Molecular Orbital Theory – LCAO Based Approach

1. Decompose into AOs
2. Combine AOs of appropriate Symmetry w/ one another to build MOs
3. Fill MOs w/ available e^-

Lets Consider H_2: $H_A - H_B$ formed from constructive interference of $1s_A + 1s_B$

Above wavefunctions for AOs

$$\psi = C_a\psi_a + C_b\psi_b$$

Molecular wavefunction

Coefficients (Adjustable) – Related to AOs size, energy, electronegativity, type

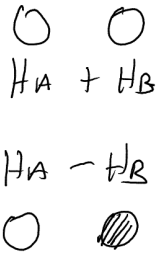
2 Hydrogen atoms ($H_A + H_B$) $1s_A$ $1s_B$

Overlap of $\psi(1s_A) + \psi(1s_B)$ constructive or destructive

N = Normalization Constant

$\int \psi\psi^* d\tau \approx 1$

Build 2 linear combinations



Constructive $\psi(\sigma) = N[C_A\psi(1s_A) + C_B\psi(1s_B)]$ $H_A + H_B$

Destructive $\psi(\sigma^*) = N[C_A\psi(1s_A) - C_B\psi(1s_B)]$ $H_A - H_B$

$N = \left(\sqrt{\Sigma C_i^2}\right)^{-1}$

$\sqrt{\Sigma(1^2)} \rightarrow \sqrt{1^2 + 1^2}$

$C_A = C_B$

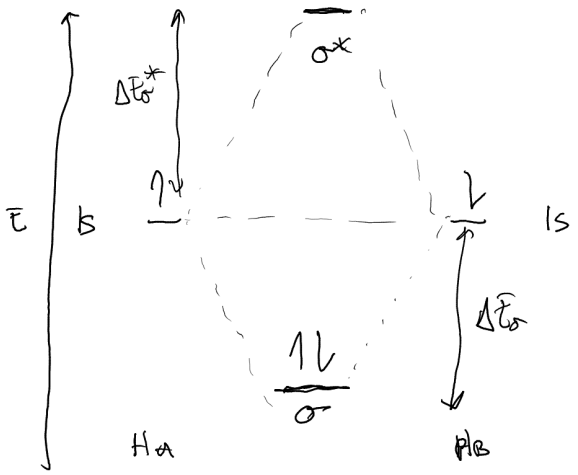
$\hookrightarrow N = 1/\sqrt{2}$

3 Conditions are essential for orbital overlap + bonding

1. Symmetry of the constituent AOs must be appropriate to allow overlap
2. Energies of AOs must be similar
3. Proximity → distance between AOs must be close enough to allow for bonding

$\sigma = 1/\sqrt{2}\,\psi(1s_A) + 1/\sqrt{2}\,\psi(1s_B)$ $1s_A$ $1s_B$

$\sigma^* = 1/\sqrt{2}\,\psi(1s_A) - 1/\sqrt{2}\,\psi(1s_B)$



$1/\sqrt{2}(\psi(1s_A) - \psi(1s_B))$

* Denote Antibonding orbitals

P + d Basis sets ⇒ Nonbonding orbitals

$|\Delta E_\pi| > |\Delta E_\sigma|$

$1/\sqrt{2}(\psi(1s_A) + \psi(1s_B))$ $1s_A$ $1s_B$ =

P + d orbitals

P – P σ – interaction (g)

P – P π – interactions (u)

P – P σ* interaction (u)

P – P π* interaction (g)

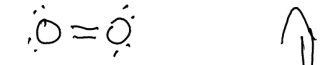
P – S σ – interaction

P – P nonbonding

P – S σ* – interaction

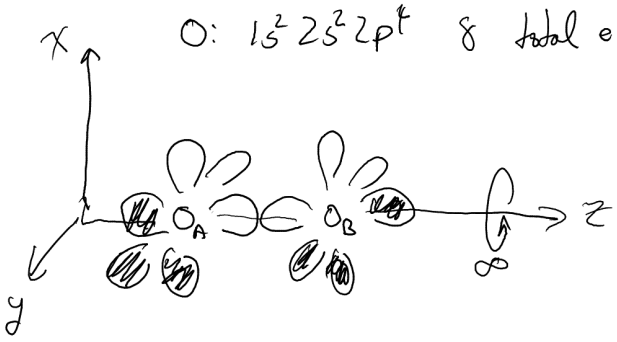
P – S nonbonding

O_2 Doon (& Non-bonding e^-)

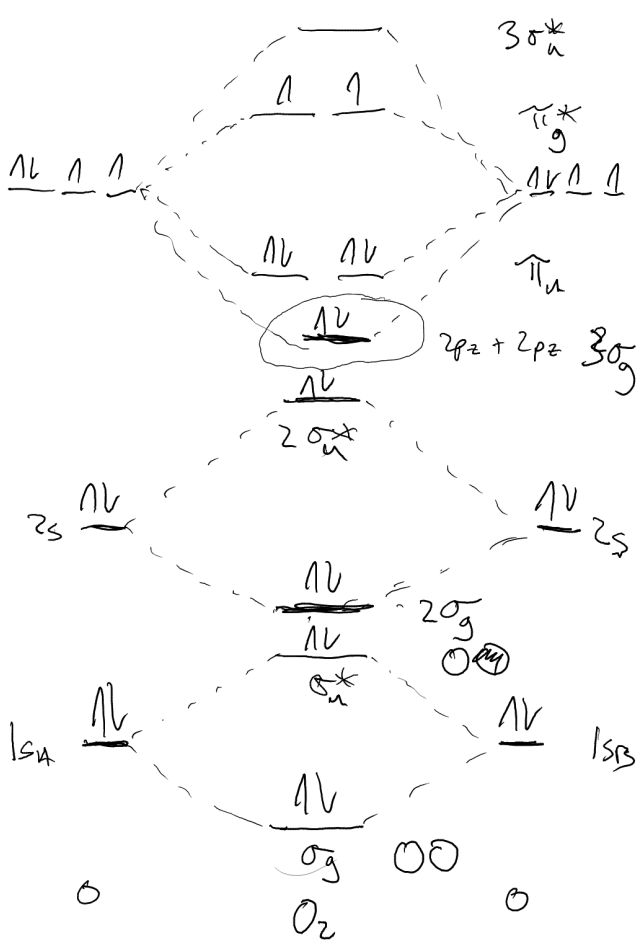


2 Bonds + 4 lone pairs
$1\sigma + 1\pi$

O: $1s^2 2s^2 2p^4$ & total e^-



1s, 2s, 2pz, 2py, 2px



Bond Order

$\frac{1}{2}$ (# Bonding e^- − # Antibonding e^-)

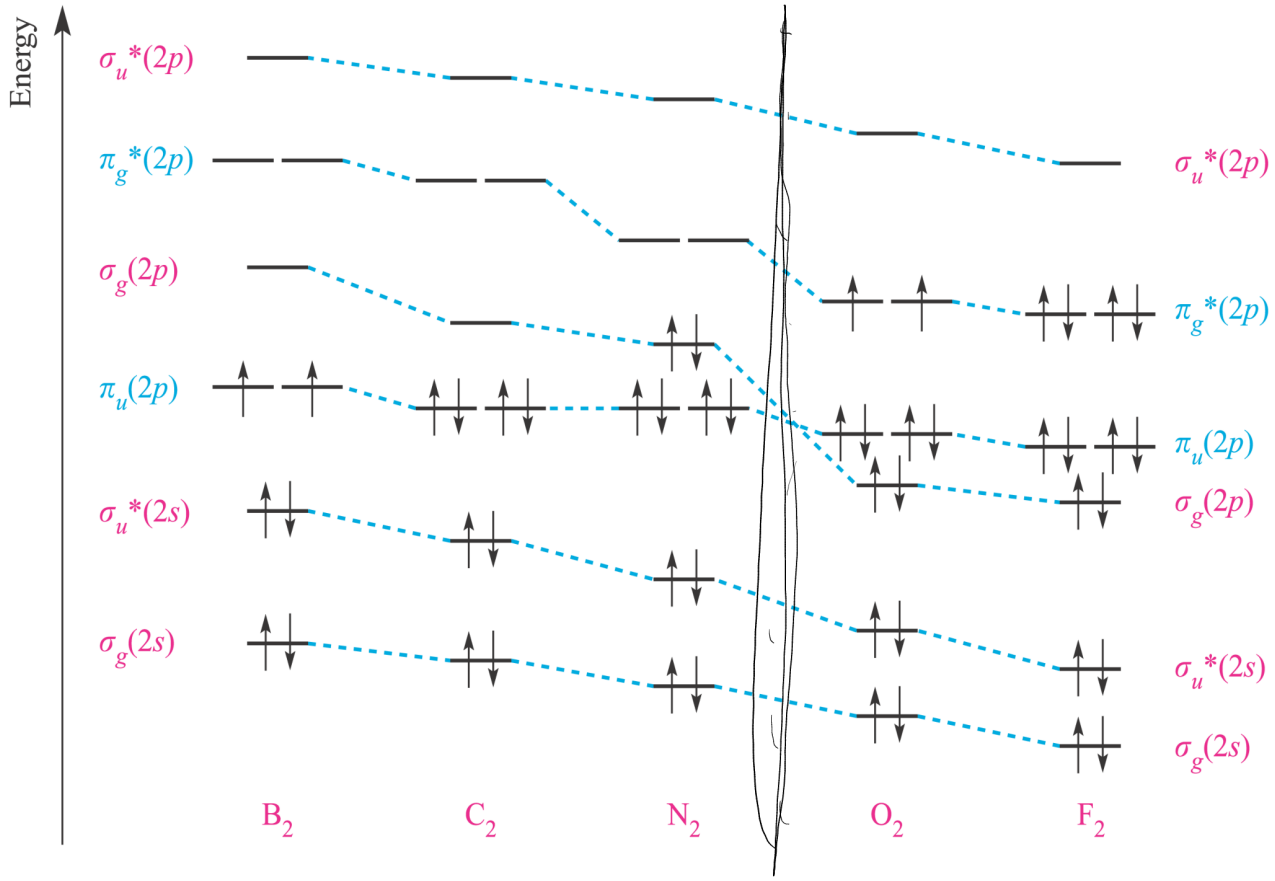
$\frac{1}{2}(10 - 6) = 4/2 = 2$

Oxygen should be a ground state triplet

$1\sigma_g^2\, 1\sigma_u^{*2}\, 2\sigma_g^2\, 2\sigma_u^{*2}\, 3\sigma_g^2\, 1\pi_u^4\, 1\pi_g^{*2}$

Mixing ⇒ Related to hybridization

↳ orbitals of the same symmetry interact. Here energies diverge


Energy
$\sigma_u^*(2p)$
$\pi_g^*(2p)$
$\sigma_g(2p)$
$\pi_u(2p)$
$\sigma_u^*(2s)$
$\sigma_g(2s)$
$\sigma_u^*(2p)$
$\pi_g^*(2p)$
$\pi_u(2p)$
$\sigma_g(2p)$
$\sigma_u^*(2s)$
$\sigma_g(2s)$
B_2
C_2
N_2
O_2
F_2

Photoelectron Spectroscopy (UV- X-Ray)

UPS ⇒ ejecting valence e^-

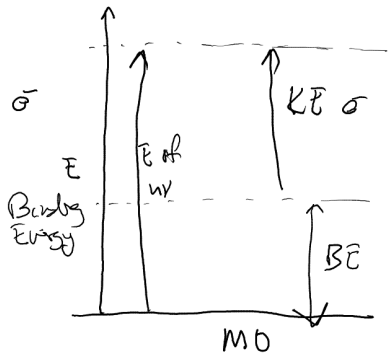
XPS ⇒ ejects core e^-

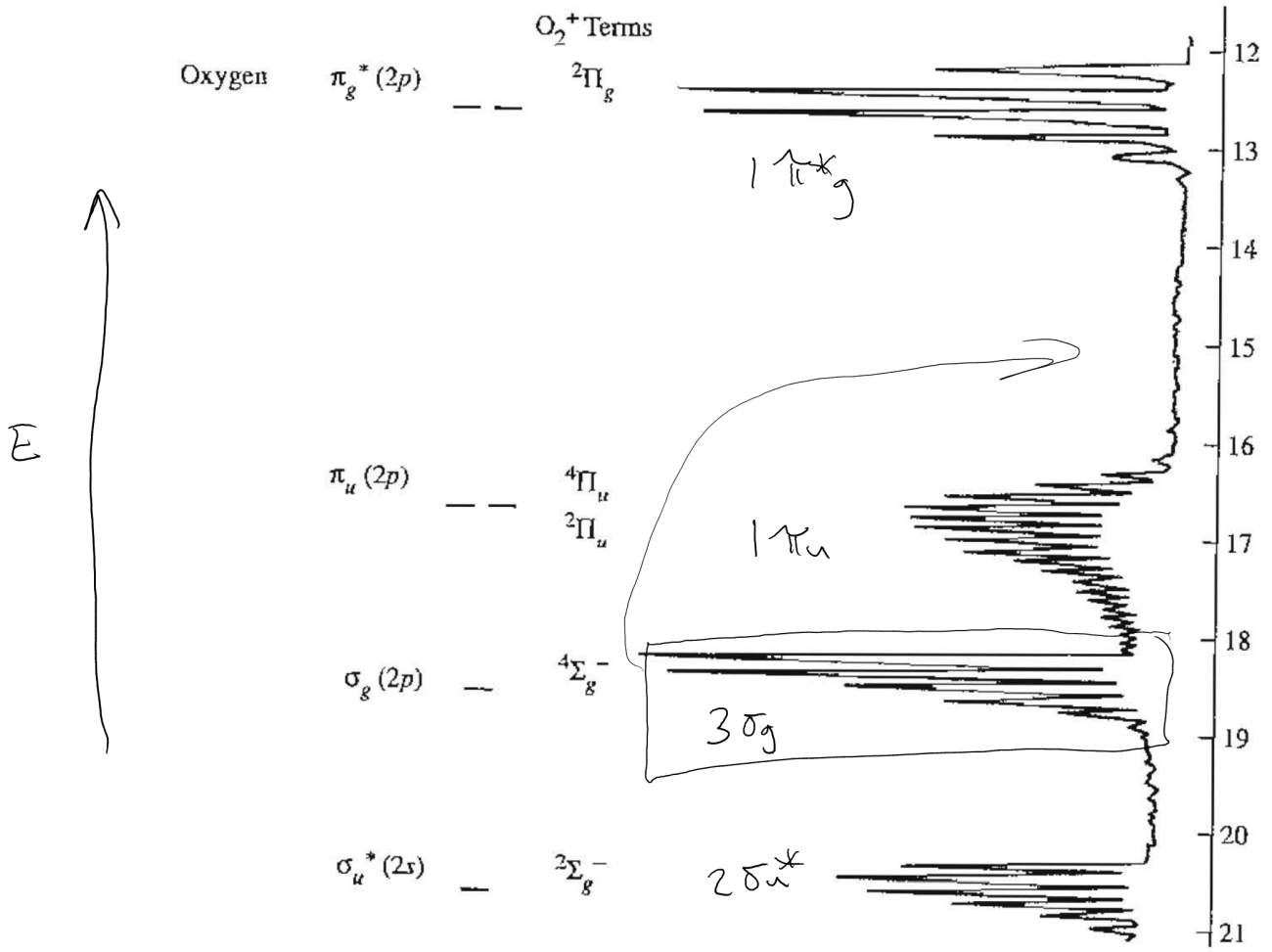
Sample + $h\nu$ ⟶ Sample^{+} + e^-

Ionization energy

$IE \simeq h\nu - KE$ of e^-

↑ we know this





Fine splittings correspond to vibrational states

2 degenerate π-Bonds

From: *Physical Chemistry – A Molecular Approach* by D. A. McQuarrie and J. D Simon

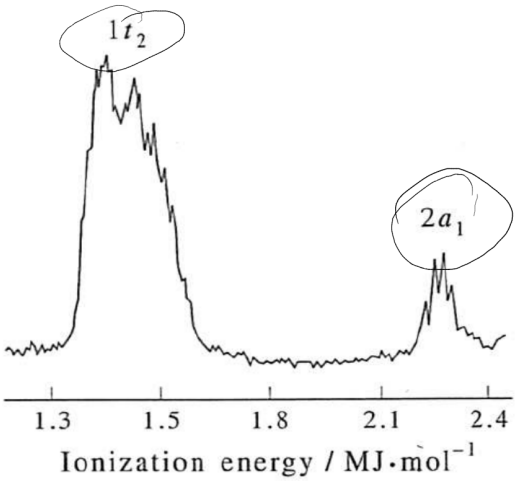


FIGURE 10.16
The photoelectron spectrum of methane. The two bands observed in the photoelectron spectrum reflect the ionization of electrons from the $1t_2$ and $2a_1$ molecular orbitals. The energy difference between these two bands corresponds to the energy difference between the $1t_2$ and $2a_1$ molecular orbitals (see Figure 10.15). The bands are broad because ionization occurs to many different vibrational levels of the molecules.

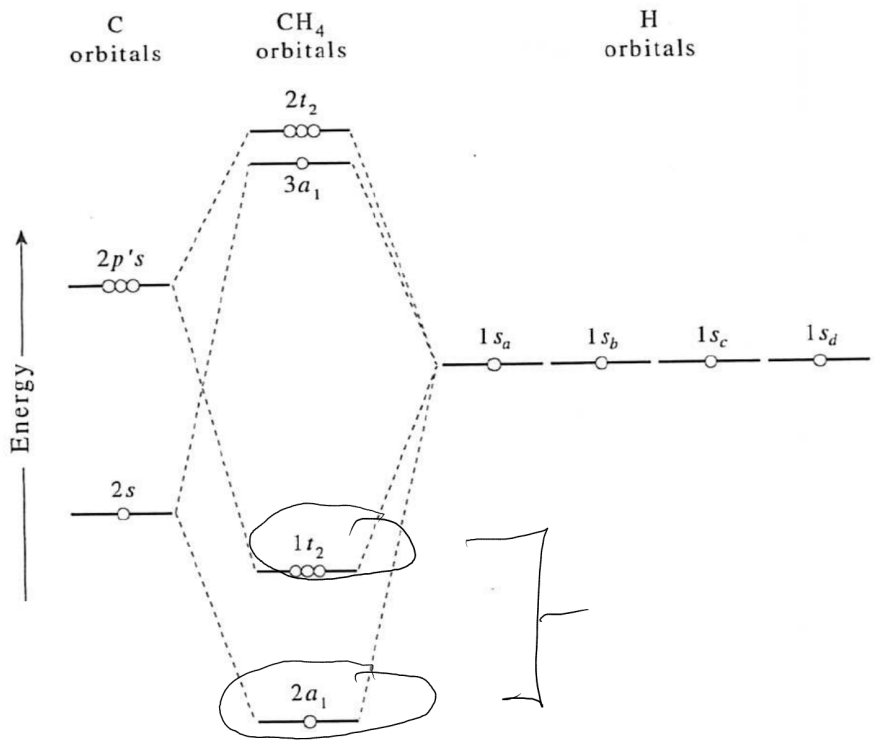


FIGURE 10.15
A molecular-orbital energy-level diagram for the valence electrons in CH_4.