>Eigenfunctions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \psi_{100} = \frac{1}{\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/2a_0} )</td>
</tr>
<tr>
<td>0</td>
<td>( \psi_{200} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} )</td>
</tr>
<tr>
<td>0</td>
<td>( \psi_{210} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos \theta )</td>
</tr>
<tr>
<td>±1</td>
<td>( \psi_{21 \pm 1} = \frac{1}{8\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\phi} )</td>
</tr>
<tr>
<td>0</td>
<td>( \psi_{300} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 27 - 18 \frac{Zr}{a_0} + 2 \left( \frac{Zr}{a_0} \right)^2 \right) e^{-Zr/3a_0} )</td>
</tr>
<tr>
<td>0</td>
<td>( \psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/3a_0} \cos \theta )</td>
</tr>
<tr>
<td>±1</td>
<td>( \psi_{31 \pm 1} = \frac{1}{81\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/3a_0} \sin \theta e^{\pm i\phi} )</td>
</tr>
<tr>
<td>0</td>
<td>( \psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} (3 \cos^2 \theta - 1) )</td>
</tr>
<tr>
<td>±1</td>
<td>( \psi_{32 \pm 1} = \frac{1}{81\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin \theta \cos \theta e^{\pm i\phi} )</td>
</tr>
<tr>
<td>±2</td>
<td>( \psi_{32 \pm 2} = \frac{1}{162\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2 \theta e^{\pm 2i\phi} )</td>
</tr>
</tbody>
</table>

Figure 2: One-Electron Wavefunctions
These wavefunctions are orthogonal and normalized, hence
\[
\int_0^\infty \int_0^{2\pi} \int_0^\pi \Psi_{n_f,l_f,m_{f}}^*(r, \theta, \phi) \Psi_{n_i,l_i,m_{i}}(r, \theta, \phi) r^2 \sin \theta \, d\theta \, d\phi \, dr = \delta_{n_f,n_i} \delta_{l_f,l_i} \delta_{m_{f},m_{i}}
\]

\[
E_n = -\frac{\mu Z^2 e^4}{(4 \pi \epsilon_o)^2 2 \hbar^2 n^2} = -\frac{13.6 Z^2}{n^2} \, eV \quad n = 1, 2, 3, \ldots
\]

\[
a_o = \frac{4 \pi \epsilon_o \hbar^2}{\mu e^2} = 0.529 \, \text{Å} \quad \text{Bohr’s radius}
\]

\[
L = \sqrt{l(l+1)} \hbar, \quad l = 0, \ldots, n - 1
\]

\[
L_z = m_l \hbar, \quad m_l = -l, -l+1, \ldots, l-1, l
\]

\[
\text{degeneracy} = (2l + 1)
\]

**Magnetic Properties**

\[
E_{mag} = -\vec{\mu} \cdot \vec{B}
\]

orbital \quad \vec{\mu}_L = -g_l \mu_B \frac{\vec{L}}{\hbar}

magnetic moment \quad \text{intrinsic} \quad \vec{\mu}_S = -g_s \mu_B \frac{\vec{S}}{\hbar}

Total \quad \vec{\mu} = \vec{\mu}_L + \vec{\mu}_S

magnetic moment \quad \vec{J} = \vec{L} + \vec{S}

Total \quad g\text{-factors}

orbital \quad g_l = 1

electron spin \quad g_s = 2

**Spin-Orbit Coupling**

\[
\Delta E = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}
\]
OPERATORS

\[ P_x = -i\hbar \frac{\partial}{\partial x} \]
\[ E = i\hbar \frac{\partial}{\partial t} \]
\[ \Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \]

In spherical polar coordinates

\[ L_x = i\hbar \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \]
\[ L_y = i\hbar \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \]
\[ L_z = -i\hbar \frac{\partial}{\partial \phi} \]

Using that \( L^2 = L_x^2 + L_y^2 + L_z^2 \),

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