PHY 745 Group Theory
11-11:50 AM MWF Olin 102

Plan for Lecture 13:

Group properties of atomic orbitals and crystals

Reading: Chapter 5 in DDJ

1. **Correction: Cambell-Baker-Hausdorff equation**
2. **Group properties of atomic orbitals**
3. **Atomic orbitals in crystal fields**

Course schedule for Spring 2017

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	DDJ Reading	Topic	HW	Due date
1	Wed: 01/11/2017	Chap. 1	Definition and properties of groups	#1	01/20/2017
2	Fri: 01/13/2017	Chap. 1	Theory of representations		
	Mon: 01/16/2017		*MLK Holiday - no class*		
3	Wed: 01/18/2017	Chap. 2	Theory of representations		
4	Fri: 01/20/2017	Chap. 2	Proof of the Great Orthonality Theorem	#2	01/23/2017
5	Mon: 01/23/2017	Chap. 3	Notion of character of a representation	#3	01/25/2017
6	Wed: 01/25/2017	Chap. 3	Examples of point groups	#4	01/27/2017
7	Fri: 01/27/2017	Chap. 4 & 8	Symmetry of vibrational modes	#5	01/30/2017
8	Mon: 01/30/2017	Chap. 4 & 8	Symmetry of vibrational modes	#6	02/01/2017
9	Wed: 02/01/2017	Chap. 8	Vibrational excitations	#7	02/03/2017
10	Fri: 02/03/2017	Notes	Continuous groups	#8	02/06/2017
11	Mon: 02/06/2017	Notes	Group of three-dimensional rotations	#9	02/08/2017
12	Wed: 02/08/2017	Notes	Continuous groups	#10	02/10/2017
13	Fri: 02/10/2017	Chap. 5	Atomic orbitals	#11	02/14/2017
14	Mon: 02/13/2017				
15	Wed: 02/15/2017				

Correction to previous lecture notes

Simplifying notation for spin-angular operators: $\bar{J}_i \equiv J_i / \hbar$

Cambell-Baker-Hausdorff relation

$$e^{-i\alpha_1\bar{J}_1} e^{-i\alpha_2\bar{J}_2} = e^{-i\left(\alpha_1\bar{J}_1 + \alpha_2\bar{J}_2 - iF(\alpha_1,\alpha_2,\bar{J}_1,\bar{J}_2,[\bar{J}_1,\bar{J}_2])\right)}$$

$$\text{where } F = \frac{\alpha_1\alpha_2}{2}\left[\bar{J}_1,\bar{J}_2\right] + \frac{\alpha_1\alpha_2}{12}\left(\alpha_1\left[\bar{J}_1,\left[\bar{J}_1,\bar{J}_2\right]\right] - \alpha_2\left[\bar{J}_2,\left[\bar{J}_1,\bar{J}_2\right]\right]\right) + \frac{\alpha_1^2\alpha_2^2}{24}\left[\bar{J}_1,\left[\bar{J}_2,\left[\bar{J}_2,\bar{J}_1\right]\right]\right] + \ldots..$$

Note that when the generators satisfy a commutation relation such as $\left[\bar{J}_a,\bar{J}_b\right] = if_{abc}\bar{J}_c$, the group multiplication property follows.

Symmetry properties of electronic states in an atom

For a hydrogen atom:

$$H\Psi_{nlm}(\mathbf{r}) = E_{nl}\Psi_{nlm}(\mathbf{r})$$

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{r}$$

$$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$$

For a multi-electron atom in a mean-field approximation:

$$H\Psi_{nlm}(\mathbf{r}) = E_{nl}\Psi_{nlm}(\mathbf{r})$$

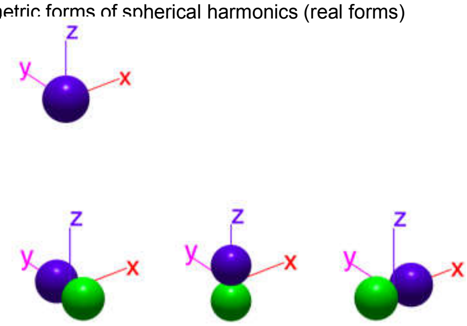
$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r)$$

$$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$$

Geometric forms of spherical harmonics (real forms)

l=0

l=1



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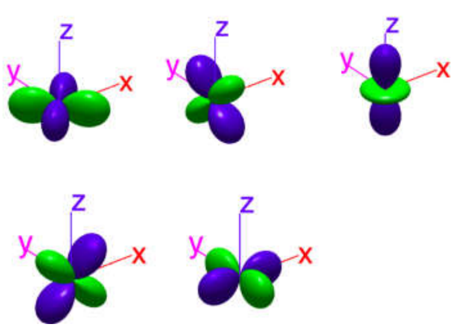
Geometric forms of spherical harmonics (real forms)

l=2



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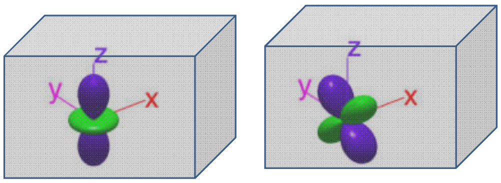
Symmetry of a spherical atom

$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$

$\Rightarrow$ states have degeneracy of $2l+1$

What happens when that atom is placed in a lower symmetry environment?



Symmetry of a spherical atom

$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$

$\Rightarrow$ states have degeneracy of $2l+1$

In terms of the spherical harmonic basis functions, the state have characters for rotation by an angle α :

$$\chi^l(\alpha) = \frac{\sin\left[\alpha\left(l+\frac{1}{2}\right)\right]}{\sin\left(\alpha/2\right)}$$

Using character tables to analyze the “crystal field” effects on atomic symmetry

The point symmetries are described by rotations, inversions, and reflections.

Rotation by an angle α :

$$\chi^l(\alpha) = \frac{\sin\left[\alpha\left(l+\frac{1}{2}\right)\right]}{\sin\left(\alpha/2\right)}$$

Inversion $\Im$:

Since $Y_{lm}(-\hat{\mathbf{r}}) = (-1)^l\, Y_{lm}(\hat{\mathbf{r}}), \quad \chi^l(\Im) = (2l+1)(-1)^l$

Decomposition of the continuous rotation representations into irreducible representations of the crystallographic point group:

$$\chi(R) = \sum_i a_i \chi^i(R)$$

$$a_i = \frac{1}{h}\sum_R \left(\chi^i(R)\right)^* \chi(R)$$

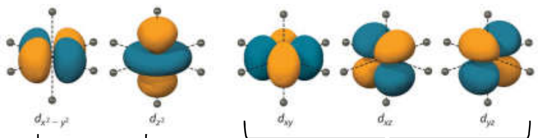
Example for the group O_h (48 group members)

Compatibility of continuous rotation group with the cubic group:

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0
l=0	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
l=1	*3*	*-1*	*1*	*-1*	*0*	*-3*	*1*	*-1*	*1*	*0*
l=2	*5*	*1*	*-1*	*1*	*-1*	*5*	*1*	*-1*	*1*	*-1*

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$	
Γ_1	1	1	1	1	1	1	1	1	1	1	
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1	
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1	
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0	
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0	
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1	
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1	
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1	
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0	
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0	
l=0	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	Γ_1
l=1	*3*	*-1*	*1*	*-1*	*0*	*-3*	*1*	*-1*	*1*	*0*	Γ_{15}
l=2	*5*	*1*	*-1*	*1*	*-1*	*5*	*1*	*-1*	*1*	*-1*	$\Gamma_{12}+\Gamma_{25'}$

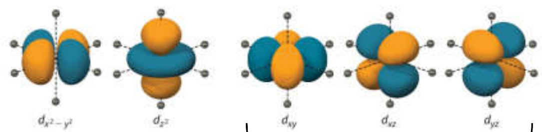
Visualization of *l=2* orbitals from
http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Crystal_Field_Theory/Crystal_Field_Theory



Γ_{12} $\Gamma_{25'}$

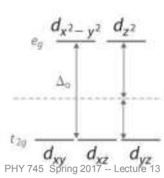
Octahedral symmetry

Octahedral symmetry effects on d-orbitals

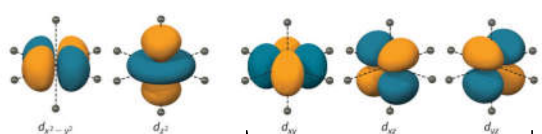


$\Gamma_{12}=e_g$ $\Gamma_{25'}=t_{2g}$

Energy diagram



Tetrahedral symmetry effects on d-orbitals



$\Gamma_{12}=e_g$ $\Gamma_{25'}=t_{2g}$