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

Plan for Lecture 22:

“Addition” of angular momenta – Chap. 15

1. **States of multi-electron atoms**
2. **Atomic term analysis**

12	Fri, 9/22/2017	Chap. 10	Quantum mechanics of multiparticle systems	#9	9/25/2017
13	Mon, 9/25/2017	Chap. 10-12	Multiparticle systems and angular momentum		
14	Wed, 9/27/2017	Chap. 12	Eigenstates of angular momentum		
15	Fri, 9/29/2017	Chap. 1,4,5,7,9,10,12	Review		
	Mon, 10/02/2017		*Take-home exam -- No class*		
	Wed, 10/04/2017		*Take-home exam -- No class*		
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				
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				

“Addition” of angular momentum

Clebsch-Gordan coefficients

$$|JM, j_1 j_2\rangle = \sum_{m_1, m_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2 | JM, j_1 j_2\rangle$$

A more symmetric coefficient is the so-called 3-j symbol:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

Clebsch-Gordan 3-j

$$\left(j_1\, m_1\, j_2\, m_2 | j_1\, j_2\, j_3\, m_3\right) = (-1)^{j_1 - j_2 + m_3}(2j_3 + 1)^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}$$

link to more information: http://dlmf.nist.gov/34.1

Some symmetry properties of 3-j symbols:

$$|j_r - j_s| \le j_t \le j_r + j_s,$$

$$m_1 + m_2 + m_3 = 0.$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix},$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix}.$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix},$$

Some orthogonality properties of 3-j symbols:

$$\sum_{m_1 m_2} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \delta_{j_3, j_3'} \delta_{m_3, m_3'},$$

$$\sum_{j_3 m_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1, m_1'} \delta_{m_2, m_2'},$$

$$\sum_{m_1 m_2 m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 1.$$

Relationship of 3-j symbols to integrals over spherical harmonics and related functions

$$\int_0^{\pi} P_{l_1}(\cos\theta) P_{l_2}(\cos\theta) P_{l_3}(\cos\theta) \sin\theta \, d\theta = 2 \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}^2,$$

Gaunt Coefficient

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

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

$$\equiv \frac{1}{\sqrt{4\pi}} G(l_1 m_1, l_2 m_2, l_3 m_3)$$

Explicit formula for Clebsch-Gordon coefficients:

Reference: Abramowitz & Stegum – pg. 1006

Original formula:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle = \delta_{m,m_1+m_2}\sqrt{\frac{(j_1+j_2-j)!(j_1-j_2+j)!(-j_1+j_2+j)!(2j+1)}{(j_1+j_2+j+1)!}}$$
$$\times \sum_k \frac{(-1)^k\sqrt{(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!}}{k!(j_1+j_2-j-k)!(j_1-m_1-k)!(j_2+m_2-k)!(j-j_2+m_1+k)!(j-j_1-m_2+k)!}$$

Working formula:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m\rangle = \delta_{m,m_1+m_2}\sqrt{\frac{(j_1-j_2+j)!(-j_1+j_2+j)!(2j+1)}{(j_1+j_2-j)!(j_1+j_2+j+1)!}}$$
$$\times\sqrt{\frac{(j_1+m1)!(j_2-m_2)!(j+m)!}{(j_1-m1)!(j_2+m_2)!(j-m)!}}$$
$$\times \sum_k \frac{(-1)^k}{k!}\frac{(j_1+j_2-j)!}{(j_1+j_2-j-k)!}\frac{(j_1-m_1)!}{(j_1-m_1-k)!}\frac{(j_2+m_2)!}{(j_2+m_2-k)!}\frac{(j-m)!}{(j-j_2+m_1+k)!(j-j_1-m_2+k)!}$$

Coupling of orbital angular momenta of multiple electrons

$$\mathbf{J} = \mathbf{L}_1 + \mathbf{L}_2$$
$$J = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, (l_1 + l_2)$$

Example: $l_1 = l_2 = 1$ total of 9 orbital states

$J = 0$ 1 state

$J = 1$ 3 states

$J = 2$ 5 states

Consequences of orbital coupling on energies of multi-electron atoms

Example C $1s^2\ 2s^2\ 2p^2$

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Primary data source	Query NIST Bibliographic Database for **C I** (new window)
Moore 1993	Literature on C I Energy Levels

Configuration	Term	J	Level (eV)	Reference
$2s^2 2p^2$	^3P	0	0.00000	L7288
		1	0.002033	
		2	0.005381	
$2s^2 2p^2$	^1D	2	1.263725	
$2s^2 2p^2$	^1S	0	2.684011	

Atomic term notation: $^{(2S+1)}L_J$

L	symbol	spin
0	S	S=0
1	P	S=1
2	D	S=0
3	F	S=1

Example for C *1s² 2s² 2p²*

States of total orbital momentum: $(2l_1+1)(2l_2+1)=9$

Total number of orbital and spin configurations: $6\cdot 5/2=15$

$^1D \Rightarrow 5$ states

$^1S \Rightarrow 1$ states

$^3P \Rightarrow 9$ states

Energetic differences are due to the electron-electron Coulomb repulsion:

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

Example for ^1D state

$$|JM;l_1l_2\rangle=|22;11\rangle=\sum_{m_1,m_2}|l_1m_1,l_2m_2\rangle\langle l_1m_1,l_2m_2|JM;l_1l_2\rangle$$
$$=|11,11\rangle=R_{2p}(r_1)R_{2p}(r_2)Y_{11}(\hat{\mathbf{r}}_1)Y_{11}(\hat{\mathbf{r}}_2)$$

Need to evaluate: $\langle 11,11|V_{ee}|11,11\rangle$

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

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

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

$$\langle 11,11|V_{ee}|11,11\rangle = e^2\mathcal{R}^0(2p,2p;2p,2p)G^2(1-1,00,11)$$
$$+e^2\mathcal{R}^2(2p,2p;2p,2p)\frac{G^2(1-1,20,11)}{5}$$
$$E(D) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p)+\frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

Similarly, can show that:

$$E(P) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p)-\frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$
$$E(S) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p)+\frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

Summary of results:

$$\mathcal{R}^\lambda(n_a l_a, n_b l_b; n_c l_c, n_d l_d)$$
$$=\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{r_<^\lambda}{r_>^{\lambda+1}} R_{n_a l_a}(r_1) R_{n_b l_b}(r_2) R_{n_c l_c}(r_1) R_{n_d l_d}(r_2)$$
$$\mathcal{R}^\lambda(2p,2p;2p,2p)$$
$$=\int_0^\infty r_1^2 dr_1 R_{2p}^2(r_1)\left(\int_0^{r_1} r_2^2 dr_2 \frac{r_2^\lambda}{r_1^{\lambda+1}} R_{2p}^2(r_2) + \int_{r_1}^\infty r_2^2 dr_2 \frac{r_1^\lambda}{r_2^{\lambda+1}} R_{2p}^2(r_2)\right)$$

$$E(P) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p)-\frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$
$$E(D) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p)+\frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$
$$E(S) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p)+\frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

Taking into account anti-symmetry of two-particle wavefunction

More details of the total angular momentum $L = 2$ case:

$$|JM;l_1l_2\rangle = |22;11\rangle = \sum_{m_1,m_2} |l_1m_1,l_2m_2\rangle\langle l_1m_1,l_2m_2|JM;l_1l_2\rangle$$
$$=|11,11\rangle = R_{2p}(r_1)R_{2p}(r_2)Y_{11}(\hat{\mathbf{r}}_1)Y_{11}(\hat{\mathbf{r}}_2)$$

Note that $\psi_D(\mathbf{r}_1,\mathbf{r}_2) = \psi_D(\mathbf{r}_2,\mathbf{r}_1)$

Full wavefunction including spin

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\sigma_1,\sigma_2)=\psi_{L=2}(\mathbf{r}_1,\mathbf{r}_2)\chi(\sigma_1,\sigma_2)$$

Must be anti-symmetric

Summary of results for two spin-$\frac{1}{2}$ particle states:

$$\left.\begin{aligned}
&\left|11;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\left|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\right\rangle\\
&\left|10;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\right\rangle+\left|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\right\rangle\right)\\
&\left|1-1;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\right\rangle
\end{aligned}\right\}$$

S=1, symmetric degeneracy: *2S+1=3*

$$\left|00;\tfrac{1}{2}\tfrac{1}{2}\right\rangle=\frac{1}{\sqrt{2}}\left(\left|\tfrac{1}{2}-\tfrac{1}{2},\tfrac{1}{2}\tfrac{1}{2}\right\rangle-\left|\tfrac{1}{2}\tfrac{1}{2},\tfrac{1}{2}-\tfrac{1}{2}\right\rangle\right)\Big\}$$

S=0, anti-symmetric degeneracy: *2S+1=1*

Extending these arguments, Condon and Shortley concluded that in general *L+S=even*

➔Valid atomic terms for Carbon:

$$^{(2S+1)}L_J$$

$$^3P=E_0-5\mathcal{R}^2/25=0.00\text{ eV}$$
$$^1D=E_0+1\mathcal{R}^2/25=1.26\text{ eV}$$
$$^1S=E_0+10\mathcal{R}^2/25=2.68\text{ eV}$$
$$\Rightarrow\mathcal{R}^2/25\sim0.19\text{ eV}$$

Another example – Ti^{+2} ($1s^2\ 2s^2\ 3s^2\ 2p^6\ 3p^6\ 3d^2$)

Condon & Shortley analysis:

$$^3F=E_0-8\mathcal{R}^2/49-9\mathcal{R}^4/441$$
$$^1D=E_0-3\mathcal{R}^2/49+36\mathcal{R}^4/441$$
$$^1G=E_0+4\mathcal{R}^2/49+1\mathcal{R}^4/441$$
$$^3P=E_0+7\mathcal{R}^2/49-84\mathcal{R}^4/441$$
$$^1S=E_0+14\mathcal{R}^2/49+126\mathcal{R}^4/441$$

From NIST:

Configuration	Term	J	Level (eV)
$3p^63d^2$	^3F	2	0.0000
		3	0.02292
		4	0.05212
$3p^63d^2$	^1D	2	1.05058
$3p^63d^2$	^3P	0	1.30660
		1	1.31468
		2	1.32926
$3p^63d^2$	^1G	4	1.78507
$3p^63d^2$	^1S	0	4.02645