Atomic Structure and Spectra
Electronic Spin, Pauli Exclusion Principle, Multielectron Atom

Daniele Toffoli

Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste

October 16, 2024

Outline

Outline

The Hydrogen Spectrum
Recap

- Energy levels in hydrogen atom are given by:

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$

- The energy of transitions between levels is:

$$\Delta E = E_f - E_i = h\nu$$

- The Rydberg formula for spectral lines:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- In the electronic emission and absorption of H, not all transitions are visible. Some transitions are *forbidden*.

The Hydrogen Spectrum
Interaction of Light with a Hydrogen Atom

- Absorption: Photon with energy $h\nu$ interacts with a hydrogen atom $\rightarrow$ Excites electron from E_1 to E_2 ($E_1 < E_2$).
- Spontaneous Emission: Excited electron in a state E_2 spontaneously transitions to a state E_1 ($E_1 < E_2$).
- Stimulated Emission: Incident photon with energy interacts with an excited atom $\rightarrow$ stimulates the electron to drop from E_2 to E_1 ($E_1 < E_2$).
- In all three cases: $h\nu = E_2 - E_1$
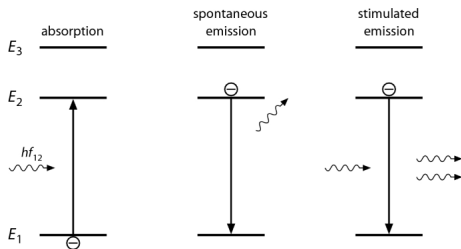
Hydrogen Spectrum
Electromagnetic Waves and the Vector Potential

- Electromagnetic wave: $\vec{E}(\vec{r}, t)$ and $\vec{B}(\vec{r}, t)$ components perpedicular to each other and the direction of propagation.
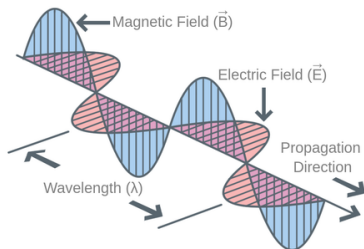
- $\vec{E}$ and $\vec{B}$ fields can be written in terms of the *vector* and *scalar* potentials.

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}$$

The Hydrogen Spectrum
Interaction of Electrons with Electromagnetic Waves

- For a plane electromagnetic wave, the vector potential can be expressed as a sinusoidal function:

$$\vec{A}(\mathbf{r}, t) = \vec{A}_0 \cos(\vec{k} \cdot \vec{r} - \omega t)$$

  where $\vec{A}_0$ is the amplitude, $\vec{k}$ is the wave vector, and ω is the angular frequency of the wave.

- The electric and magnetic fields can be derived from $\vec{A}$, and describe the oscillating behavior of the electromagnetic wave.

The Hydrogen Spectrum
The Dipole Approximation

- The interaction of the electron in the hydrogen with the EM wave is represented quantum mechanically via an extra term in the Hamiltonian:
$$\hat{H} = \hat{H}_0 - \frac{i\hbar e}{\mu}\vec{A} \cdot \vec{\nabla}$$
where $\hat{H}_0$ is the usual hydrogen Hamiltonian, μ is the reduced mass and $\vec{A}$ is the vector potential.

- In most atomic transitions, the wavelength of radiation is much larger than the size of the atom:
$$\lambda \gg a_0$$

- This allows us to approximate the interaction between the atom and the electromagnetic field using the *dipole approximation.*
$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \left[\hat{H}_0 + e\vec{A}_0 \cdot \vec{r}\right]\Psi(\vec{r}, t)$$

The Hydrogen Spectrum
Selection Rules

- Fermi's Golden Rule: The transition probability depends on the matrix element of the dipole operator between initial and final states.

$$W_{i \to f} \propto |\langle \psi_f | \vec{d} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \qquad \vec{d} = e\vec{r}$$

- Only transitions for which this matrix element is non-zero are allowed, leading to selection rules.
- The selection rules are:

$$\Delta l = \pm 1 \text{ and } \Delta m = 0, \pm 1.$$

Outline

1. The Hydrogen Spectrum

2. **Orbital Angular Momentum**

3. Electron Spin

4. The Helium Atom

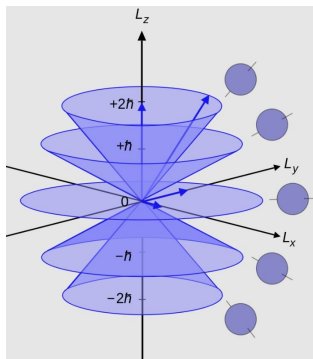# Orbital Angular Momentum in Hydrogen
Introduction and Quantization

- The orbital angular momentum, $\hat{L}$, of an electron is associated with its motion around the nucleus.

    Classical: $\vec{L} = \vec{r} \times \vec{p}$, where $\vec{r}$ is the position vector and $\vec{p}$ is the momentum vector.

    QM: $\hat{L} = \vec{r} \times \hat{\vec{p}}$, where the variables are replaced by operators.

- Unlike the classical case, where $\vec{L}$ can take any value, the magnitude of the orbital angular momentum is quantized.

- There are two levels of quantization: the first has to do with the magnitude.

$$L^2 = \hbar^2 l(l+1),$$

where l is the orbital quantum number, $l = 0, 1, 2, \ldots$.

Orbital Angular Momentum in Hydrogen
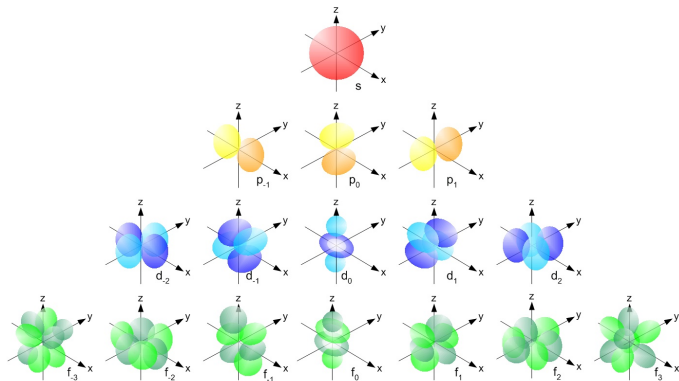
Introduction and Quantization

- The projection of the orbital angular momentum on the z-axis, $\hat{L}_z$, is also quantized:

$$\hat{L}_z \psi = m_l \hbar \psi,$$

- m_l is the magnetic quantum number, $m_l = -l, -(l-1), \dots, l$.
- Only specific orientations of $\vec{L}$ are allowed in space: $(2l + 1)$ orientations

Orbital Angular Momentum in Hydrogen
Connection to orbitals

- For $l = 0$, there is no angular momentum (s-orbitals).
- For $l = 1$, three possible values of m_l (p-orbitals).
- For $l = 2$, five possible values of m_l (d-orbitals).

Daniele Toffoli (UniTS)   Atomic Structure and Spectra   October 16, 2024   13 / 25

Orbital Angular Momentum in Hydrogen

Spherical Harmonics and Angular Wavefunctions

- The angular part of the wavefunction in hydrogen is described by spherical harmonics, $Y_l^{m_l}(\theta, \phi)$.
- Spherical harmonics are solutions to the angular part of the Schrödinger equation for the hydrogen atom.
- They depend on the angular quantum numbers l and m_l and are functions of the polar angles θ and ϕ.
- Examples:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \quad \text{(spherically symmetric)}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \quad \text{(p}_z \text{ orbital)}$$

Orbital Angular Momentum in Hydrogen
Coupling of Angular Momenta

- When an atom has multiple electrons, their individual angular momenta couple to form the total angular momentum.

- The orbital angular momenta of two electrons, $\vec{L}_1$ and $\vec{L}_2$, combine to form the total angular momentum:

$$\vec{L}_{\text{tot}} = \vec{L}_1 + \vec{L}_2.$$

- Similarly, the total angular momentum quantum number, L, follows the rules of vector addition:

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2.$$

- This applies to both orbital angular momentum and spin angular momentum.

Outline

Electron Spin
Introduction to Electron Spin

- Spin is an intrinsic form of angular momentum carried by electrons, independent of their orbital motion.
- Unlike orbital angular momentum, which arises from spatial movement, spin is a quantum property that does not have a classical counterpart.
- The spin angular momentum is quantized, with the quantum number $s = \frac{1}{2}$ for electrons.
- The possible values of the spin projection on the z-axis are:

$$m_s = \pm\frac{1}{2}.$$

Electron Spin
Spin Angular Momentum and Spin Operators

- The magnitude of the spin angular momentum is given by:

$$S^2 = s(s+1)\hbar^2,$$

where $s = \frac{1}{2}$ for electrons.

- The projection of spin angular momentum along the z-axis is quantized:

$$\hat{S}_z \psi = m_s \hbar \psi, \quad m_s = \pm \frac{1}{2}.$$

Electron Spin

Pauli Exclusion Principle and Electron Spin

- The Pauli Exclusion Principle in its simpler form states that no two electrons in an atom can have the same set of quantum numbers.
- Since each electron has a unique set of quantum numbers (n, l, m_l, m_s), this principle directly involves the electron's spin.
- In the context of multi-electron atoms, spin is essential for determining the electron configurations:
    - Electrons with the same orbital quantum numbers (n, l, m_l) must have opposite spin values ($m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$).
- The antisymmetric nature of the wavefunction for fermions, like electrons, reflects the Pauli Exclusion Principle.

Outline

1. The Hydrogen Spectrum

2. Orbital Angular Momentum

3. Electron Spin

4. The Helium Atom

Helium Atom: Introduction

- Helium atom: simplest multi-electron atom $\rightarrow$ two electrons and a nucleus.
- The Hamiltonian for the Helium atom (ignoring relativistic effects and spin-orbit coupling) is:

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where r_1 and r_2 are the distances of the two electrons from the nucleus, and r_{12} is the distance between the two electrons.
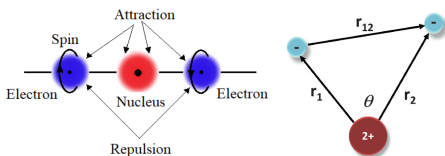
Ground State of the Helium Atom

- In the ground state, both electrons occupy the $1s$ orbital. The electronic configuration is $1s^2$.

- The wavefunction for the spatial part of the ground state can be approximated by:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)$$

where ψ_{1s} is the hydrogen-like wavefunction for each electron.

- The energy of the ground state is approximately:

$$E_0 = -2 \times 13.6\,\text{eV} + \langle \frac{e^2}{4\pi\epsilon_0 r_{12}}\rangle$$

where the second term accounts for the electron-electron repulsion.

Excited States of the Helium Atom

- In excited states, one or both electrons can occupy higher orbitals.
- For example, the first excited state corresponds to the configuration $1s^1 2s^1$.
- The spatial wavefunction for an excited state is:

$$\psi(\vec{r_1}, \vec{r_2}) = \psi_{1s}(\vec{r_1})\psi_{2s}(\vec{r_2}) \pm \psi_{2s}(\vec{r_1})\psi_{1s}(\vec{r_2})$$

  where the plus or minus sign corresponds to whether the state is symmetric or antisymmetric with respect to particle exchange.

- The energy of excited states depends on both the electron-nucleus and electron-electron interactions, making it more complex than in hydrogen.

Pauli Exclusion Principle and Antisymmetry Principle

- The Pauli Exclusion Principle states that no two fermions (electrons) can occupy the same quantum state.
- The total wavefunction for the two-electron system must be antisymmetric under the exchange of the two electrons:

$$\Psi(\vec{r}_1, \vec{r}_2, \sigma_1, \sigma_2) = -\Psi(\vec{r}_2, \vec{r}_1, \sigma_2, \sigma_1)$$

- The total wavefunction is the product of a spatial part and a spin part:

$$\Psi_{\text{total}} = \psi_{\text{spatial}} \chi_{\text{spin}}$$

- If the spatial part is symmetric, the spin part must be antisymmetric (singlet state), and vice versa (triplet state).

Spin States of the Helium Atom

- The spin part of the wavefunction describes the spin states of the two electrons.
- There are four possible spin states:
  - One antisymmetric singlet state:

$$\chi_{\text{singlet}} = \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) - \beta(1)\alpha(2) \right)$$

  - Three symmetric triplet states:

$$\chi_{\text{triplet},+1} = \alpha(1)\alpha(2), \quad \chi_{\text{triplet},-1} = \beta(1)\beta(2)$$

$$\chi_{\text{triplet},0} = \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) + \beta(1)\alpha(2) \right)$$

- The singlet state corresponds to the total spin $S = 0$, while the triplet states correspond to $S = 1$.
- The antisymmetry of the total wavefunction ensures compliance with the Pauli Exclusion Principle.