Lecture 24 – 12/4

Remember: Final presentations !!

Timeline:
- → suggestion of topic (in person or via email): Wednesday
- → first draft (in person or via email): Tu next week
- → Presentation: Thu, Dec 7,
  - 10 am – 2 pm
  - will provide lunch
  - Science Center 309

Topics today:
Molecules

Energy levels of molecules

Overview

Electronic Transitions:

ΔE = 1-15 eV

Visible-UV

Vibrational Transitions:

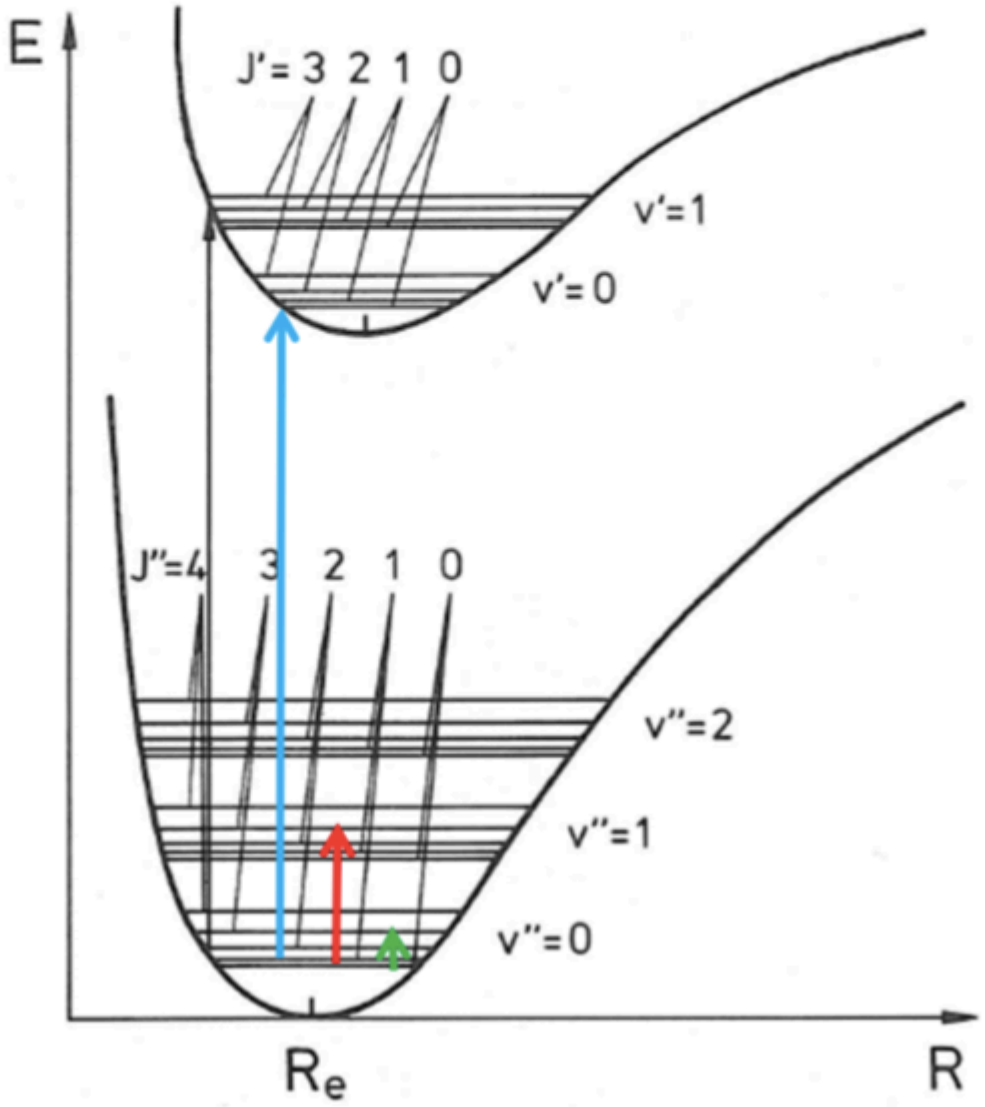
ΔE = 0.1-1 eV

Infrared

Rotational Transitions:

ΔE = 0.01-0.1 eV

(sub)-Millimeter



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Symmetry in molecular physics

no spherical symmetry $\Rightarrow$ $\vec{L}_i^2, \vec{L}^2$ not good q. numbers

but L_z, L_z along symmetry is!

Examples by symmetry:

(i) homonuclear diatomic molecules

$\circ\!-\!\circ$ $D_{\infty h}$

classes: e, C_∞, σ_v, i, ...

(see table next page)

What is "analogue" of n (principal q. number) in atoms

2 limits: (a) n of separated atoms

(b) n of combined atoms

Example: H_2^+

4_b: g.s.: (a) "σ_g 1s" (b) "1s σ_g"

4_{ab}: (a) σ_u 1s (b) 2p σ_u

1s: rel. to each nucleus

2p σ_u: combined orb. has symmetry of p, second electronic level

cf. "correlation diagram"

Example: H_2: g.s. spins opposed

$\Lambda = 0 \Rightarrow (\sigma_g 1s)^2$, $1s\sigma_g \rightarrow {}^1\Sigma_g^+$

$S = 0$

$\oplus + \oplus$

$\rightarrow$ symm. under i, σ_v

"configuration" "term"

1

$D_{\infty h}$

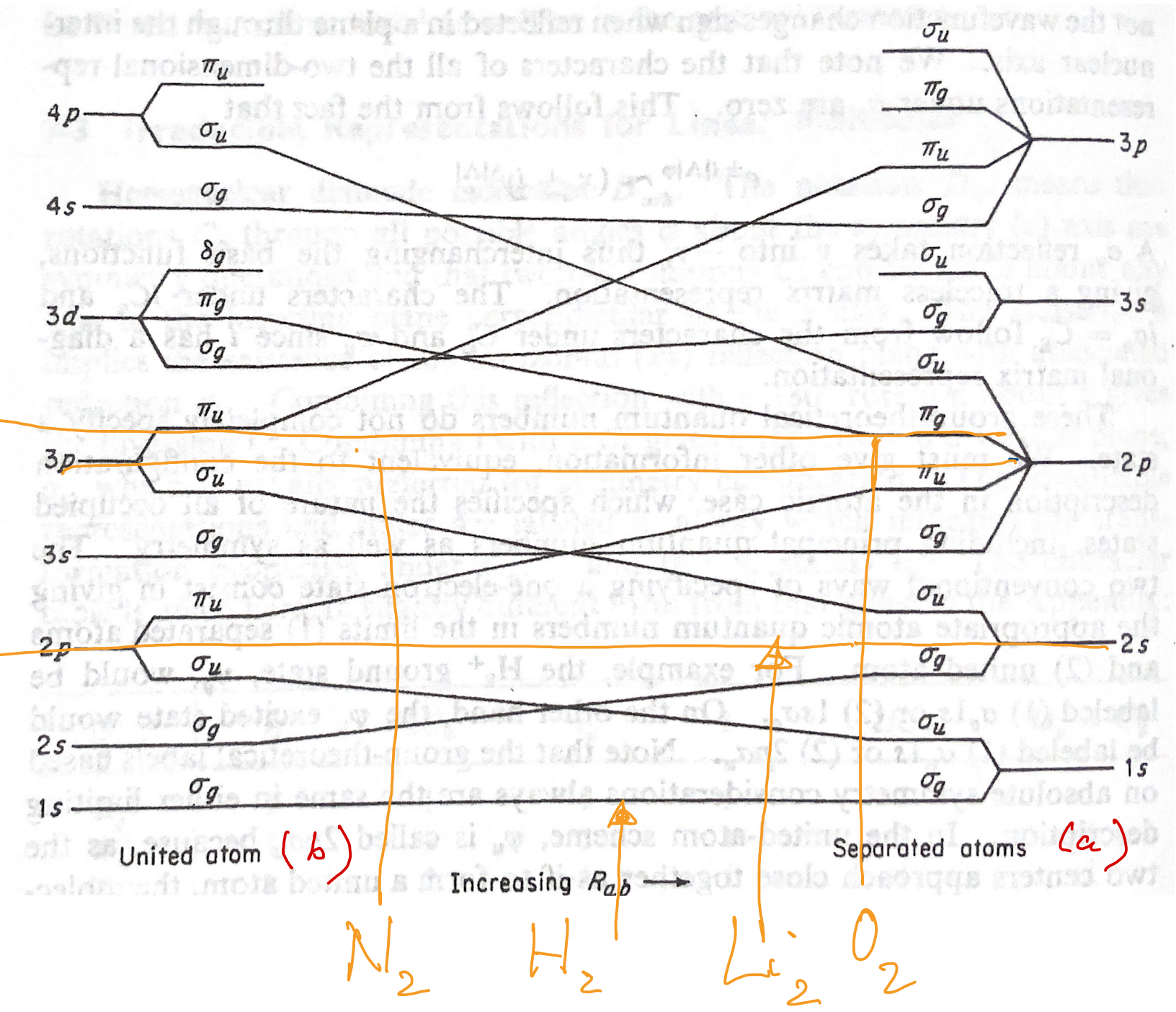
$D_{\infty h}$	E	$2C_\varphi$	σ_v	i	$2iC_\varphi$	$i\sigma_v = C_2'$
A_{1g} Σ_g^+	1	1	1	1	1	1
A_{1u} Σ_u^+	1	1	1	−1	−1	−1
A_{2g} Σ_g^-	1	1	−1	1	1	−1
A_{2u} Σ_u^-	1	1	−1	−1	−1	1
E_{1g} Π_g	2	$2\cos\varphi$	0	2	$2\cos\varphi$	0
E_{1u} Π_u	2	$2\cos\varphi$	0	−2	$-2\cos\varphi$	0
E_{2g} Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
E_{2u} Δ_u	2	$2\cos 2\varphi$	0	−2	$-2\cos 2\varphi$	0
$E_{\dots}$ ...	...	...	...	...	...	...

i "g" : gerade (even) } under i
"u" : ungerade (odd) }
"+" : even under σ_v
"-" odd

Ml $\Lambda > 1$ ah 2D (Σ)

(2)

"correlation diagram"



N_2 H_2 Li_2 O_2

Example O_2 (16 e$^-$) g.S.

look only @ partially: 2e$^-$ in π_g $(\pi_g 2p)^2$

Hund's rule: $S=1$: $\psi_S^{spin} \cdot \psi_A^{space}$

opposing angular momenta: $\Lambda = 0$

$\Rightarrow {}^3\Sigma_g^-$

"3" $\hat{=} 2S+1$

"g": stems from π_g

$-$: changes sign under σ_v

(ii) <u>diatomic heteronuclear:</u> $C_{\infty v}$ $(= C_\infty \times \sigma_v)$

$\bullet\!\!-\!\!\circ$

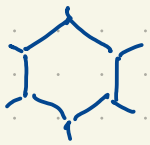
no parity / inversion symmetry ($\Rightarrow$ no "g" / "u")

$\Rightarrow {}^{1D}\Sigma^{\pm}$, ${}^{2D}\Pi$, ${}^{2D}\Delta$, ...

(table ③)

(iii) <u>Connection of mol. spatial symm. + basis function</u>

(Hückel theory)

Example:  C_6H_6

Benzene

Symmetry: D_{6h} (direct product group of D_6 with σ_h $\Rightarrow$ look only @ D_6)

<u>Task</u>: Build six orthonormal orbitals (belonging to rep's of D_6) from six C 2s-orbitals

3

$C_{\infty v}$	E	$2C_{\varphi}$	σ_v
Σ^+	1	1	1
Σ^-	1	1	−1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos 2\varphi$	0
...	...	...	...

(using projection method for basis functions)

Starting point: all symmetry operations can be described by the permutation rep. ("Γ_S") – ($\chi(E) = 6$, $\chi(g \neq E) = 0$: change / permute location of atoms)

reduce $\Gamma_S = \underset{1D}{\Gamma_1} + \underset{1D}{\Gamma_3} + \underset{2D}{\Gamma_5} + \underset{2D}{\Gamma_6}$ } see table ④

Use these 3 projection operators in the space of superpositions of the six C 2s orbitals (call them a, b, c, d, e, f):

$$\psi(\Gamma_1) = \frac{a + b + c + d + e + f}{\sqrt{6(1+2S)}}$$

S: overlap integral for neighboring atoms

$$\psi_2(\Gamma_3) = \frac{a - b + c - d + e - f}{\sqrt{6(1-2S)}}$$

$$\psi_3(\Gamma_5) = \frac{a - b + d - e}{\sqrt{4(1-S)}}$$

$$\psi_4(\Gamma_5) = \frac{a + b - 2c + d + e - 2f}{\sqrt{16(1-S)}}$$

$$\psi_5(\Gamma_6) = \frac{a + b - d - e}{\sqrt{4(1-S)}}$$

$$\psi_6(\Gamma_6) = \frac{a - b - 2c - d + e + 2f}{\sqrt{16(1-S)}}$$

These are already six basis fcts ⇒ done ☺

Energies: $Q \equiv \langle a|H|a\rangle = \langle b|H|b\rangle = \ldots$

$\beta \equiv \langle a|H|b\rangle = \langle b|H|c\rangle = \ldots$

(overlap of non-neighboring neglected)

$$E(\Gamma_1) = \langle \psi_1|H|\psi_1\rangle = \frac{Q + 2\beta}{1+2S}$$

$$E(\Gamma_3) = \frac{Q - 2\beta}{1-2S}$$

$$E(\Gamma_5) = \frac{Q - \beta}{1-S}$$

$$E(\Gamma_6) = \frac{Q + \beta}{1+S}$$

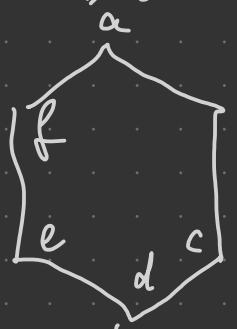
see Fig. ⑤

Projection:

$$P^{(i)} = \sum_R P^{(i)}_{\mu\mu} = \frac{l_i}{h} \sum_R \chi^{(i)}(R) \cdot P_R$$

Example: $\Gamma^{(3)}$: $l^{(3)} = 1$, $h = 6$, use single-e^- 1s orbital μ as start

$$\Rightarrow P^{(3)} = \frac{1}{12}\left(1\cdot a - C_2 a + C_3 a + C_3^2 a - C_6 a - C_6^5 a + C_2' a + \right.$$



$$\left. + C_2' a + C_2' a - C_2'' a - C_2'' a - C_2'' a\right) =$$

$$= \frac{1}{12}\left(a - d + c + e - b - f + a + c + e - d - f - b\right) =$$

$$= \frac{1}{6}\left(a - b + c - d + e - f\right)$$

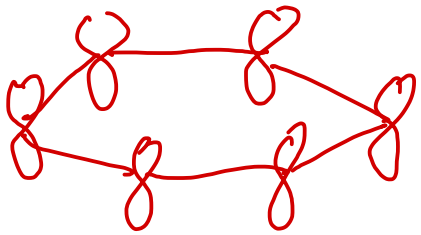
Overlap: $S = \int a^* b \, dV$

neighbouring

4

D_6	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
$\Gamma_1(A_1)$	1	1	1	1	1	1
$\Gamma_2(A_2)$	1	1	1	1	−1	−1
$\Gamma_3(B_1)$	1	−1	1	−1	1	−1
$\Gamma_4(B_2)$	1	−1	1	−1	−1	1
$\Gamma_5(E_2)$	2	2	−1	−1	0	0
$\Gamma_6(E_1)$	2	−2	−1	1	0	0
Γ_S	6	0	0	0	2	0

Γ_S : permutation representation of 6 points



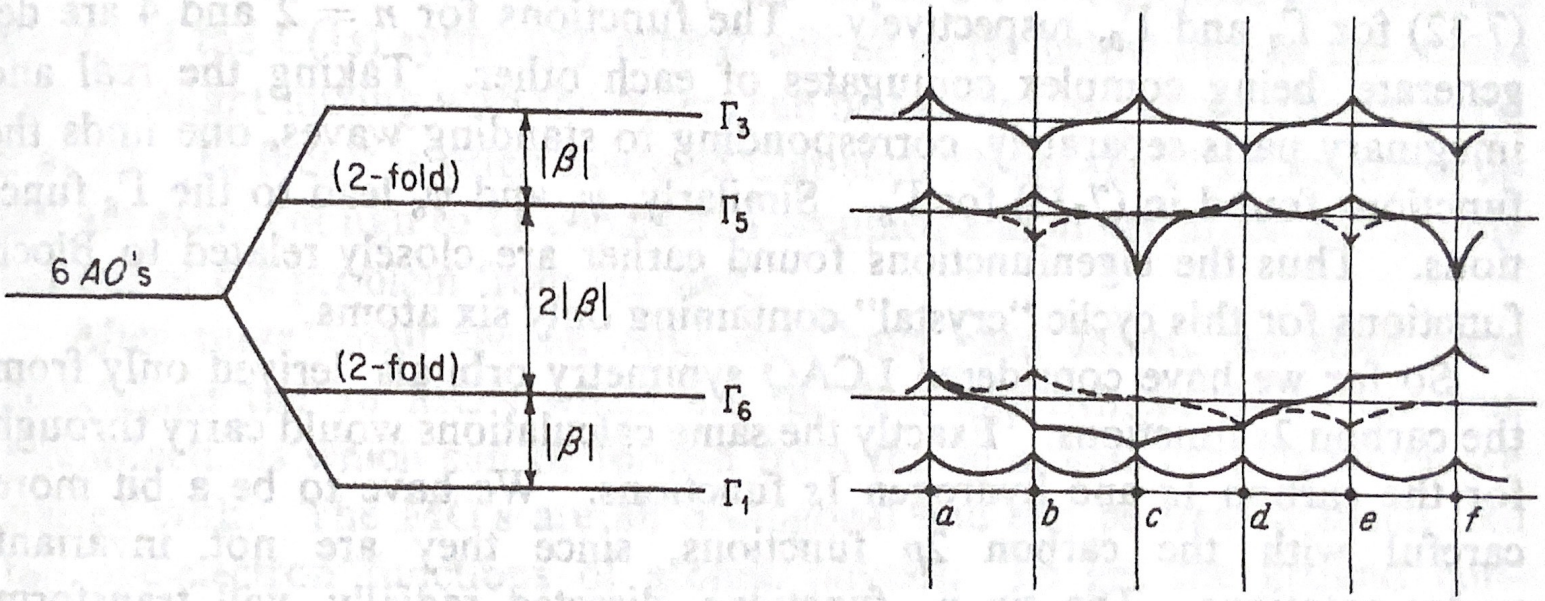
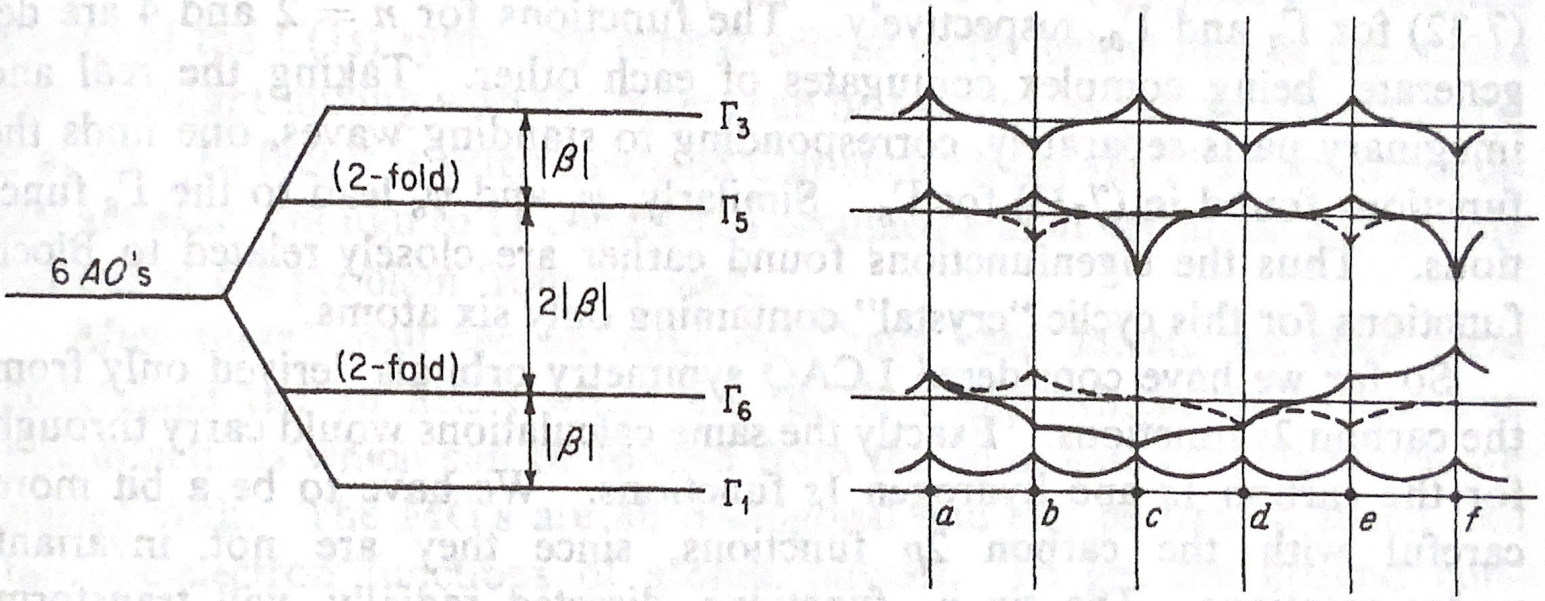


Fig. 7-7. *Molecular-orbital energy-level scheme for benzene, with overlap integrals neglected. The form of the MO is also shown schematically in each case, a 1s atomic orbital being used for simplicity. In case of degeneracy, the two functions are distinguished by solid and dashed curves.*



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