BONDING:

WHY DOES A BOND FORM?

H_2:

TWO ELECTRONS

TWO PROTONS

$$H\psi = E\psi$$

$$H = \underbrace{\sum_i T_i}_{\text{SUM OVER ALL ELECTRONS AND NUCLEI. } \Rightarrow \text{ KINETIC ENERGY CONTRIBUTION.}} + \underbrace{\sum_{i,j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}}_{\text{ELECTROSTATIC POTENTIAL ENERGY TERM, V, BETWEEN ALL CHARGED PARTICLES}}$$

$$H = \sum_i \frac{-\hbar^2}{2m_i}\nabla_i^2 + \left[\underbrace{\frac{-e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}}}_{\Leftarrow\Rightarrow \text{ ATTRACTIVE}} + \underbrace{\frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}}}_{\Rightarrow\Leftarrow \text{ REPULSIVE}}\right]$$

UNFORTUNATELY WE CANNOT SOLVE THIS PROBLEM ANALYTICALLY.

∴ APPROXIMATE THE ANSWER.

VALENCE BOND APPROACH:

$$\Psi = 1s_A(1)\ 1s_B(2)$$

ELECTRON 1 IN 1S ORBITAL OF PROTON A

ELECTRON 2 IN 1S ORBITAL OF PROTON B

TOTAL WAVE FUNCTION IS THE PRODUCT.

BUT

$$\Psi = 1s_A(2)\ 1s_B(1)$$

EXACTLY EQUIVALENT

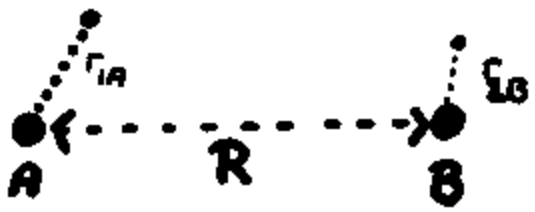
ELECTRON 2 IN 1S ORBITAL OF PROTON A

ELECTRON 1 IN 1S ORBITAL OF PROTON B

$$\Psi = N\left(1s_A(1)1s_B(2) \oplus 1s_A(2)1s_B(1)\right)$$

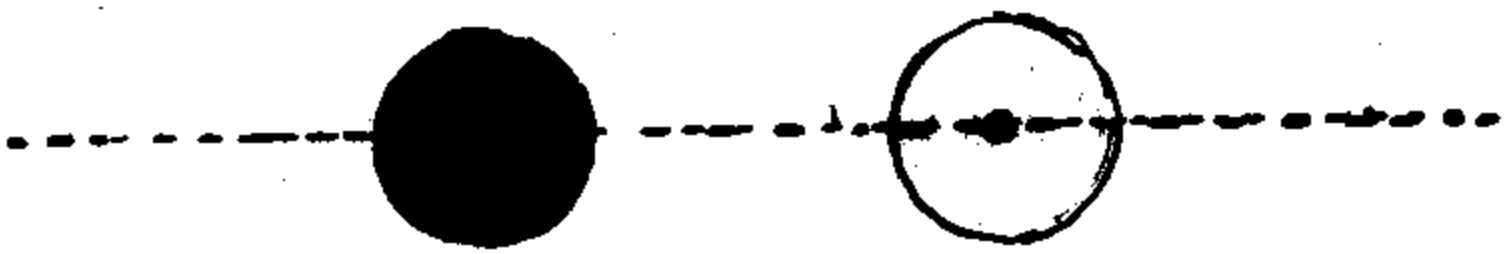
STABLE GROUND STATE.

N: NORMALIZATION

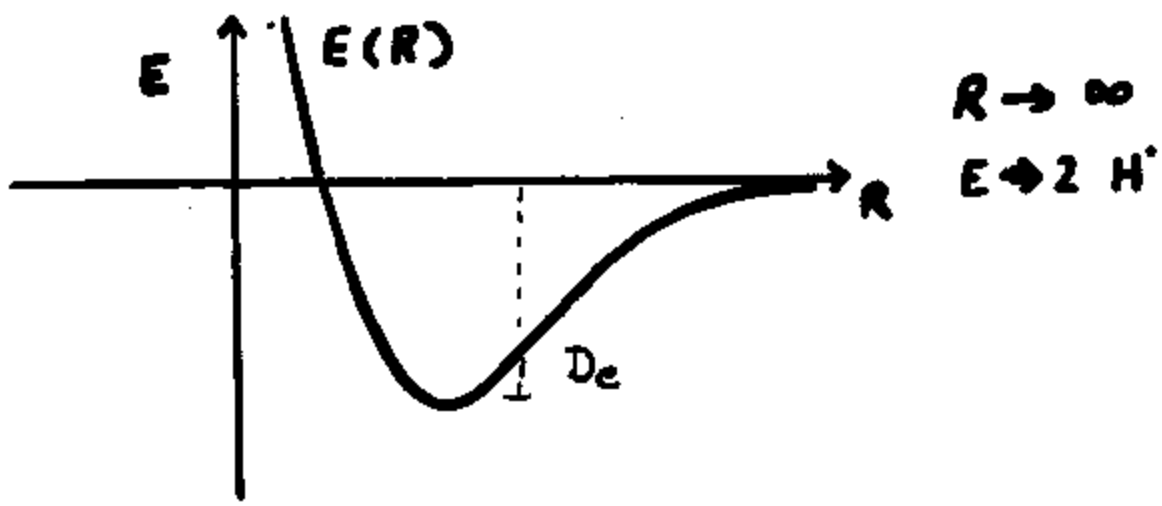


$$\psi = \frac{1}{\sqrt{2(1+S^2)}} \left(1s_A(1)\,1s_B(2) + 1s_A(2)\,1s_B(1) \right)$$

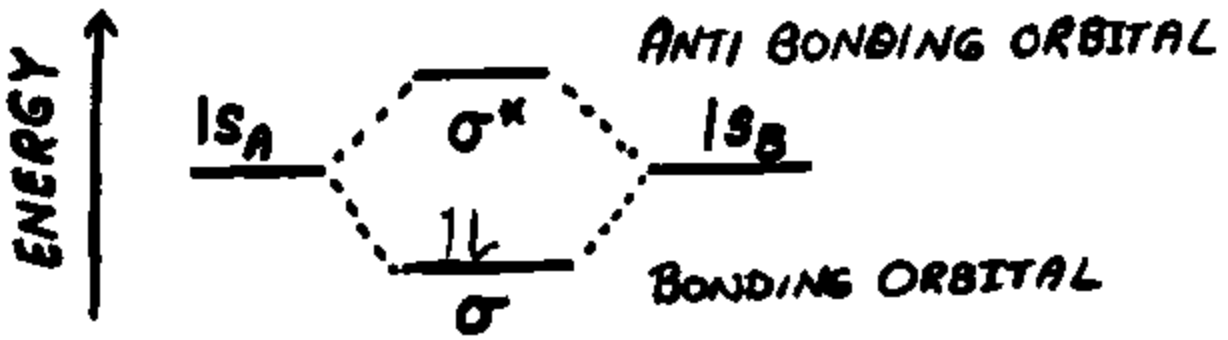
OVERLAP $\int dr\; 1s_A\, 1s_B$



$H\psi = \underline{E(R)}\psi$ ENERGY DEPENDS ON S & R



MOLECULAR ORBITAL APPROACH:

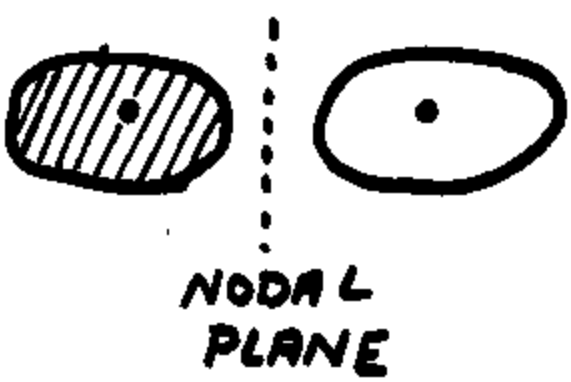


$\sigma = N(1s_A + 1s_B)$

$\sigma^* = N(1s_A - 1s_B)$

LINEAR COMBINATION OF ATOMIC ORBITALS
LCAO

BONDING ORBITAL



ANTI-BONDING ORBITAL

MO THEORY CONTINUED

$\psi = \sigma(1)\,\sigma(2)$ PUT BOTH ELECTRONS IN THE BONDING ORBITAL

$$\psi = N\underbrace{\left(1s_A(1) + 1s_B(1)\right)}_{\text{ELECTRON 1 IN BONDING ORBITAL}}\underbrace{\left(1s_A(2) + 1s_B(2)\right)}_{\text{ELECTRON 2 IN BONDING ORBITAL}}$$

$$\psi = N\Big(\underbrace{1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)}_{\text{SAME AS VB WAVE FUNCTION}} + \underbrace{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)}_{\text{IONIC CONTRIBUTION}}\Big)$$

BOTTOM LINE:

VB THEORY UNDERESTIMATES IONIC TERM

MO THEORY OVERESTIMATES IONIC TERM

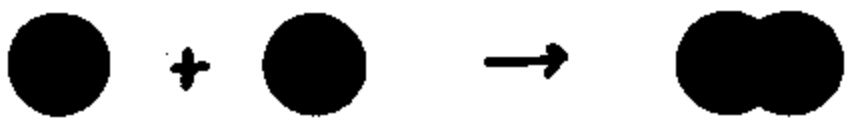
* BOTH APPROACHES ARE USEFUL FOR QUALITATIVE INTUITIVE UNDERSTANDING *

SECOND PERIOD DIATOMIC MOLECULES

- VALENCE BOND APPROACH

* V.B. EMPHASIZES THE BOND *

BUILDING BONDS FROM SINGLY OCCUPIED ATOMIC ORBITALS



$Li^{\bullet}$ 2s + $Li^{\bullet}$ 2s → Li-Li σ-BOND

CYLINDRICAL SYMMETRY

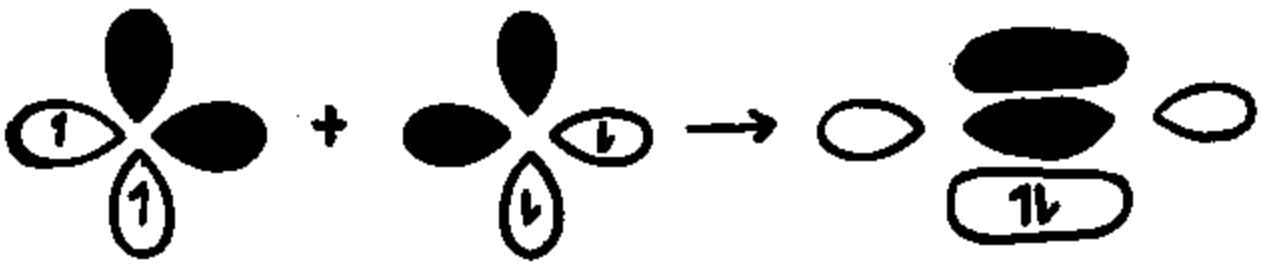
$Be^{\bullet}$ + $Be^{\bullet}$ ↛ NO BOND

$F_2 \Rightarrow F: 1s^2 2s^2 2p^5$

$F^{\bullet}$ $2p_z$ + $F^{\bullet}$ $2p_z$ → σ-BOND

SECOND PERIOD DIATOMICS CONTINUED

$O_2 \Rightarrow O: 1s^2 2s^2 2p^4 \Rightarrow 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$



$2p_y$ $2p_y$ σ - BOND

$2p_z$ $2p_z$ π - BOND

O O "DOUBLE BOND"

$N_2 \Rightarrow N: 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

σ-BOND π_y-BOND

π_x-BOND

"TRIPLE BOND"

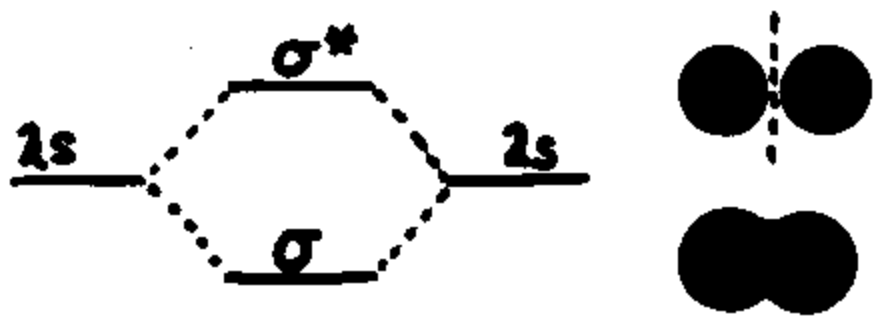
SECOND PERIOD DIATOMIC MOLECULES

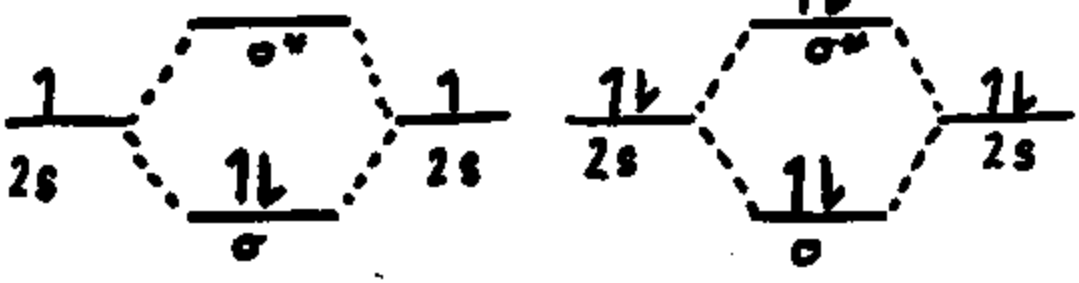
- MOLECULAR ORBITAL APPROACH

*** M.O. EMPHASIZES THE MOLECULE ***

BOILDING MOLECULAR ORBITALS AND ADDING ELECTRONS

Li:





Li_2

BOND ORDER = 1

Be_2

BOND ORDER = 0

NO NET BOND

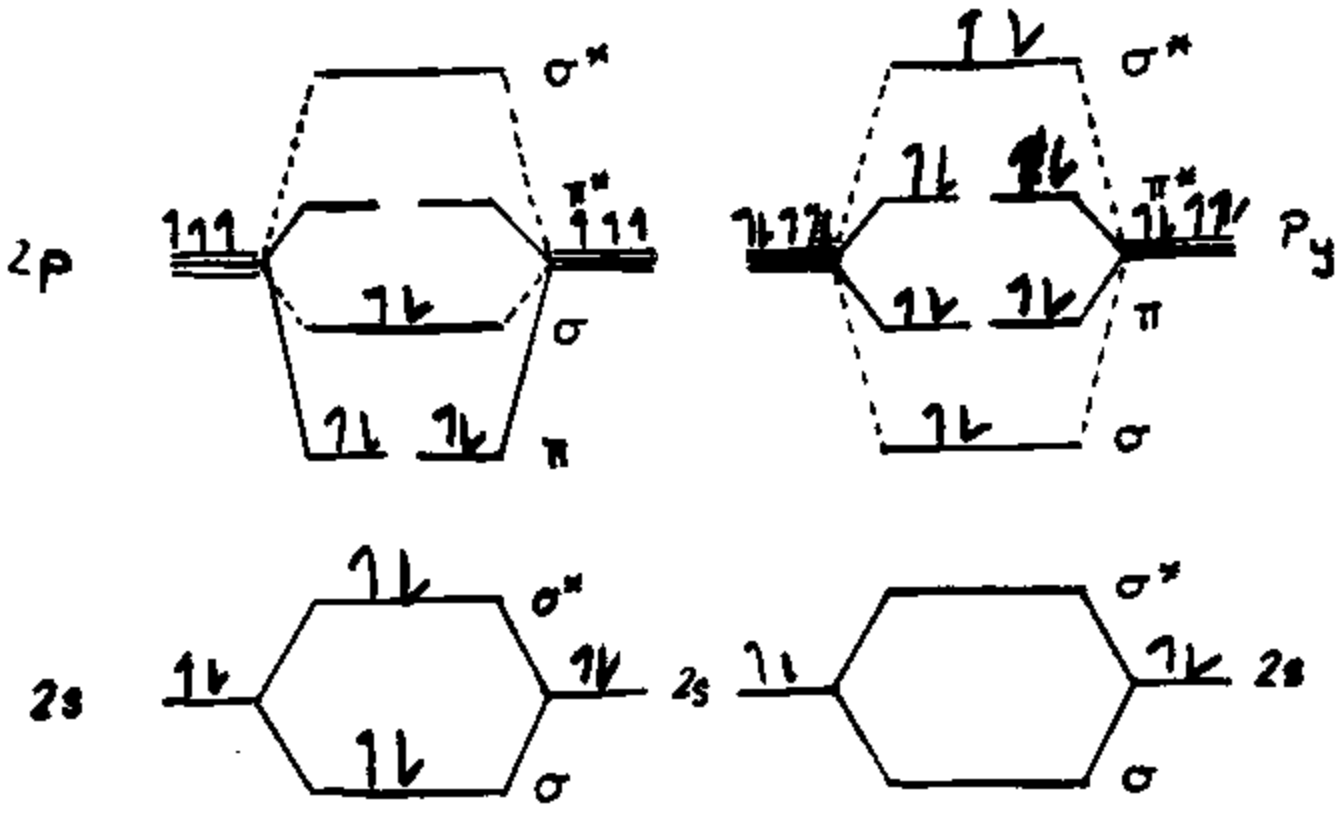
$\frac{1}{2}$ { # bonding e⁻'s − # antibonding electrons }

SECOND PERIOD DIATOMICS CONTINUED

B	$2s^2\,2p^1$
C	$2s^2\,2p^2$
N	$2s^2\,2p^3$
O	$2s^2\,2p^4$
F	$2s^2\,2p^5$
Ne	$2s^2\,2p^6$

BASIS SET OF $n=2$ ATOMIC ORBITALS FOR ALL OF THESE:

$$\phi = (a2s + b2p_x + c2p_y + d2p_z)$$



B, C, N

O, F, Ne