Addition of Angular Momentum

➢ We've learned that angular momentum is important in quantum mechanics
- Orbital angular momentum L
- Spin angular momentum S

➢ For multielectron atoms, we need to learn to add angular momentum
- Multiple electrons, each with l_i and s_i
- Spin-orbit interaction couples L and S to form a total angular momentum J

Addition of Angular Momentum

➢ What is the total spin of two electrons?

➢ Again we must take into account that electrons are identical particles

Symmetric spin wave functions

Symmetric under interchange of particles $1 \leftrightarrow 2$

$$\uparrow\uparrow, \ \downarrow\downarrow, \ \frac{1}{\sqrt{2}}\left(\uparrow\downarrow + \downarrow\uparrow\right)$$

Antisymmetric spin wave functions

Antisymmetric under interchange of particles $1 \leftrightarrow 2$

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right)$$

Addition of Angular Momentum

➢ Comments

The symmetric spin state is called the triplet state

$S = 1$

$\uparrow\uparrow$ corresponds to $m_s = 1$

$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow + \downarrow\uparrow\right)$ corresponds to $m_s = 0$

$\downarrow\downarrow$ corresponds to $m_s = -1$

The antisymmetric spin state is called the singlet state

$S = 0$

$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right)$ corresponds to $m_s = 0$

Addition of Angular Momentum

➢ Comments

■ The symmetry properties under particle interchange of the wave function for fermions and bosons refers to the TOTAL wave function ψ(space)χ(spin)

♦ For fermions, since the overall wave function must be antisymmetric under interchange of particles 1 and 2, we can have either

$$\psi(\text{symmetric})\chi(\text{antisymmetric})\,\text{or}$$
$$\psi(\text{antisymmetric})\chi(\text{symmetric})$$

Addition of Angular Momenta

➢ The complete wave functions are

$$\Psi_a = \frac{1}{\sqrt{2}}(\psi_m(x_1)\psi_n(x_2) + \psi_m(x_2)\psi_n(x_1))\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

$$\Psi_a = \frac{1}{\sqrt{2}}(\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1))\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$$

  ▪ The symmetric spin function could be any of the S=1 triplet states

➢ Note that for the S=1 triplet state the spatial wave function has low probability for $x_1 \sim x_2$

  ▪ Parallel spins repel

➢ Note that for the S=0 singlet state the spatial wave function has high probability for $x_1 \sim x_2$

  ▪ Opposite spins attract

➢ This spin pairing arises from the exchange "force" we talked about earlier

Addition of Angular Momentum

➢Comments

- Look at the He atom again ($1s^2$)
  - ◆ What is the spin of the ground state of He?
  - ◆ What is the spin of the first excited state of He?
  - ◆ Estimate the ground state energy of He
  - ◆ Estimate for the first excited state of He

Addition of Angular Momentum

➢ Comments

- Based on this example, the rules for addition of (spin) angular momentum are

$$\vec{S} = \vec{s}_1 + \vec{s}_2$$

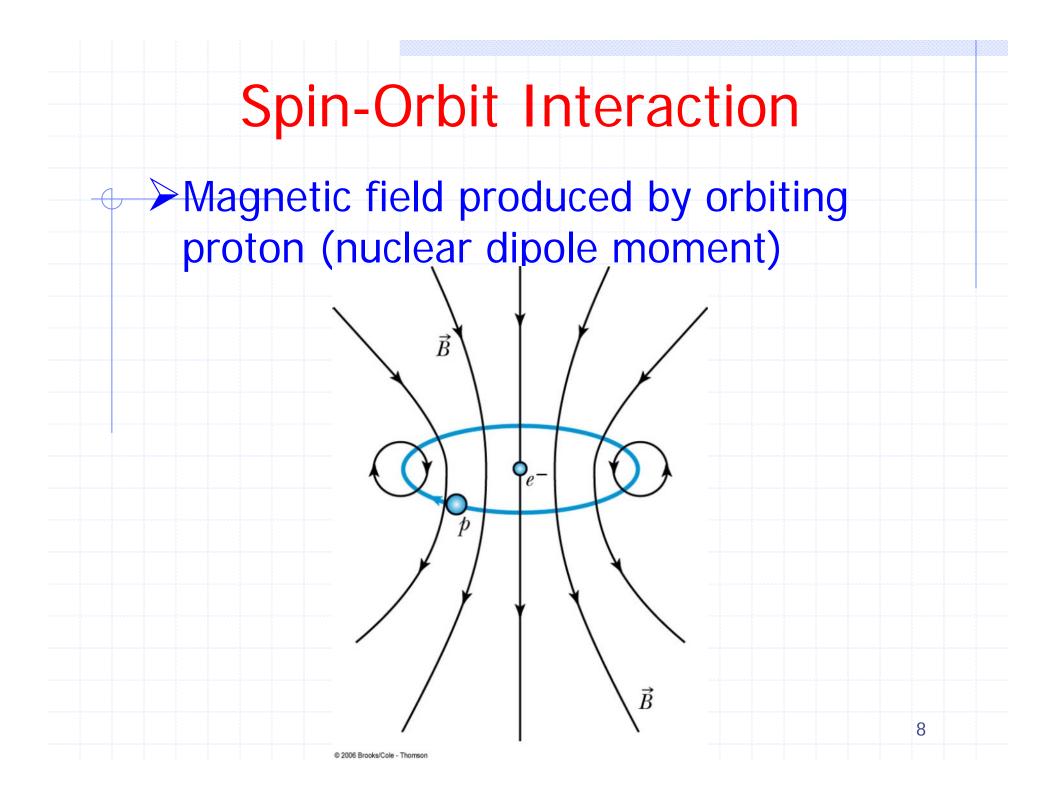$$S \text{ runs from } s_1 + s_2, \, ..., \, \left| s_1 - s_2 \right|$$

$$m_s \text{ runs from } + S, \, ..., \, -S$$

$$\text{Eigenvalues of } S^2 \text{ are } S(S+1)\hbar^2$$

$$\text{Eigenvalues of } S_z \text{ are } m_s \hbar$$

- The same rules hold for the addition of any two (or more) angular momenta

Spin-Orbit Interaction

➢ Magnetic field produced by orbiting proton (nuclear dipole moment)

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Spin Orbit Interaction

➢ Quick review of orbital and spin magnetic moments

Orbital magnetic moment

$$\vec{\mu}_l = -\frac{g_l \mu_B}{\hbar} \vec{L} \text{ where } g_l = 1$$

$$\mu_{l_z} = -\frac{g_l \mu_B}{\hbar} L_z = -g_l \mu_B m_l$$

$$\Delta E = -\vec{\mu}_l \cdot \vec{B}$$

Spin magnetic moment

$$\vec{\mu}_s = -\frac{g_s \mu_B}{\hbar} \vec{S} \text{ where } g_s = 2$$

$$\mu_{s_z} = -\frac{g_s \mu_B}{\hbar} S_z = -g_s \mu_B m_s$$

$$\Delta E = -\vec{\mu}_s \cdot \vec{B}$$

Spin-Orbit Interaction

➢ This internal magnetic field gives rise to a spin-orbit interaction term in the Hamiltonian

$$\Delta E = -\vec{\mu}_s \cdot \vec{B}$$

$$B = \frac{\mu_0 I}{2r} \text{ (Biot - Savart law)}$$

$$I = \frac{Ze}{T} \text{ and } L = mvr = \frac{m2\pi r^2}{T} \text{ and } c^2 = \frac{1}{\mu_0 \varepsilon_0}$$

$$\Rightarrow \vec{B} = \frac{1}{4\pi\varepsilon_0} \frac{Ze}{mc^2 r^3} \vec{L}$$

$$\vec{\mu}_s = -\frac{g_s \mu_B}{\hbar} \vec{S} = -\frac{e}{m} \vec{S}$$

$$\Rightarrow \Delta E = \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

Spin-Orbit Interaction

➢ Actually this isn't quite right since the electron is in a non-inertial frame

- The correct result differs by a factor of ½ and is know as the Thomas precession

$$\Delta E = \frac{Ze^2}{8\pi\varepsilon_0} \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

Spin-Orbit Interaction

➢ Aside

Estimate $\Delta E = \dfrac{Ze^2}{8\pi\varepsilon_0}\dfrac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}$ for $n,l = 2,1$

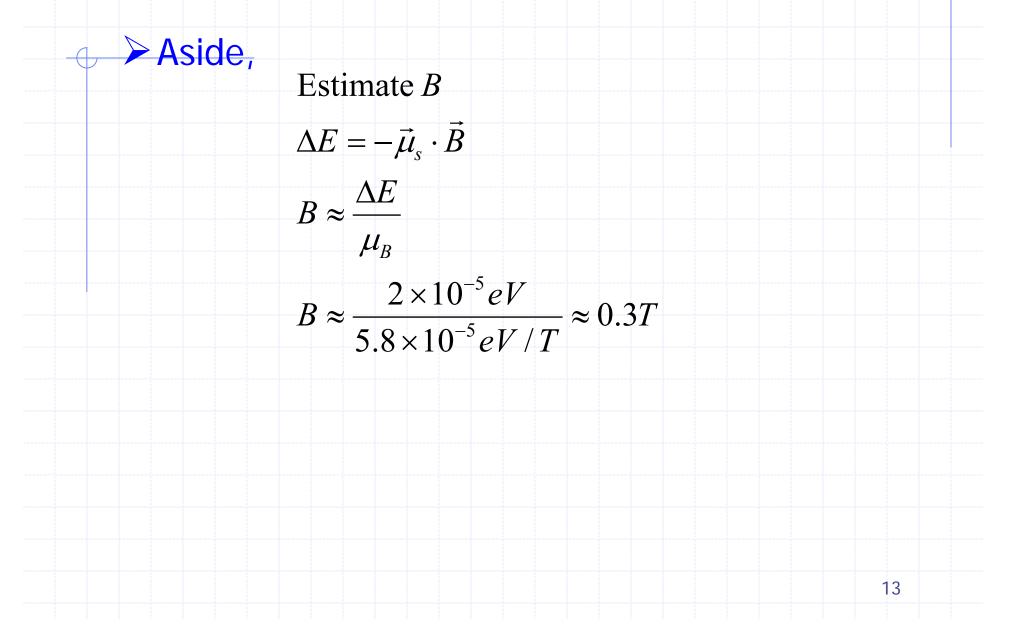$$\Delta E = \frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2c^2}\left(\frac{1}{3a_0}\right)^3\hbar^2$$

$$\Delta E = \frac{me^2}{\hbar^2 4\pi\varepsilon_0}\frac{1}{2m^3c^2}\left(\frac{1}{3a_0}\right)^3\hbar^4$$

$$\Delta E = \frac{1}{a_0}\frac{1}{2m^3c^6}\left(\frac{1}{3a_0}\right)^3\hbar^4c^4$$

$$\Delta E = \frac{1}{2(mc^2)^3}\frac{1}{27}\left(\frac{1}{a_0}\right)^4\hbar^4c^4$$

$$\Delta E = (0.5)\left(\frac{1}{.511 MeV}\right)^3\left(\frac{1}{27}\right)\left(\frac{1}{0.53\times10^{-10}m}\right)^4\left(197\times10^{-9}\,eVm\right)^4$$

$$\Delta E = 2\times10^{-5}\,eV$$

Spin-Orbit Interaction

➢ Aside,

Estimate B

$$\Delta E = -\vec{\mu}_s \cdot \vec{B}$$

$$B \approx \frac{\Delta E}{\mu_B}$$

$$B \approx \frac{2 \times 10^{-5} eV}{5.8 \times 10^{-5} eV / T} \approx 0.3T$$

Spin-Orbit Interaction

➤ We left the spin-orbit interaction out of the Hamiltonian the first time we did the hydrogen atom

  ▪ In part, because it's a small correction

➤ The full Schrodinger equation for the hydrogen atom is (neglecting a relativistic correction)

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \left(-\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2 r^3}\vec{S}\cdot\vec{L}\right)\psi = E\psi$$

Spin-Orbit Interaction

➢ Our original quantum numbers for the hydrogen atom were n, l, m_l, s, m_s

➢ And $[H, L^2] = [H, S^2] = [H, L_z] = [H, S_z] = 0$

➢ But with the spin-orbit term in the Hamiltonian, H no longer commutes with some of these operators

➢ Before you answer note that

$$\text{For } \vec{J} = \vec{L} + \vec{S}$$

$$\vec{J}^2 = \left(\vec{L} + \vec{S}\right)^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$

Total Angular Momentum

➢ The spin-orbit interaction couples the orbital (L) and spin (S) angular momentum to form the total angular momentum (J)

- The internal magnetic field is determined by L and this acts on the spin magnetic dipole of the electron determined by S so the two angular momenta are not independent

$$\vec{J} = \vec{L} + \vec{S}$$

➢ The new "good" quantum numbers of the hydrogen atom are n, l, s, j, m_j

Total Angular Momentum

➢ Coupling of L and S to form J

- L and S precess around J

- J precesses around the z axis

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