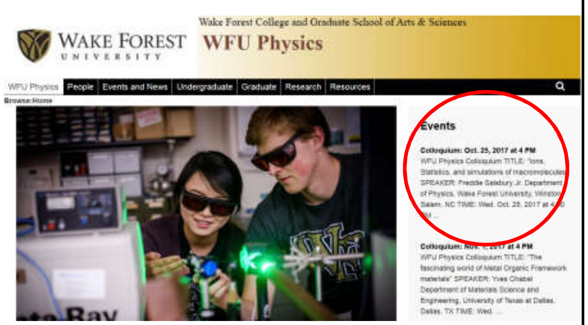
PHY 741 Quantum Mechanics
12-12:50 AM MWF Olin 103

Plan for Lecture 23:

"Addition" of angular momenta – Chap. 15

1. **States of multi-electron atoms**
2. **Atomic term analysis**
3. **Rotation of angular momentum eigenstates**
4. **Quantum states of a diatomic molecule**



16	Fri, 10/06/2017	Chap. 12-13	Spherically symmetric systems		
17	Mon, 10/09/2017	Chap. 13	Quantum mechanics of a hydrogen atom	#10	10/16/2017
18	Wed, 10/11/2017	Chap. 13	Quantum mechanics of multi-electron atoms		
	Fri, 10/13/2017		*Fall break – No class*		
19	Mon, 10/16/2017		Discuss exam questions and topics for presentations	Topic	10/18/2017
20	Wed, 10/18/2017	Chap. 14	Intrinsic spin	#11	10/20/2017
21	Fri, 10/20/2017	Chap. 15	Addition of Angular Momentum	#12	10/23/2017
22	Mon, 10/23/2017	Chap. 15	Multi-electron atoms	#13	10/25/2017
23	Wed, 10/25/2017	Chap. 15	Multi-electron atoms	#14	10/30/2017
24	Fri, 10/27/2017				
25	Mon, 10/30/2017				
26	Wed, 11/01/2017				
27	Fri, 11/03/2017				
28	Mon, 11/06/2017				
29	Wed, 11/08/2017				
30	Fri, 11/10/2017				
31	Mon, 11/13/2017				
32	Wed, 11/15/2017				

Summary of results for analysis of atomic term energies

$$\mathcal{H} = \underbrace{\sum_i h(\mathbf{r}_i)}_{\text{single electron terms}} + \underbrace{\sum_{i,j<i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{electron-electron interaction}}$$

Evaluating expectation values: $\langle LM|\mathcal{H}|LM\rangle$ for $2p^2$

$$E(P) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) - \frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

$$E(D) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

$$E(S) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

In this case, the Hamiltonian does not depend on spin, and the Hamiltonian commutes with total orbital angular momentum

$$[\mathcal{H}, \mathbf{L}] = 0$$

$$\Rightarrow [\mathcal{H}, L_\pm] = 0$$

Suppose $\mathcal{H}|LM\rangle = E|LM\rangle$

$$\mathcal{H}L_\pm|LM\rangle = L_\pm\mathcal{H}|LM\rangle = E\left(L_\pm|LM\rangle\right)$$

$\Rightarrow \left(L_\pm|LM\rangle\right)$ is an eigenvector of $\mathcal{H}$ with eigenvalue E

Some details of two-electron matrix elements: $\langle LM|V_{ee}|LM\rangle$

$$V_{ee} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = e^2\sum_{\lambda\mu}\frac{4\pi}{2\lambda+1}\frac{r_<^\lambda}{r_>^{\lambda+1}}Y_{\lambda\mu}(\hat{\mathbf{r}}_1)Y^*_{\lambda\mu}(\hat{\mathbf{r}}_2)$$

$$|LM\rangle = \sum_{m_a m_b} R_{n_a l_a}(r_1)R_{n_b l_b}(r_2)Y_{l_a m_a}(\hat{\mathbf{r}}_1)Y_{l_b m_b}(\hat{\mathbf{r}}_2)\langle l_a m_a, l_b m_b|LM; l_a l_b\rangle$$

Define: $\mathcal{R}^\lambda(n_a l_a, n_b l_b; n_c l_c, n_d l_d)$

$$= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{r_<^\lambda}{r_>^{\lambda+1}} R_{n_a l_a}(r_1)R_{n_b l_b}(r_2)R_{n_c l_c}(r_1)R_{n_d l_d}(r_2)$$

Gaunt Coefficients

$$\int_0^{2\pi}\int_0^{\pi} Y_{l_1,m_1}(\theta,\phi)Y_{l_2,m_2}(\theta,\phi)Y_{l_3,m_3}(\theta,\phi)\sin\theta\, d\theta\, d\phi$$

$$= \left(\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}\right)^{\frac{1}{2}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

$$\equiv \frac{1}{\sqrt{4\pi}} G\left(l_1m_1, l_2m_2, l_3m_3\right)$$

Two types of radial components:

$\mathcal{R}^\lambda(n_al_a, n_bl_b; n_cl_c, n_dl_d)$

$$= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{r_<^\lambda}{r_>^{\lambda+1}} R_{n_al_a}(r_1)R_{n_bl_b}(r_2)R_{n_cl_c}(r_1)R_{n_dl_d}(r_2)$$

Direct interaction: $\mathcal{F}^\lambda(n_al_a, n_bl_b) = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{r_<^\lambda}{r_>^{\lambda+1}} R^2_{n_al_a}(r_1)R^2_{n_bl_b}(r_2)$

Exchange interaction: $\mathcal{G}^\lambda(n_al_a, n_bl_b)$

$$= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{r_<^\lambda}{r_>^{\lambda+1}} R_{n_al_a}(r_1)R_{n_bl_b}(r_1)R_{n_al_a}(r_2)R_{n_bl_b}(r_2)$$

Rotation of eigenstate of angular momentum

Rotation of a vector in Cartesian coordinates:

$$\begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x\cos\alpha - y\sin\alpha \\ x\sin\alpha + y\cos\alpha \\ z \end{pmatrix}$$

Relationship of spherical harmonics to Cartesian vectors

$Y_{00}(\hat{\mathbf{r}}) = \frac{1}{\sqrt{4\pi}}$ (invariant under rotation)

$$Y_{11}(\hat{\mathbf{r}}) = -\frac{3}{\sqrt{8\pi}}\left(\frac{x+iy}{r}\right)$$

$$Y_{10}(\hat{\mathbf{r}}) = \frac{3}{\sqrt{4\pi}}\left(\frac{z}{r}\right)$$

$$Y_{1-1}(\hat{\mathbf{r}}) = \frac{3}{\sqrt{8\pi}}\left(\frac{x-iy}{r}\right)$$

Effects of rotating by α about $\hat{\mathbf{z}}$

$$Y_{11}(R(\hat{\mathbf{r}})) = -\frac{3}{\sqrt{8\pi}}\left(\frac{x+iy}{r}\right)e^{i\alpha} = R\left(Y_{11}(\hat{\mathbf{r}})\right)$$

$$Y_{10}(R(\hat{\mathbf{r}})) = \frac{3}{\sqrt{4\pi}}\left(\frac{z}{r}\right) = R\left(Y_{10}(\hat{\mathbf{r}})\right)$$

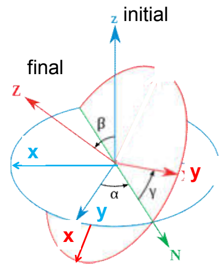
$$Y_{1-1}(R(\hat{\mathbf{r}})) = \frac{3}{\sqrt{8\pi}}\left(\frac{x-iy}{r}\right)e^{-i\alpha} = R\left(Y_{1-1}(\hat{\mathbf{r}})\right)$$

Generator for rotations:

$e^{i\alpha\hat{\mathbf{n}}\cdot\mathbf{J}/\hbar}$

For $\hat{\mathbf{n}} = \hat{\mathbf{z}}$: $\quad e^{i\alpha J_z/\hbar}\left|JM\right\rangle = e^{i\alpha M}\left|JM\right\rangle$

Euler angles --



$$R(\alpha,\beta,\gamma) = e^{i\gamma J_z/\hbar} e^{i\beta J_y/\hbar} e^{i\alpha J_z/\hbar}$$

$$R(\alpha,\beta,\gamma)\left|JM\right\rangle = \sum_{M'} \left|JM'\right\rangle e^{i\gamma M'} \left\langle JM'\right| e^{i\beta J_y/\hbar} \left|JM\right\rangle e^{i\alpha M}$$

$$\left\langle JM'\right| e^{i\beta J_y/\hbar} \left|JM\right\rangle \equiv d^J_{M'M}(\beta)$$

According to Rose, "Elementary Theory of Angular Momentum"

$$d^J_{M'M}(\beta) = \sqrt{(J+M)!(J-M)!(J+M')!(J-M')!}$$

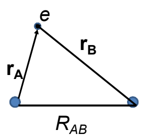
$$\times \sum_m \frac{(-1)^m \left(\cos\frac{\beta}{2}\right)^{2J+M-M'-2m} \left(\sin\frac{\beta}{2}\right)^{M'-M+2m}}{(J+M-m)!(J-M'-m)!(m+M'-M)!m!}$$

Rotation matrix for *J=1/2:*

$$d^{1/2}(\beta) = \begin{pmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix}$$

$$d^1(\beta) = \frac{1}{2}\begin{pmatrix} 1+\cos\beta & -\sqrt{2}\sin\beta & 1-\cos\beta \\ \sqrt{2}\sin\beta & 2\cos\beta & -\sqrt{2}\sin\beta \\ 1-\cos\beta & \sqrt{2}\sin\beta & 1+\cos\beta \end{pmatrix}$$

Quantum states of H_2^+



$$r_A \equiv r$$
$$r_B \equiv |\mathbf{r} - \mathbf{R}|$$
$$\mathbf{R}_{AB} \equiv \mathbf{R} = R\hat{\mathbf{z}}$$

Assuming that the nuclear positions are fixed:
Schroedinger equation for electron

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} + \frac{e^2}{R}$$
$$H\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

10/25/2017 PHY 741 Fall 2017 -- Lecture 23 13