

**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**

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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				


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DREST Department of Physics

News



Angela Harper named Churchill scholar

Major Manal Abumoush featured in article on women diversity in STEM

Congratulations to Dr. Alex Taylor, recent Ph.D. Recipient

Events

Wed, Feb. 15, 2017
Career Advising Event
Andrea Eslinger
Univ of Texas, Dallas
12:00pm - Olin Lounge
Dinner will be served

Wed, Feb. 15, 2017
Electrochemical Energy Storage
Professor Augustyn,
NCSCU
4:50pm - Olin 101
Refreshments served
3:30pm - Olin Lounge

Wed, Feb. 22, 2017
Data Compression Methods
Professor Ballard, WFU

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Electronic structure of an atom

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

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad E_{100} = -13.60569253 Z^2 \text{ eV}$$

$$a_0 = 0.52917721092 \text{ \AA}$$

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

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

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

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

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

$$\Psi_{211}(r, \theta, \phi) = \mp \sqrt{\frac{Z^3}{64\pi a_0^3}} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\phi} \quad E_{211} = \frac{E_{100}}{4}$$

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Example – 1s state of hydrogen-like atom

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

The graph shows the radial wavefunction $\Psi_{100}(r, \theta, \phi)$ as a function of r/a_0 . The x-axis ranges from -4 to 4, and the y-axis ranges from 0 to 1.4. The curve starts at 0 for negative r , reaches a maximum of approximately 1.27 at $r=0$, and then decays exponentially towards zero as r increases.

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

The diagram shows two nuclei, labeled $Z_A e$ and $Z_B e$, separated by a distance R_{AB} . A single electron, labeled $-e$, is positioned between them. Distances r_A and r_B are shown from the electron to the nuclei. The vector \mathbf{R}_A points from the origin to the nucleus $Z_A e$, and \mathbf{R}_B points from the origin to the nucleus $Z_B e$.

$$r_A = |\mathbf{r} - \mathbf{R}_A| \quad r_B = |\mathbf{r} - \mathbf{R}_B|$$

$$R_{AB} = |\mathbf{R}_B - \mathbf{R}_A|$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Z_A e^2}{4\pi\epsilon_0 r_A} - \frac{Z_B e^2}{4\pi\epsilon_0 r_B} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$$

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

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

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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:

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

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

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Electronic structure of H-like molecular ion – continued

antibonding Ψ_-

bonding Ψ_+

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LCAO methods -- continued -- angular variation
<http://winter.group.shef.ac.uk/orbital/>

$l=0$ $l=1$ $l=2$

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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		
	<i>m</i>	symbol		λ	symbol
<i>l</i> =0	<i>m</i> =0	<i>s</i>	<i>l</i> =0	λ =0	σ
<i>l</i> =1	<i>m</i> =0	<i>p</i>	<i>l</i> =1	λ =0	σ
	<i>m</i> = ± 1	<i>p</i>		λ =1	π
<i>l</i> =2	<i>m</i> =0	<i>d</i>	<i>l</i> =2	λ =0	σ
	<i>m</i> = ± 1	<i>d</i>		λ =1	π
	<i>m</i> = ± 2	<i>d</i>		λ = 2	δ

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LCAO methods -- continued -- bond types

ss σ

pp σ

pp π

dd π

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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}

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

$$\chi^{a.s.}(E) = 3$$

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

$$\chi^{a.s.}(C_3) = 0$$

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

$$\chi^{a.s.}(\sigma_v) = 1$$

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

$C_{3v}(3m)$		E	$2C_3$	$3\sigma_v$
$x^2 + y^2, z^2$	A_1	1	1	1
$(x^2 - y^2, xy)$	A_2	1	1	-1
(xz, yz)	E	2	-1	0

$$\chi^{a.s.}(R) \quad 3 \quad 0 \quad 1$$

atomic site character

Decomposition of the atomic site representation into irreducible representations

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

In this case:

$$a_i = \frac{1}{h} \sum_R (\chi^i(R))^* \chi^{a.s.}(R) \quad \chi^{a.s.} \rightarrow A_1 + E$$

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

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

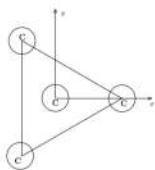


Figure 8.17: Schematic diagram of a carbon atom forming bonds to 3 other carbon atoms at the corners of an equilateral triangle.

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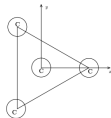
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Character table

$D_{3h}(6m2) \equiv D_3 \otimes \sigma_h$		E	σ_h	$2C_3$	$2S_6$	$3C_2$	$3\sigma_v$
$x^2 + y^2, z^2$	A_1'	1	1	1	1	1	1
	A_2'	1	1	1	1	-1	-1
	A_1''	1	-1	1	-1	1	-1
	A_2''	1	-1	1	-1	-1	1
$(x^2 - y^2, xy)$	E'	2	2	-1	-1	0	0
(xz, yz)	E''	2	-2	-1	1	0	0

$$\chi^{a.s.} \quad 3 \quad 3 \quad 0 \quad 0 \quad 1 \quad 1 \rightarrow A_1' + E'$$



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

Diagram from DDJ textbook (earlier version)

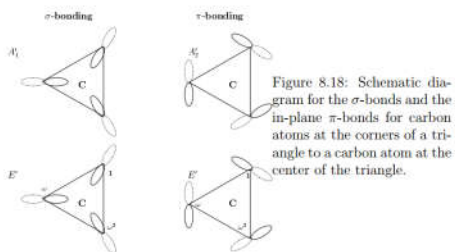


Figure 8.18: Schematic diagram for the σ -bonds and the in-plane π -bonds for carbon atoms at the corners of a triangle to a carbon atom at the center of the triangle.

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Analysis of LCAO symmetries for this case

$$\chi^{\text{atom sites}} \otimes \chi_s = (A'_1 + E') \otimes A'_1 = A'_1 + E'$$

$$\chi^{\text{atom sites}} \otimes \chi_{p_z} = (A'_1 + E') \otimes A''_2 = A''_2 + E''.$$

$$\chi^{\text{atom sites}} \otimes \chi_{p_x, p_y} = (A'_1 + E') \otimes E' = A'_1 + A'_2 + 2E'.$$

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