PH102, 2012W, Lecture Notes: January 25, Wed, Class 7

Hydrogen Atom: Orbital and spin angular momentum quantization and LS coupling
Objectives:

- Define what the Spin angular momentum represents and how it is quantized.
- Define the total angular momentum, how it is quantized, and how it is related to L and S.
- Understand what LS coupling represents and how it is done.

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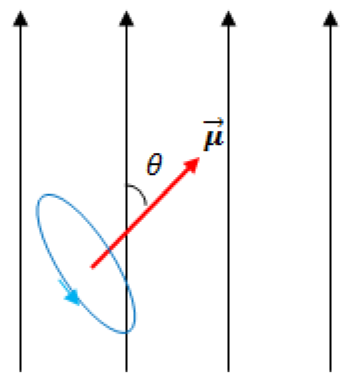
7.1. Why Spin?

An electron revolving around a nucleus in an atom can be considered as a minute current loop and has a magnetic field of a magnetic dipole $\vec{\mu}$. In an external $\vec{B}$ (magnetic) field, the potential of the magnetic dipole can be defined as:



$$U = -\vec{\mu} \cdot \vec{B} = \left(\frac{e}{2m}\right)\vec{L} \cdot \vec{B} = \left(\frac{e}{2m}\right) L_z B_z$$

Since $\vec{\mu} = -\left(\frac{e}{2m}\right)\vec{L}$

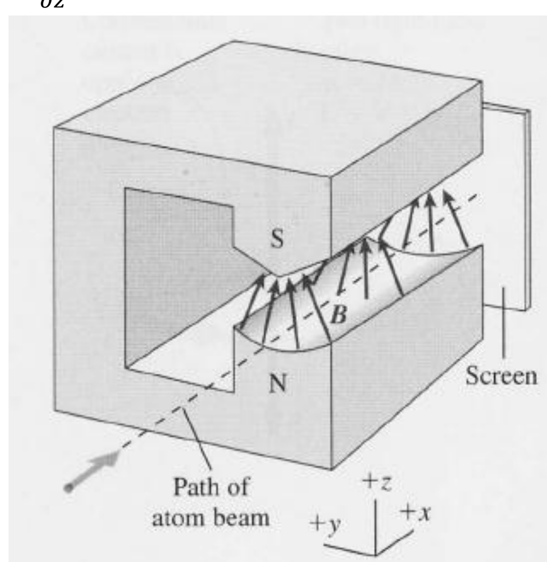
Why? The magnetic moment of a current loop is

$$\mu = i(\pi r^2) = -e\left(\frac{v}{2\pi r}\right)(\pi r^2) = -e\left(\frac{vr}{2}\right) = -\frac{eL}{2m}$$

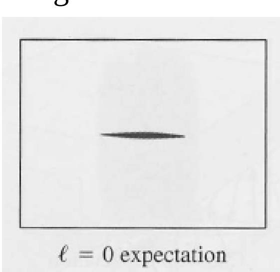
The force exerting on the magnetic dipole is

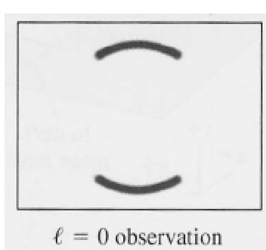
$$F = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right) = -\left(\frac{e}{2m}\right) L_z \frac{\partial B_z}{\partial z}\hat{z} = -\left(\frac{e}{2m}\right)(m_l \hbar)\frac{\partial B_z}{\partial z}\hat{z}$$ where $m_l = -l, \dots, +l$.

$\vec{B} = B_z \hat{z}$ Since $L_z = m_l \hbar$



In a uniform $\vec{B}$ field, there is no force exerting on the magnetic dipole. In a non-uniform $\vec{B}$ field, the force varies by m_l.
If l=0 → m_l. = 0 → no orbital motion → no magnetic moment → one spectral line


$\ell = 0$ expectation


$\ell = 0$ observation

However, the Stern-Gerlach experiment shows that two split lines are present when l=0.

When the spin angular momentum is considered, then the electron in the atomic beam in the experiment can be solved by replacing $-\vec{\mu}$ *with* $\vec{\mu}_s = -\frac{e}{2m}\vec{S}$

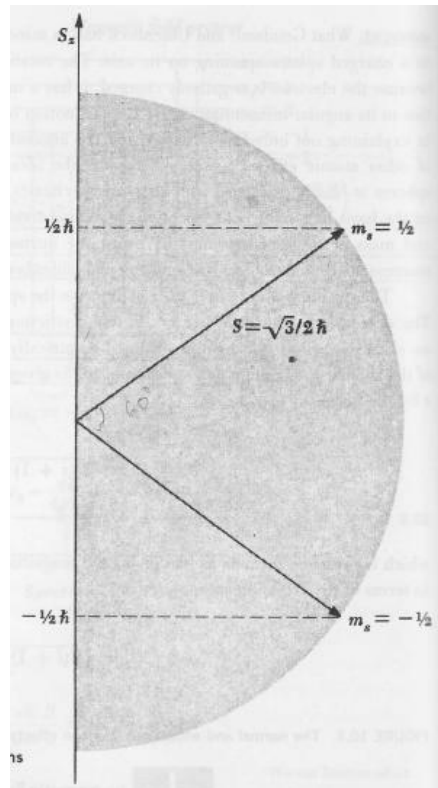
$F = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right) = -\left(\frac{e}{2m}\right) S_z \frac{\partial B_z}{\partial z}\hat{z} = -\left(\frac{e}{m}\right)(m_s\hbar)\frac{\partial B_z}{\partial z}\hat{z}$ where $m_s = \pm\frac{1}{2}$ → two lines justified!

To account for this, an intrinsic angular momentum called Spin (S) was introduced by Goudsmit and Uhlenbeck in 1925:

- The intrinsic angular momentum is one of fundamental properties of a particle such as mass and charge.
  - Fermions (Half-integral spin): Electron, proton, neutron, neutrino, and Omega = ½
  - Bosons (integral spin): pion and alpha particle = 0
  - Bosons: Photon, Deutron = 1
- Magnitude of $\vec{S}$, $|\vec{S}| = \sqrt{s(s+1)}\,\hbar$

  $(e.g.\, electron\ |\vec{S}| = \frac{\sqrt{3}}{2}\hbar)$
- Direction is quantized by $S_z = m_s\hbar$ where $m_s = -s, . -s+1, \ldots s-1, s$ (e.g. electron -1/2 and 1/2)
- A given particle has intrinsic magnetic dipole moment due to its intrinsic angular momentum:

  $\vec{\mu}_s = g\frac{q}{2m}\vec{S}$ (e.g. electron $\vec{\mu}_s = -\frac{e}{m}\vec{S}$)
- Spin is not classical, so an analogy of rotating its own axis does not properly describe it.
- Now the wave function for the Schrodinger Equation can be completely described using four quantum numbers, n, l, m_l, m_s.



$$\psi_{n,l,m_l,m_s} = \psi_{n,l,m_l}(r,\theta,\phi)m_s$$

OR

$$\psi_{n,l,m_l,+\frac{1}{2}} = \psi_{n,l,m_l}(r,\theta,\phi)\uparrow$$

$$\psi_{n,l,m_l,-\frac{1}{2}} = \psi_{n,l,m_l}(r,\theta,\phi)\downarrow$$

- Spin should increase the degeneracy in the hydrogen atom. The number of states with the same n would increase the degeneracy from n^2 to $2n^2$. But, due to interactions between orbital and spin angular momentums, degeneracy can be broken.
- Photon's Spin is 1. When an atom undergoes a transition in which a photon is produced, there is a limit on how much the atom's angular momentum can change: no more than 1, which creating selection rules for spectral emissions.

Spin-Orbit Coupling (Spin-Orbit Interaction) OR LS Coupling

In a weak external magnetic field where the external magnetic field does not overwhelm the magnetic field internal to the atom, we do not observe separate quantization of $\vec{L}$ and $\vec{S}$. Rather, we observe the combined angular momentum:

Total Angular Momentum ($\vec{J}$) $\vec{J} = \vec{L} + \vec{S}$

$$|\vec{J}| = \sqrt{j(j+1)}\hbar \qquad where\ j = |l-s|, |l-s|+1, \ldots |l+s|-1, |l+s|$$
$$J_z = m_j\hbar \qquad \text{where } m_j = -j, -j+1, \ldots, j-1, j$$
$$J_z = L_z \pm S_z$$
$$m_j\hbar = m_l\hbar + m_s\hbar$$

$$|\vec{L}| = \sqrt{l(l+1)}\hbar \qquad where\ l = 0, 1, 2, \ldots n-1$$
$$L_z = m_l\hbar \qquad where\ m_l = -l, -l+1, \ldots l-1, l$$

$$|\vec{S}| = \sqrt{s(s+1)}\hbar \qquad where\ s\ is\ a\ number\ intrinsic\ to\ a\ given\ particle$$
$$S_z = m_s\hbar \qquad where\ m_s = -s, -s+1, \ldots s-1, s$$

- In a strong magnetic field, LS coupling breaks. In that case, $\vec{L}$ and $\vec{S}$ are independently quantized.
- Good quantum numbers refer to quantities which can be assigned simultaneously to describe a quantum system at any time. In a weak B field, n, l, j, m_j $are\ good\ quantum\ numbers$. In a strong B field, $n, l, m_l, and\ m_s\ are\ good\ quantum\ numbers$.
- The effect of LS coupling is very small compared to the electron energies allowed in the hydrogen atom around 2 x $10^{-5}\ eV$. (compare this with -13.6 eV).--> the effect is observed in the fine structure of hydrogen spectral lines. When L and S are aligned, the energy is slightly higher than when L and S are anti-aligned.

Exercise: Identify the different total angular momentum states possible for $l = 2\ and\ s = \frac{1}{2}$

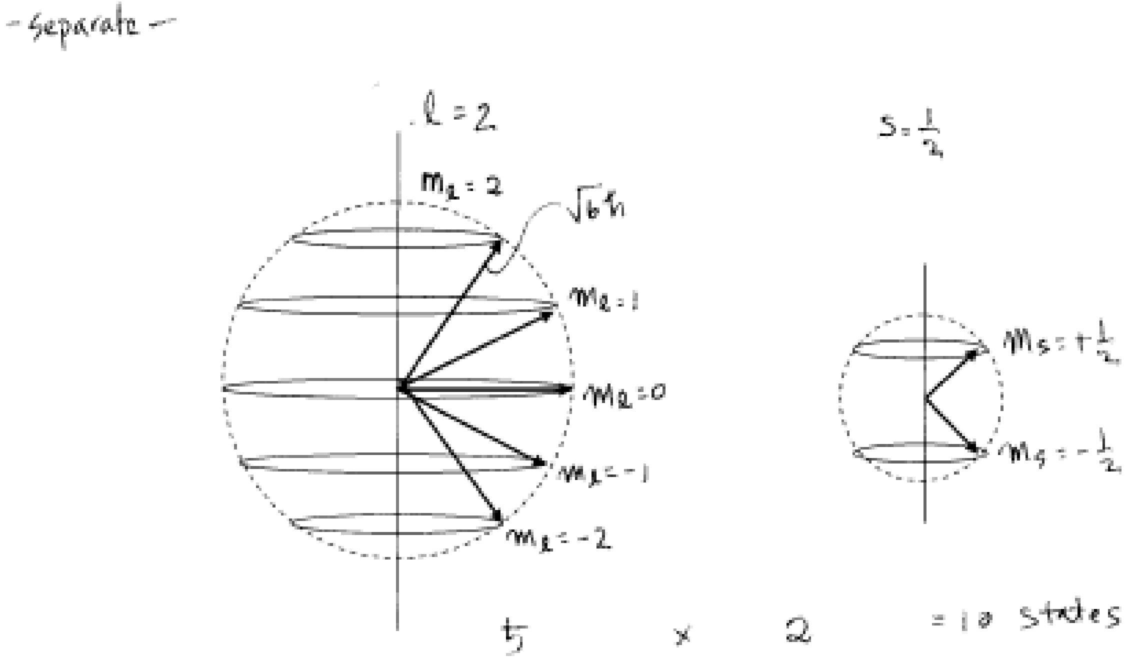
j can be $l + s\ or\ l - s \rightarrow 2 + \frac{1}{2}\left(= \frac{5}{2}\right)\ or\ 2 - \frac{1}{2}\ (= \frac{3}{2})$

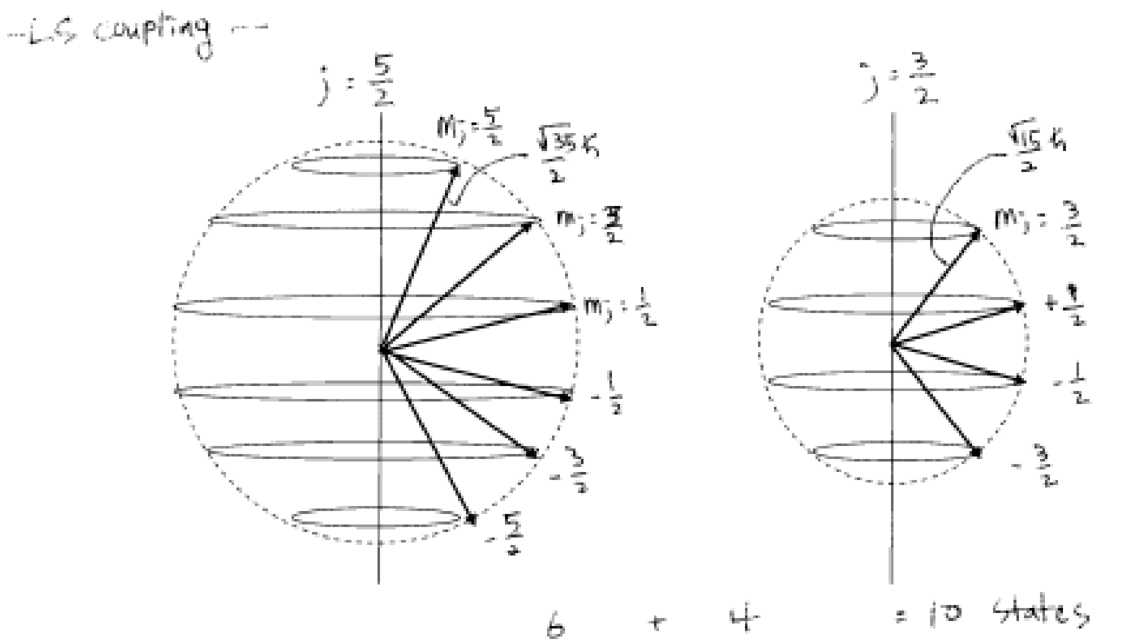
- for $j = \frac{5}{2} \rightarrow m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$ $\quad |\vec{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{5}{2}\frac{7}{2}}\hbar = \frac{\sqrt{35}}{2}\hbar$ → 6 possible states (2j+1)
- for $j = \frac{3}{2} \rightarrow m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ $\quad |\vec{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{3}{2}\frac{5}{2}}\hbar = \frac{\sqrt{15}}{2}\hbar$ → 4 possible states
- A total of 10 states are possible.

If we consider $\vec{L}$ and $\vec{S}$ $separately,$

- For l = 2 → 5 states are possible
- For s = ½ →2 states are possible

- When adding $\vec{L} + \vec{S}$, a total of 5x2 = 10 states are possible. This number agrees to the number of states possible with J.





$$n = 2, l = 1 \rightarrow R_{21} = \frac{1}{(2a_0)^{\frac{3}{2}}} \frac{r}{\sqrt{3}a_0} e^{-\frac{r}{2a_0}}$$

$$\int_0^\infty r \cdot r^2 \cdot \frac{1}{(2a_0)^3}\frac{r^2}{3a_0^2} e^{-\frac{r}{a_0}}\, dr = \frac{1}{3 \cdot 2^3 a_0^5}\int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = \frac{1}{3 \cdot 2^3 a_0^5} 5!\, a_0^6 = 5\, a_0$$

$$\int_0^\infty x^m e^{-bx} dr = \frac{m!}{b^{m+1}} = 5\, a_0$$