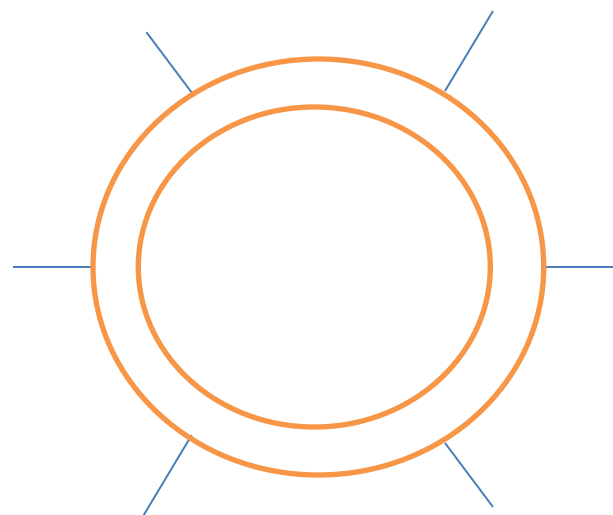


# Molecular Orbitals of Benzene

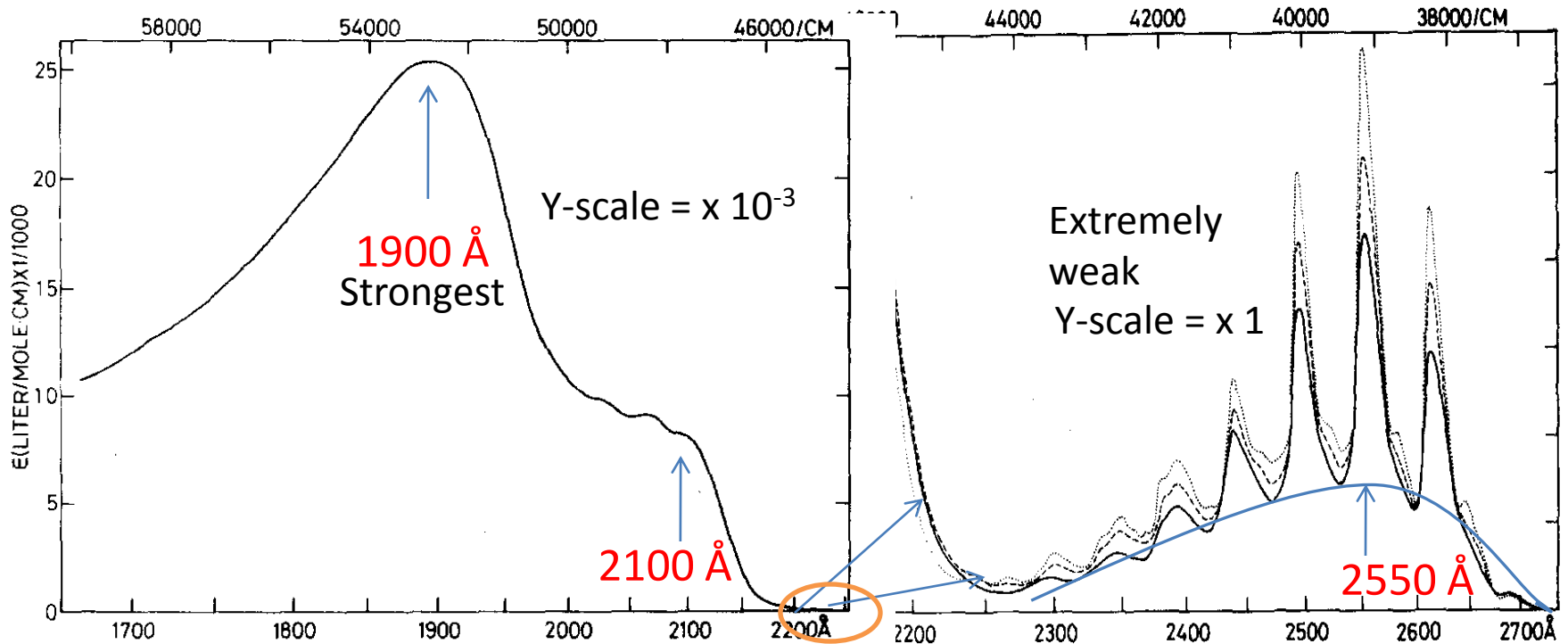
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Nov 18, 2009  
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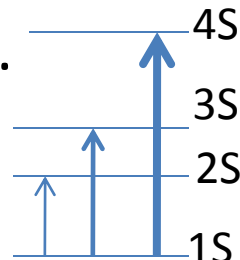
# Overview

- Absorption spectrum of benzene film
- Molecular Orbitals
  - Quantum Problem
  - Approximations
    - Linear Combination of Atomic Orbitals (LCAO)
  - Assignment of absorption bands

# UV Absorption Spectrum (thin film of Benzene between quartz plates)



What are the origins of these bands? (known since 1880s).  
Three transitions from ground state to low lying states.



# Electronic problem of benzene

- Full electronic Hamiltonian for 54 particles (42 e and 12 nuclei)

1.  $H = T_e + T_n + V_{nn} + V_{en} + V_{ee}$

$$T = KE = \frac{1}{2} m v^2;$$

$$V = PE = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_{12}};$$

(e = electrons; n = nuclei).

2. Solve for stationary states :

$$H\Psi(r,R) = E\Psi(r,R)$$

# Assumptions

1. Divide the electrons into **valence (e')** and **core electrons (e<sub>0</sub>)**.

2. **Born-Oppenheimer adiabatic approximation.**

– Expand around equilibrium positions of the nuclei.

→  $H \approx T_{e'} + V_{e'n_0} + V_{e'e'}$  (no vibrations) (6+24 = 30 e problem!)

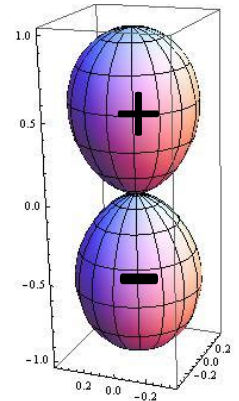
3. Chemical properties linked to  **$\pi$  electrons (e'')** of **C only.**

→  $H = T_{e''} + V_{e''n_0} + V_{e''e''}$  (6 e + 12 nuclei).

4. **Mean Field Approximation** . Assume each of the six electrons moves in some effective potential called mean field.

→ (1 e + 12 nuclei)

5. **Ignore H-nuclei.** → (1 e moving in potential of 6 nuclei)



# Electronic problem of benzene

## (Summary)

1. Solve  $H_0 \Psi_n = E_{0n} \Psi_n$  with  $H_0 = T_{e''} + V_{e''n0}$  (1 e in the field of 6 nuclei).
2. Solutions are 1-e states, called Molecular Orbitals  $\Psi_n$ .

3. **Fill MOs one e at a time** to obtain the effective ground state of the molecule  $|0\rangle$ .

**Achtung!! Achtung!!** Molecular orbitals are not quantum states of the molecule!

4. Treat  $H_1 (= V_{e''e''})$  perturbatively:  
$$\Delta E_{0n} = \langle \Psi_n | H_1 | \Psi_n \rangle.$$

# Use symmetry to solve $H_0 \Psi_n = E_0 \Psi_n$

- Point Symmetry Group  $D_{6h}$
- $H_0$  is the Hamiltonian with e-e interactions ignored.
  - $[H_0, R_i] = 0$  for all operations  $R_i$  in  $D_{6h}$ .
  - Simultaneous eigenstates of  $H_0$  and  $R_i$ .
  - Stationary states form basis for irreducible representations of  $D_{6h}$ .

There are 12 irreducible reps of  $D_{6h}$ . Which ones will be useful for benzene?

# Character Table of $D_{6h}$

Character table for  $D_{6h}$  point group

	E	$2C_6$	$2C_3$	$C_2$	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$	Linear, rotations	Quadratic
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1		$x^2+y^2, z^2$
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2-y^2, xy)$
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	$(x, y)$	
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

# Irreps of point group $D_{6h}$

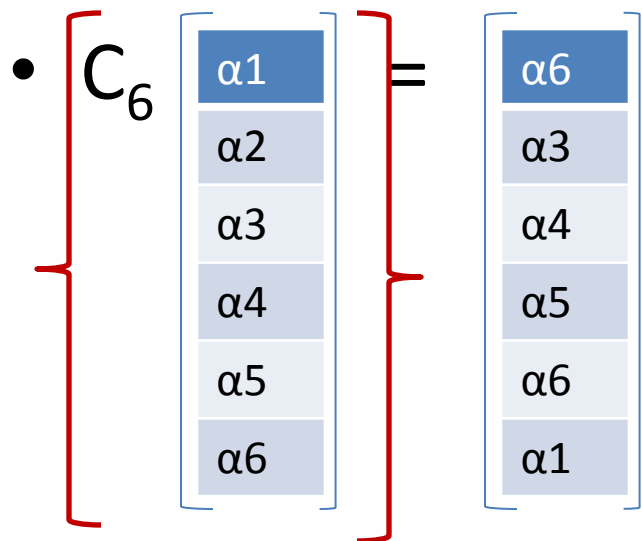
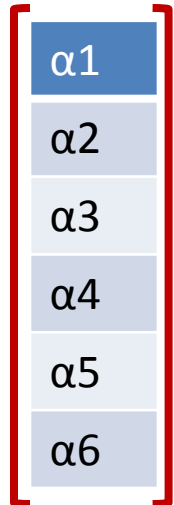
$D_{6h}$	E	$2C_6$ (z)	$2C_3$ (z)	$C_2$ (z)	$3C_2'$ (c)	$3C_2''$ (b)	i	$2S_3$ (z)	$2S_6$ (z)	$\sigma_h$ (c)	$3\sigma_d$ (b)	$3\sigma_v$ (c)
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0
$A_{1u}$	1						-1					
$A_{2u}$	1	same					-1		times -1			
$B_{1u}$	1						-1					
$B_{2u}$	1						-1					
$E_{1u}$	2						-2					
$E_{2u}$	2						-2					

# Steps in solution (Once again)

- **Pick atomic orbitals (AO) of interest**
  - In benzene, the low lying excited states “must” involve only  $p\pi$  atomic orbitals. We denote them here by  $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6\}$ .
- **Construct Molecular Orbitals**
  - by forming linear combinations (LCAO) that transform according to “relevant” **irreducible representations** of the symmetry group.
  - LCAO is one among many other ways of obtaining MOs, which are loosely defined as wavefunctions that extend over a molecule. [Block wave would be an example of a MO extending over a very large molecule].
- **Energy of orbitals**
  - Find the **expectation value of Hamiltonian** in these molecular orbitals.
- **Aufbau principle**
  - **Fill each orbital with one up spin and one down spin** electron till all electrons get used up.
- **Construct the ground state**
  - From the electron configuration **construct the ground state** of the molecule by properly symmetrizing the product of orbitals.
- **Generate first excited state**
  - Promote one electron from highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO) to **generate first excited state**. Symmetrize properly and find energy of excited state(s).

# Construct MO : Full representation $\Gamma_{\pi}$

- Arrange orbitals on C atoms in a vector.
- How does this vector change when you act on the molecule by operations of  $D_{6h}$  ?



$C_6$  represented by:

0	0	0	0	0	1
0	0	1	0	0	0
0	0	0	1	0	0
0	0	0	0	1	0
0	0	0	0	0	1
1	0	0	0	0	0

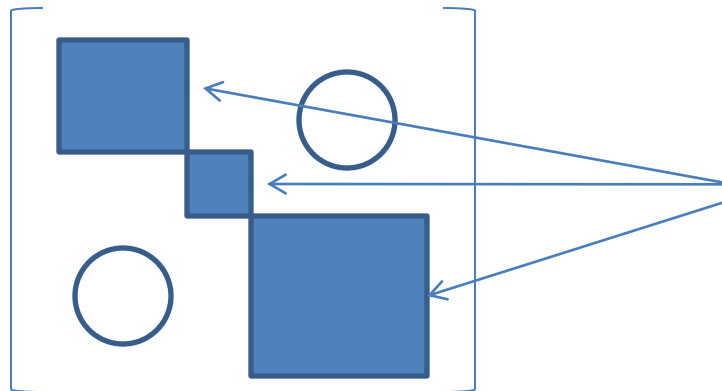
Same procedure for other operations.

The 6x6 matrices “represent” the operations in the space of the atomic orbitals  $\alpha_i$ .

# Finding relevant irreducible (1)

- Reducible representation  $\Gamma_\pi$  based on atomic orbitals  $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6\}$ .
  - Each of the operations  $R_i$  represented by a 6-by-6 matrix  $S_i$ .
  - There exists a matrix  $U$  which has the same shape-changing operation on all the matrices  $S_i$ .

$US_i U^{-1} = \text{Block-diagonal Form}$ - same block-sizes for all  $S_i$



Blocks are irreducible representations we seek.

## Finding relevant irreducible (2)

- Form reducible representation based on atomic orbitals  $\{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5, \alpha_6\}$ .
  - Each of the operations  $R_i$  will be represented by a 6-by-6 matrix  $S_i$ .
  - There exists a matrix  $U$  which has the same shape-changing operation on all the matrices  $S_i$ .
    - $US_i U^{-1}$  = Block-diagonal Form- same block-sizes for all  $S_i$
- Much easier is to work with traces of the matrices  $S_i$  – called characters obtained by simply noting number of atoms which are not moved during the operation.
- Characters  $\{\chi[\Gamma_a, R]\}$  obey Great Orthogonality Theorem  $\{\chi[\Gamma_a, R]\}$  = character of operation  $R$  in representation  $\Gamma_a$ .

Theorem: 
$$\sum_R \chi[\Gamma_a, R] \chi^*[\Gamma_b, R] = h \delta_{ab} \quad h = \text{order of group.}$$

Therefore, 
$$\chi[\Gamma, R] = \sum_a n_a \chi[\Gamma_a, R] \text{ (irreps)} \rightarrow n_a = \frac{1}{h} \sum_R \chi[\Gamma, R] \chi^*[\Gamma_a, R]$$

# Decompose Reducible Rep $\Gamma_\pi$

- Six atomic orbitals,  $\{\alpha_n, n = 1, \dots, 6\}$ , one on each carbon atom gives a six-dimensional reducible representation  $\Gamma_\pi$  of  $D_{6h}$ . The traces of these matrices (characters) are:

From Group Character Table

	D <sub>6h</sub>	E	2C <sub>6</sub>	2C <sub>3</sub>	C <sub>2</sub>	3C <sub>2</sub> '	3C <sub>2</sub> ''	i	2S <sub>3</sub>	2S <sub>6</sub>	$\sigma_h$	3 $\sigma_d$	3 $\sigma_v$
$\Gamma_\pi$		<b>6</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>-2</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>-6</b>	<b>2</b>	<b>0</b>
A <sub>2u</sub>		1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B <sub>1g</sub>		1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
E <sub>1g</sub>		2	1	-1	-2	0	0	2	1	-1	-2	0	0
E <sub>2u</sub>		2	-1	-1	2	0	0	-2	1	1	-2	0	0

Therefore,  $\Gamma_\pi = A_{2u} + B_{2g} + E_{1g} + E_{2u}$ ; dim.  $6 = 1 + 1 + 2 + 2$ .

# Basis MOs for Irreps

- General Method:

- Let  $R_{mn}$  be  $mn$ -entry in the matrix for symmetry operation  $R$  in irrep  $\Gamma$  of dim  $N$  with basis  $\{\phi_1, \phi_2, \dots, \phi_N\}$ .

- Theorem:  $\left[ \frac{N}{h} \sum_R R^*_{ij} R \right]$  acting on  $\phi_j$  projects out  $\phi_i$ .

- In benzene it is enough to work with  $C_6$  subgroup of  $D_{6h}$ . Ans:

$$\phi_l = \frac{1}{\sqrt{6\sigma_l}} \sum_{k=1}^6 e^{\frac{2\pi i l k}{6}} \alpha_k$$

# Explicit calculations for MOs

- Calc for Basis for  $A_{2u}$  irrep: Act on AO  $\alpha_1$  by:

$$1E + 1 * C_6^1 + 1 * C_6^2 + 1 * C_6^3 + 1 * C_6^4 + 1 * C_6^5$$

– This yields:  $\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6$

– Normalize to obtain  $\phi_0 = (\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6) / \sqrt{6}$

- Calculation for Basis for  $B_{1g}$ : Act on AO  $\alpha_1$  by:

$$1E - 1 * C_6^1 + 1 * C_6^2 - 1 * C_6^3 + 1 * C_6^4 - 1 * C_6^5$$

– Corresponds to:  $\phi_3 = (\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6) / \sqrt{6}$

# Solution : summary

- Six atomic  $2p\pi$  orbitals:  $\alpha_n$  ( $n=1, \dots, 6$ ).
- Six mutually orthogonal LCAO ( $L=0, \pm 1, \pm 2, 3$ ): Huckel's molecular orbitals for benzene.
- Symmetry Properties:

$$\phi_0 [A_{2u}]; \phi_3 [B_{2g}];$$

$$\phi_{\pm 1} [E_{1g}]; \phi_{\pm 2} [E_{2u}]$$

$$\phi_l = \frac{1}{\sqrt{6\sigma_l}} \sum_{k=1}^6 e^{\frac{2\pi i l k}{6}} \alpha_k$$

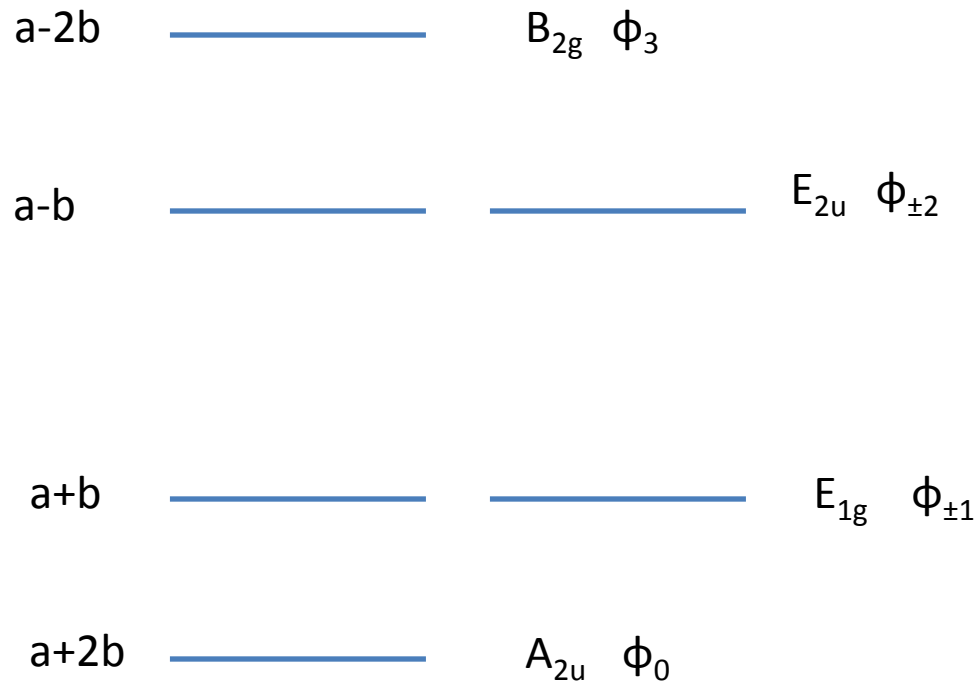
- If  $\langle \alpha_n | \alpha_m \rangle = \delta_{mn}$ , then  $\sigma_L=1$ .
- Energy of one electron in  $\phi_L$ :

$$\varepsilon_L = \langle \phi_L | T + \sum_{n0} V_{n0e''} | \phi_L \rangle$$

$$= \langle \alpha_1 | T + \sum V_{n0e''} | \alpha_1 \rangle + (2 \cos(2\pi L/6)) \langle \alpha_1 | T + \sum V_{n0e''} | \alpha_2 \rangle$$

$$= a + 2 b \cos(2\pi L/6) \text{ (upon calculation we find } b < 0 \text{ here).}$$

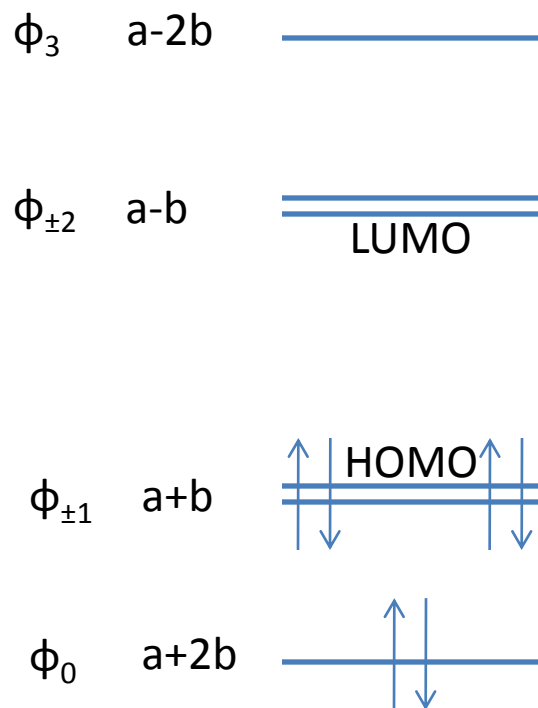
# 1-e Molecular Energy Levels



Question: What's the next step?

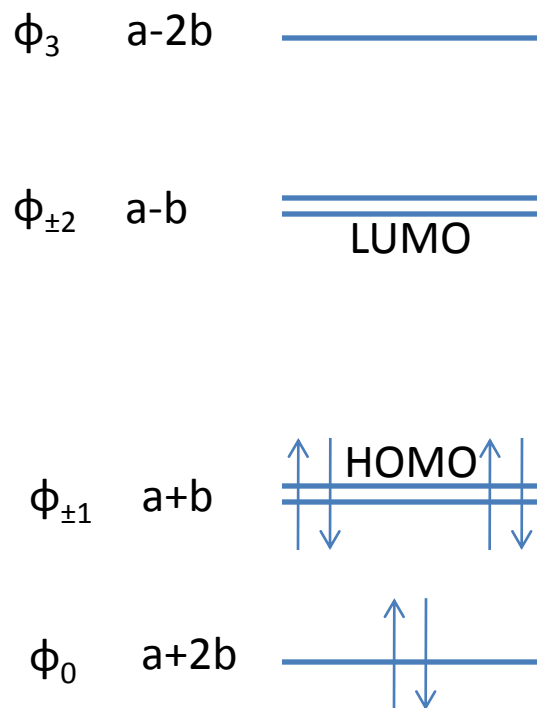
# The Ground State $|0\rangle$

Add one electron at a time in MOs paying attention to Pauli's exclusion principle



# The Ground State $|0\rangle$

Add one electron at a time in MOs paying attention to Pauli's exclusion principle



Electron configuration often written as:  
 $a_{2u}^2 e_{1g}^4$  (using small letter for the Mulliken notation for the symmetry names)  
 -a closed shell structure

Ground State:

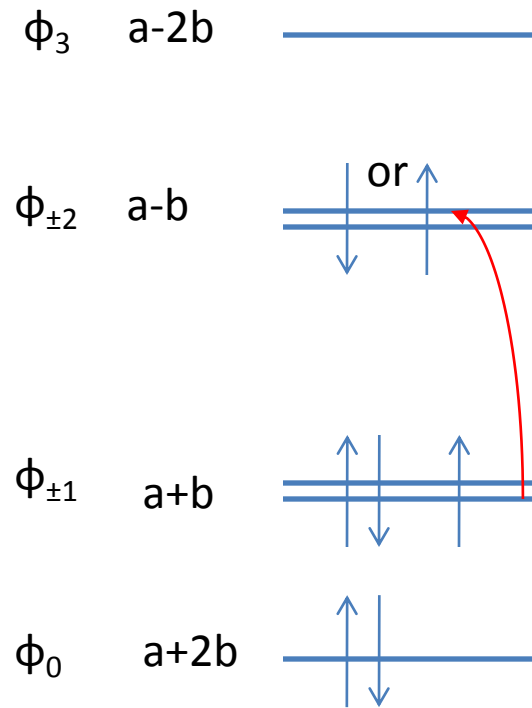
$$|0\rangle = 1/\sqrt{6!} \sum_P (-1)^P [\phi_0(1) \phi_0(2) \phi_{\pm 1}(3) \phi_{\pm 1}(4) \phi_{\pm 1}(5) \phi_{\pm 1}(6)]$$

$$[\uparrow(1) \downarrow(2) \uparrow(3) \downarrow(4) \uparrow(5) \downarrow(6)];$$

Permutations are needed to make sure Pauli's exclusion is obeyed by 6 identical electrons.

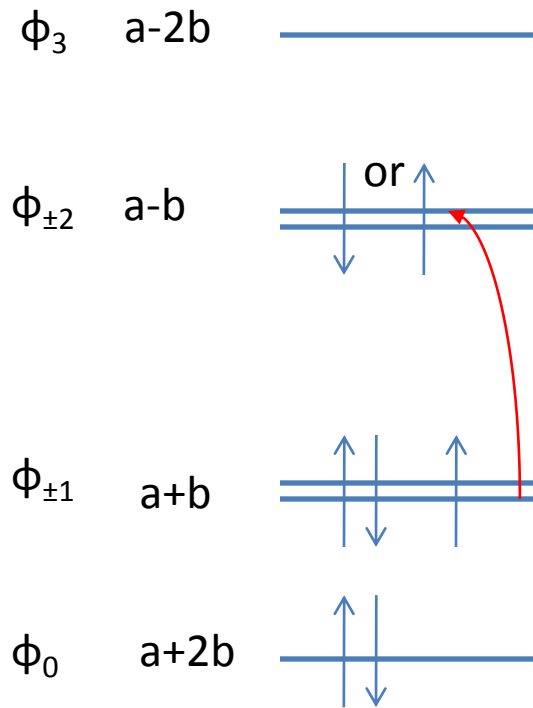
# First excited states $|1\rangle, |2\rangle, |3\rangle, |4\rangle$

- Get the first excited state of molecules by promoting one electron to the next higher level as done for atoms.



# First excited states $|1\rangle, |2\rangle, |3\rangle, |4\rangle$

- Get the first excited state of molecules by promoting one electron to the next higher level as done for atoms.



Electron configuration:  $a_{2u}^2 e_{1g}^3 e_{2u}^1$

First excited state ( four possible configurations):

$$|1\rangle = [\phi_0(1) \phi_0(2)] \phi_1(3) \phi_1(4) \phi_{-1}(5) \phi_{+2}(6);$$

$$|2\rangle = [ ] \phi_{-1}(3) \phi_{-1}(4) \phi_1(5) \phi_{-2}(6);$$

$$|3\rangle = [ ] \phi_1(3) \phi_1(4) \phi_{-1}(5) \phi_{-2}(6);$$

$$|4\rangle = [ ] \phi_{-1}(3) \phi_{-1}(4) \phi_1(5) \phi_{+2}(6);$$

Each can be singlet ( $\uparrow\downarrow$ ) or triplet ( $\uparrow\uparrow, \downarrow\downarrow, \{\uparrow\uparrow+\downarrow\downarrow\}$ ).

**$|1\rangle, |2\rangle, |3\rangle, |4\rangle$  do not have symmetry of the benzene group  $D_{6h}$**

# Transformation of excited states

## $|1\rangle, |2\rangle, |3\rangle, |4\rangle$ under $D_{6h}$

- States  $|1\rangle, |2\rangle, |3\rangle$  and  $|4\rangle$  belong to product space  $E_{1g} \times E_{2u}$  (because they are products of  $\phi_{\pm 1}$  and  $\phi_{\pm 2}$  states)
- Math:  $E_{1g} \times E_{2u} = B_{1u} + B_{2u} + E_{1u}$   
 $|1\rangle, |2\rangle, |3\rangle$  and  $|4\rangle$  separate into:  
 $|B_{1u}\rangle = (|1\rangle + |2\rangle)/\sqrt{2}$   
 $|B_{2u}\rangle = (|1\rangle - |2\rangle)/\sqrt{2}$   
 $|E_{1u}\rangle = (|3\rangle, |4\rangle)$  : two-dimensional.
- Selection rules for optical transition between states easy to work out with states of well-defined symmetry

# Selection Rules for electronic transitions

- Let  $\mathbf{P}$  be the electric dipole moment vector.
- $P_z$  transforms as  $A_{2u}$  and  $\{P_x, P_y\}$  transform as  $E_{1u}$  of  $D_{6h}$ . These are read from Character Table. [Next Slide]
- Quantum Mechanics:
  - $\langle 0 | P_z | \Psi \rangle$  and  $\langle 0 | P_{x,y} | \Psi \rangle$  determine transition between the ground state  $|0\rangle$  and state  $|\Psi\rangle$ .
  - $\langle 0 | P_z | \Psi \rangle = 0$  for all  $|\Psi\rangle$ .
  - $\langle 0 | P_{x,y} | \Psi \rangle \neq 0$  only when  $|\Psi\rangle = \{|E_{1u}\rangle, \text{singlet}\}$

Allowed transition(s):  $|0\rangle \rightarrow \{|E_{1u}\rangle, \text{singlet}\}$  only.

# Character Table of D<sub>6h</sub>

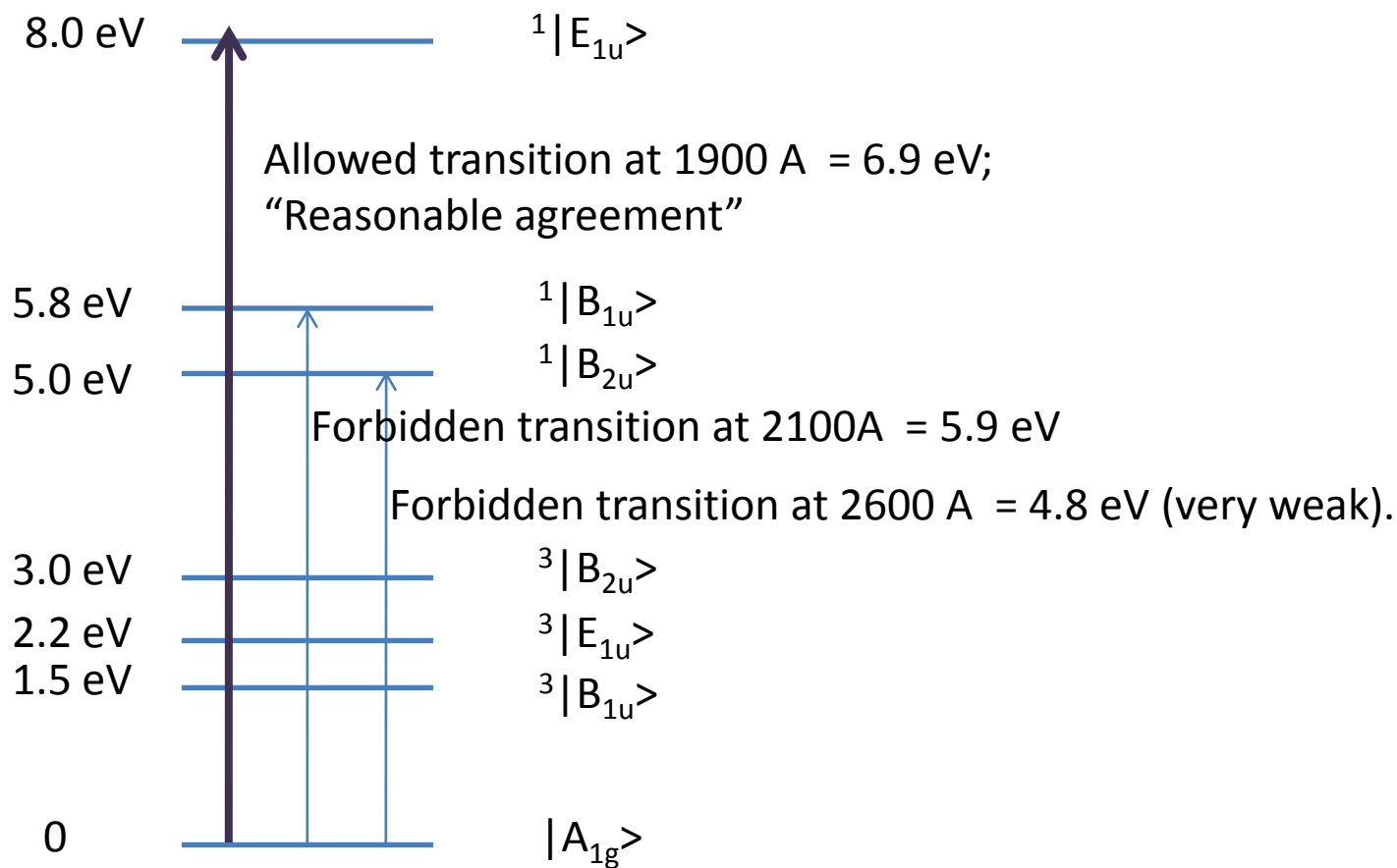
Character table for D<sub>6h</sub> point group

	E	2C <sub>6</sub>	2C <sub>3</sub>	C <sub>2</sub>	3C' <sub>2</sub>	3C'' <sub>2</sub>	i	2S <sub>3</sub>	2S <sub>6</sub>	σ <sub>h</sub>	3σ <sub>d</sub>	3σ <sub>v</sub>	Linear, rotational	Quadratic
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	1	1		x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
A <sub>2g</sub>	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R <sub>z</sub>	
B <sub>1g</sub>	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B <sub>2g</sub>	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E <sub>1g</sub>	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R <sub>x</sub> , R <sub>y</sub> )	(xz, yz)
E <sub>2g</sub>	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x <sup>2</sup> -y <sup>2</sup> , xy)
A <sub>1u</sub>	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A <sub>2u</sub>	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B <sub>1u</sub>	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B <sub>2u</sub>	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E <sub>1u</sub>	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E <sub>2u</sub>	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

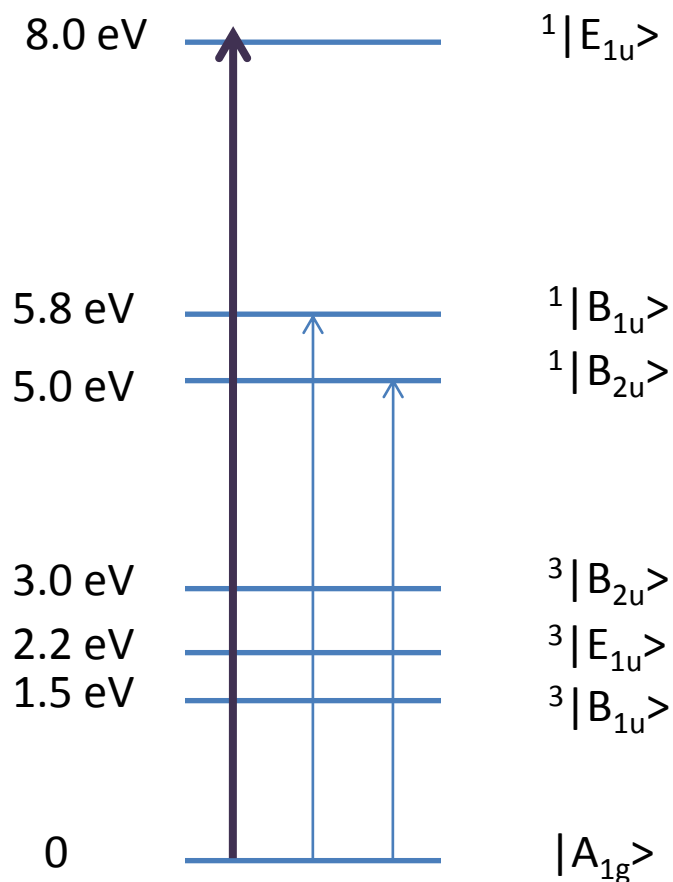
# Including e-e Interaction

- Form totally symmetric eigenfunctions to go with triplet spin states and totally antisymmetric eigenfunctions to go with the singlet states.
- Ground state  $|0\rangle$ :  ${}^1|A_{1g}\rangle$
- Excited states:  ${}^1|B_{1u}\rangle, {}^3|B_{1u}\rangle, {}^1|B_{2u}\rangle, {}^3|B_{2u}\rangle, {}^1|E_{1u}\rangle, {}^3|E_{1u}\rangle$
- Evaluate  $\Delta E = \langle \Psi | H_1 | \Psi \rangle$  in each.
- Add to  $\langle \Psi | H_0 | \Psi \rangle$
- Result next slide.

# 6-e Molecular Energy Levels of Benzene (1)



# 6-e Molecular Energy Levels of Benzene (2)



1. Is  $|A_{1g}\rangle$  to  $^1|E_{1u}\rangle$  transition equal to HOMO to LUMO gap? Why? Why not?
2. Which is more important: HOMO and LUMO or  $|0\rangle$  and  $\{|1\rangle, |2\rangle, |3\rangle, |4\rangle\}$ ?

Next Talk:  
Vibration levels of benzene.