Total Angular Momentum

- Since J is an angular momentum like L and S, its algebra is identical to that for orbital and spin angular momentum

$$j = l + s, \ldots, |l - s|$$

$$m_j = -j, \ldots, j$$

$$J^2\psi = j(j+1)\hbar^2\psi$$

$$J_z\psi = m_j\hbar\psi$$

$$J^2 = J_x^2 + J_y^2 + J_z^2$$

$$[J_x, J_y] = i\hbar J_z, [J_y, J_z] = i\hbar J_x, [J_z, J_x] = i\hbar J_y$$

$$[J^2, J_x] = [J^2, J_y] = [J^2, J_z] = 0$$

Total Angular Momentum

- We can determine the possible values of j by looking at the z components

$$J_z = L_z + S_z$$

$$m_j\hbar = m_l\hbar + m_s\hbar$$

$$m_j = m_l + m_s$$

  - The maximum value of j is the maximum value of m_j is the maximum value of m_l and m_s is l+s

- The minimum value of j can be found using the vector inequality $\left|\vec{L} + \vec{S}\right| \geq \left|\left|\vec{L}\right| - \left|\vec{S}\right|\right| = \left|l - s\right|$

- Thus j runs from $l + s, \ldots, \left|l - s\right|$ in integer steps

Addition of Angular Momentum

- These rule hold true for the addition of any two types of angular momenta
- Example
  - What are the possible s and m_s values for the combination of two spin 1/2 particles?
  - What are the possible l and m_l values for two electrons having l_1=1 and l_2=2?
  - What are the possible j and m_j values for one electron with l=2 and s=1/2?

Fine Structure

- For the hydrogen atom, we found that when one includes the spin-orbit interaction n, l, m_l, s, m_s are no longer "good" quantum numbers
- Instead we must use n, l, s, j, m_j
- We usually use spectroscopic notation to describe these states

$$n^{2S+1}L_J$$

- We'll use this notation for multielectron states as well

Fine Structure

Examples

- What are first three states (ground and first two excited states) for hydrogen?
- What are l, s, j values for $^3F_2$?

Fine Structure

- The potential energy associated with the spin-orbit interaction was calculated as

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

- Additionally we noted

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

- Hence

$$\vec{L}\cdot\vec{S} = \frac{J^2 - L^2 - S^2}{2}$$

$$\vec{L}\cdot\vec{S} = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

$$\text{And so } \Delta E = \frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2c^2r^3}\frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]$$

Fine Structure

- Furthermore, the energy eigenvalues are just the expectation values of H and with time you could show

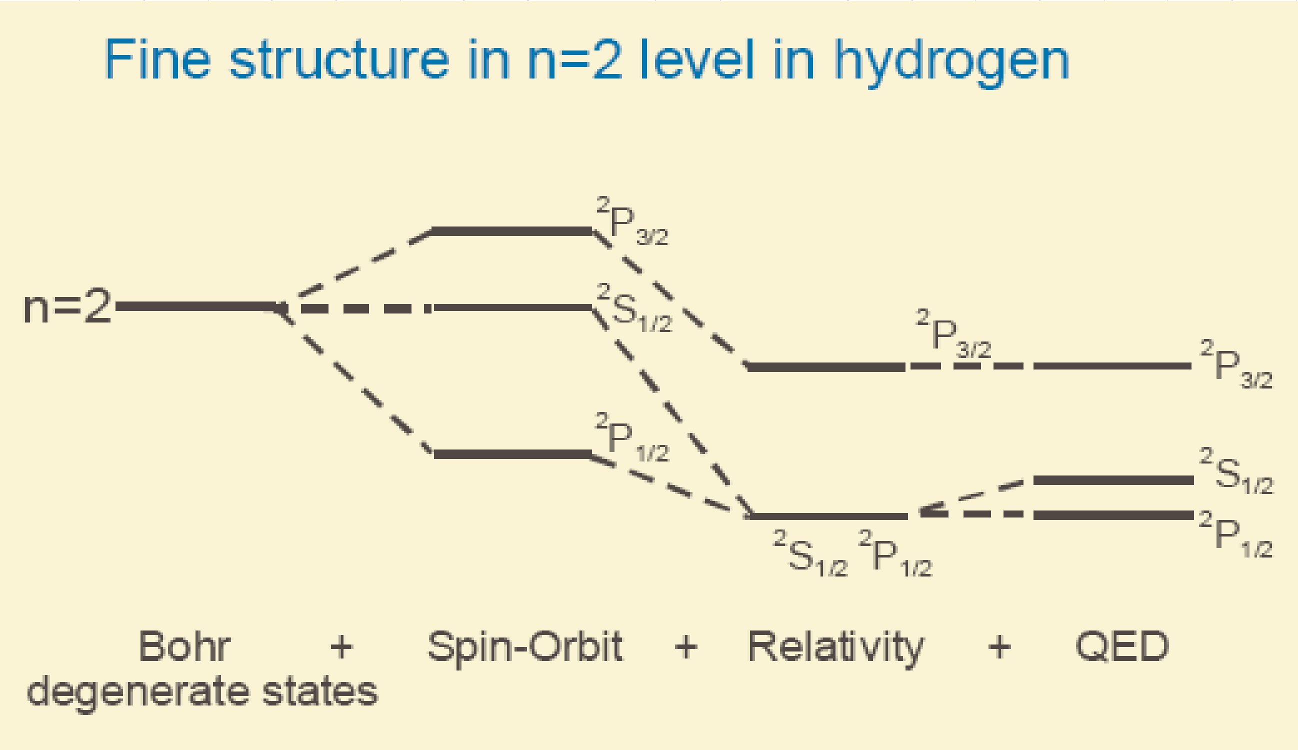
$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3 a_0^3}$$

$$\text{thus } \Delta \mathrm{E} = \frac{e^2}{8\pi\varepsilon_0} \frac{1}{m^2 c^2 r^3} \frac{\hbar^2}{2} \frac{[j(j+1) - l(l+1) - s(s+1)]}{l(l+1/2)(l+1)n^3 a_0^3}$$

- The point is that the spin-orbit interaction lifts the 2l+1 degeneracy in l

Fine Structure

- Hydrogen fine structure



Fine Structure

- The selection rules for transitions between states must be updated as well

$$\Delta n = \text{anything}$$

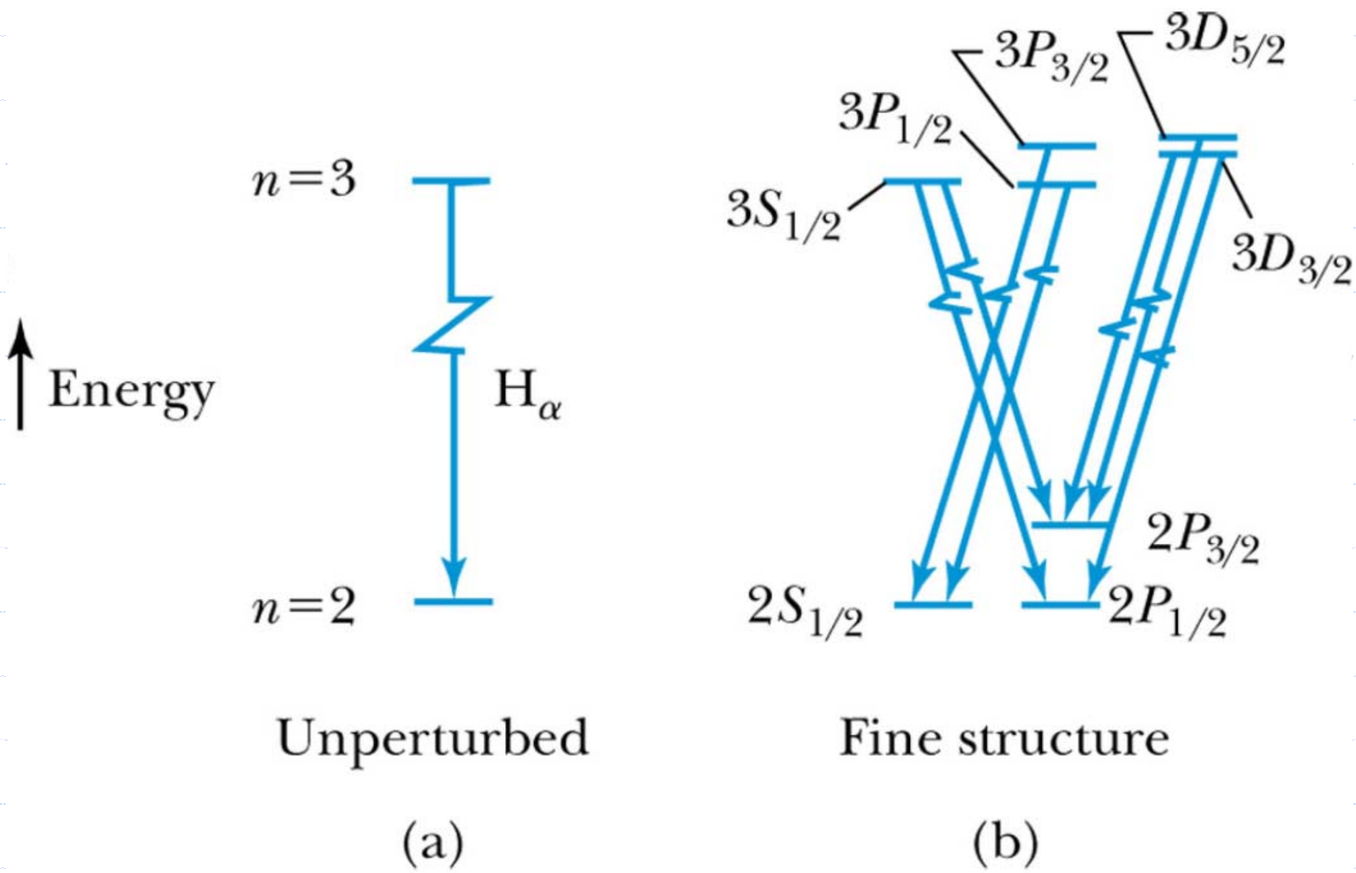
$$\Delta l = \pm 1$$

$$\Delta j = \pm 1, 0$$

$$\Delta m_j = \pm 1, 0$$

Fine Structure

- Transitions with spin-orbit interaction



Two Body Problem

- Two body systems (proton and electron, two electrons, ...) are obviously important in quantum mechanics
- A two body problem can be reduced to an equivalent one body problem if the potential energy one depends on the separation of the two particles

Two Body Problem

$$\left(-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2}-\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}\right)\psi(x_1,x_2)+V(x_1-x_2)\psi(x_1,x_2)=E\,\psi(x_1,x_2)$$

let $x = x_1 - x_2$ (relative) and $X = \dfrac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ (center - of - mass)

also let $\dfrac{1}{\mu} = \dfrac{1}{m_1} + \dfrac{1}{m_2}$ and $M = m_1 + m_2$

using the chain rule $\dfrac{\partial}{\partial x_1} = \dfrac{\partial}{\partial x}\dfrac{\partial x}{\partial x_1} + \dfrac{\partial}{\partial X}\dfrac{\partial X}{\partial x_1}$ and ditto for x_2

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}\right)\psi(x,X)+V(x)\psi(x,X)=E\,\psi(x,X)$$

Two Body Problem

- This equation is now separable

Now let $\psi(x,X) = u(x)U(X)$

$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}\right)\psi(x,X) + V(x)\psi(x,X) = E\psi(x,X)$ is separable into

$$-\frac{\hbar^2}{2M}\frac{\partial^2 U(X)}{\partial X^2} = E_{cm}U(X)$$

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 u(x)}{\partial x^2} + V(x) = E_{rel}u(x)$$

$$E = E_{cm} + E_{rel}$$

- The two equations represent
  - A free particle equation for the center-of-mass
  - A one body equation using the reduced mass and relative coordinates

Two Body Problem

- In the case of a central potential problem (like He) with $m_1=m_2=m$

$$H=\frac{\vec{p}_1^{\,2}}{2m}+\frac{\vec{p}_2^{\,2}}{2m}+V\left(\left|\vec{r}_1-\vec{r}_2\right|\right)\text{becomes}$$

$$H=\frac{\vec{P}^2}{2M}+\frac{\vec{p}^{\,2}}{2\mu}+V\left(\left|\vec{r}\right|\right)$$

$$\text{where }\frac{\vec{p}}{\mu}=\frac{\vec{p}_1}{m}-\frac{\vec{p}_2}{m}\text{ and }\vec{r}=\vec{r}_1-\vec{r}_2$$

- The point is the following: the interchange of two particles in central potential simply means

$$\vec{r}\rightarrow-\vec{r}$$

Two Body Problem

- Particle interchange in the central potential problem means $\vec{r} \rightarrow -\vec{r}$
- This means

$$r \rightarrow r$$

$$\theta \rightarrow \pi - \theta$$

$$\varphi \rightarrow \pi + \varphi$$

- Under particle interchange of 1 and 2
  - The radial wave function is unchanged
  - The symmetry of the angular wave function depends on l

$$Y_{lm}(\theta,\varphi) \rightarrow Y_{lm}(\pi-\theta,\pi+\varphi) = (-1)^l Y_{lm}(\theta,\varphi)$$