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

Plan for Lecture 15:

Symmetry properties of molecular orbitals

Reading: Chapter 7 in DDJ

1. **Linear combinations of atomic orbitals**
2. **Molecular bonds**
3. **Examples**

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	02/13/2017
14	Mon: 02/13/2017	Chap. 6	Direct product groups	#12	02/15/2017
15	Wed: 02/15/2017	Chap. 7	Molecular orbital	#13	02/17/2017
16	Fri: 02/17/2017				
17	Mon: 02/20/2017				
18	Wed: 02/22/2017				
19	Fri: 02/24/2017				
20	Mon: 02/27/2017				Exam
21	Wed: 03/01/2017				Exam
22	Fri: 03/03/2017				Exam Due
	Mon: 03/06/2017		*Spring break - no class*		
	Wed: 03/08/2017		*Spring break - no class*		
	Fri: 03/10/2017		*Spring break - no class*		
	Mon: 03/13/2017		*APS Meeting - no class*		
	Wed: 03/15/2017		*APS Meeting - no class*		
	Fri: 03/17/2017		*APS Meeting - no class*		
23	Mon: 03/20/2017				
24	Wed: 03/22/2017				

Electronic structure of an atom

For simplicity we will first consider a single electron system; a H-like ion with atomic charge *Ze*

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

E_{100}=-13. 60569253 Z^2 eV
a_0 = 0. 52917721092 Å

$$H\Psi_{nlm}(r,\theta,\phi) = E_{nlm}\Psi_{nlm}(r,\theta,\phi)$$

$$E_{nlm} = -\frac{Z^2e^2}{4\pi\epsilon_0 a_0}\frac{1}{2n^2} \equiv \frac{E_{100}}{n^2} \qquad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0} \qquad E_{100} = E_{100}$$

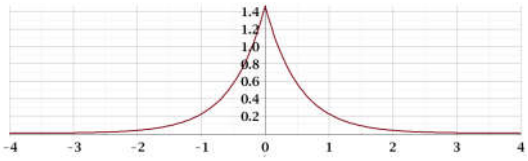
$$\Psi_{200}(r,\theta,\phi) = \sqrt{\frac{Z^3}{32\pi a_0^3}}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0} \qquad E_{200} = \frac{E_{100}}{4}$$

$$\Psi_{210}(r,\theta,\phi) = \sqrt{\frac{Z^3}{32\pi a_0^3}}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta \qquad E_{210} = \frac{E_{100}}{4}$$

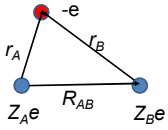
$$\Psi_{21\pm1}(r,\theta,\phi) = \mp\sqrt{\frac{Z^3}{64\pi a_0^3}}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi} \qquad E_{21\pm1} = \frac{E_{100}}{4}$$

Example – *1s* state of hydrogen-like atom

$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0}$$



Electronic structure of H-like molecular ion (within Born-Oppenheimer approximation)



$$r_A = |\mathbf{r} - \mathbf{R}_A| \qquad r_B = |\mathbf{r} - \mathbf{R}_B|$$
$$R_{AB} = |\mathbf{R}_B - \mathbf{R}_A|$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_Ae^2}{4\pi\epsilon_0 r_A} - \frac{Z_Be^2}{4\pi\epsilon_0 r_B} + \frac{Z_AZ_Be^2}{4\pi\epsilon_0 R_{AB}}$$

Approximate wavefunction:

$$\Psi(\mathbf{r},\mathbf{R}_A,\mathbf{R}_B) = X_A\Psi_{100}(\mathbf{r}-\mathbf{R}_A) + X_B\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

X_A and X_B can be determined variationally by optimizing

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

Electronic structure of H-like molecular ion – continued

Ref. Pauling and Wilson, *Introduction to Quantum Mechanics* (1935) (now published by Dover)

Necessary integrals:

$$\Delta \equiv \int d^3r \Psi^*_{100}(\mathbf{r}-\mathbf{R}_A)\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

$$H_{AA} \equiv \int d^3r \Psi^*_{100}(\mathbf{r}-\mathbf{R}_A)H\Psi_{100}(\mathbf{r}-\mathbf{R}_A) = H_{BB}$$

$$H_{AB} \equiv \int d^3r \Psi^*_{100}(\mathbf{r}-\mathbf{R}_A)H\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

Generalized eigenvalue problem for energy E in the variational approximation:

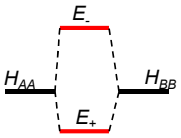
$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}\begin{pmatrix} X_A \\ X_B \end{pmatrix} = E\begin{pmatrix} 1 & \Delta \\ \Delta & 1 \end{pmatrix}\begin{pmatrix} X_A \\ X_B \end{pmatrix}$$

Eigenstates:

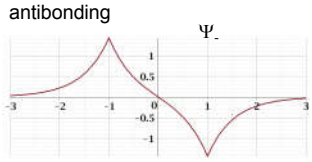
$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_+ = \frac{1}{\sqrt{2(1+\Delta)}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad E_+ = \frac{H_{AA}+H_{AB}}{1+\Delta}$$

$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_- = \frac{1}{\sqrt{2(1-\Delta)}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad E_+ = \frac{H_{AA}-H_{AB}}{1-\Delta}$$

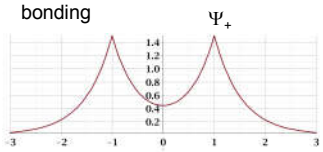
Electronic structure of H-like molecular ion – continued



antibonding

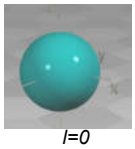


bonding

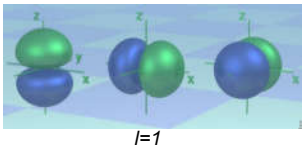


LCAO methods -- continued – angular variation

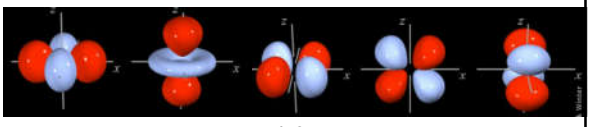
http://winter.group.shef.ac.uk/orbitron/



l=0



l=1



l=2

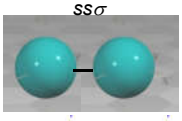
LCAO methods -- continued – angular variation

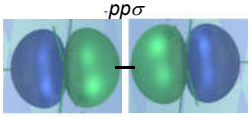
While, for atoms the "*z*" axis is an arbitrary direction, for diatomic molecules and for describing bonds, it is convenient to take the "*z*" axis as the bond direction.

Atom			Bond		
		symbol			*symbol*
l=0	*m*=0	*s*	*l*=0	λ=0	σ
l=1	*m*=0	*p*	*l*=1	λ=0	σ
	m= ±1	*p*		λ=1	π
l=2	*m*=0	*d*	*l*=2	λ=0	σ
	m= ± 1	*d*		λ=1	π
	m= ± 2	*d*		λ= 2	δ

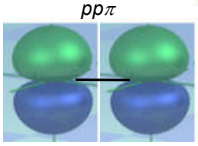
LCAO methods -- continued – bond types

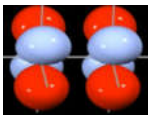
ssσ *pp*σ





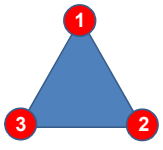
ppπ *dd*π





Extension of ideas to polyatomic molecules "atomic site" representation

$$D_{ij}^{a.s.}(R)=\begin{cases}1 & \text{if } i \xrightarrow{R} j \\ 0 & \text{otherwise}\end{cases}$$



Example: C_{3v}

$$D^{a.s.}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \quad D^{a.s.}(C_3)=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} \quad D^{a.s.}(\sigma_v)=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}$$

$$\chi^{a.s.}(E)=3 \qquad \chi^{a.s.}(C_3)=0 \qquad \chi^{a.s.}(\sigma_v)=1$$

Relationship of atomic site representation to irreducible representations for C_{3v}

C_{3v} (3m)			E	$2C_3$	$3\sigma_v$
x^2+y^2, z^2	z	A_1	1	1	1
	R_z	A_2	1	1	−1
(x^2-y^2, xy) (xz, yz)	(x, y) (R_x, R_y)	E	2	−1	0
		$\chi^{a.s.}(R)$	3	0	1

atomic site character

Decomposition of the atomic site representation into irreducible representations

$$\chi^{a.s.}(R) = \sum_i a_i \chi^i(R)$$

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

In this case:

$$\chi^{a.s.} \rightarrow A_1 + E$$

Atomic site symmetry together with internal degrees of freedom such as LCAO

Diagram (and following) from DDJ textbook (earlier version)

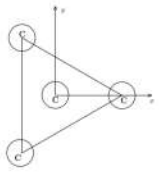
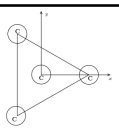


Figure 8.17: Schematic diagram of a carbon atom forming bonds to 3 other carbon atoms at the corners of an equilateral triangle.

Character table

$D_{3h}(6m2) \equiv D_3 \otimes \sigma_h$			E	σ_h	$2C_3$	$2S_3$	$3C_2''$	$3\sigma_v$
x^2+y^2, z^2		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	−1	−1
		A_1''	1	−1	1	−1	1	−1
	z	A_2''	1	−1	1	−1	−1	1
(x^2-y^2, xy)	(x, y)	E'	2	2	−1	−1	0	0
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0
		$\chi^{a.s.}$	3	3	0	0	1	1

$\rightarrow A_1' + E'$



Atomic site symmetry together with internal degrees of freedom such as LCAO

Diagram from DDJ textbook (earlier version)

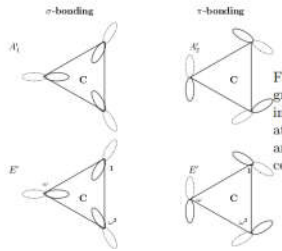


Figure 8.18: Schematic diagram for the σ-bonds and the in-plane π-bonds for carbon atoms at the corners of a triangle to a carbon atom at the center of the triangle.

Analysis of LCAO symmetries for this case

$$\chi^{\text{atom sites}} \otimes \chi_s = (A_1' + E') \otimes A_1' = A_1' + E'$$

$$\chi^{\text{atom sites}} \otimes \chi_{p_z} = (A_1' + E') \otimes A_2'' = A_2'' + E''.$$

$$\chi^{\text{atom sites}} \otimes \chi_{p_x,p_y} = (A_1' + E') \otimes E' = A_1' + A_2' + 2E'.$$