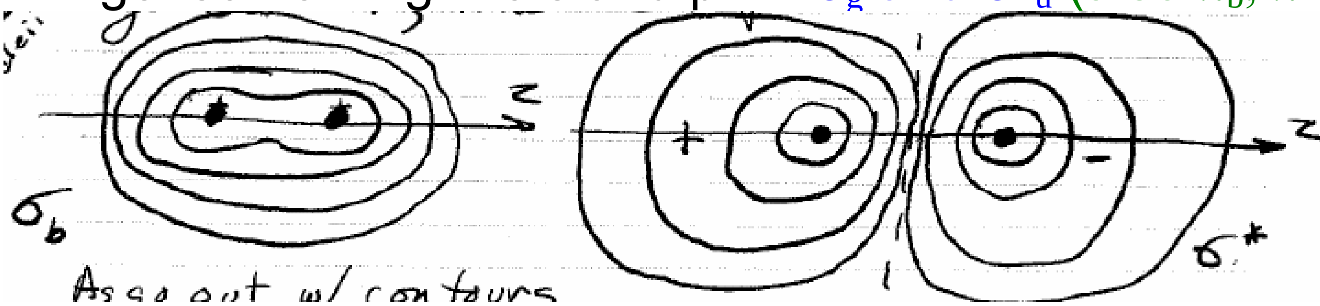
Bonding – Diatomics-09 update (Ch. 16 Engel, Ch.10-Atkins)

For multi electron atoms we built up from H-atom
For molecules take same approach
 Can solve problem for H_2^+
 (1 – e^- in non-central potential – 2 nuclei)
 get something like s and p -- σ_g and σ^*_u (also π_b, π^*)

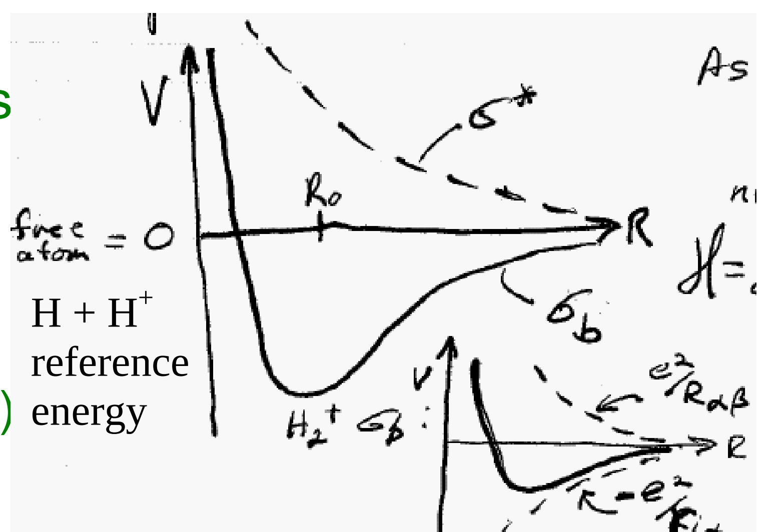


bonding -- σ
As go out with contours
gets more spherical

anti-bonding—σ*
Alternate – has nodal plane
 recall—nodes → energy

Both have <u>cylindrical symmetry</u> about z-axis –
 this is equivalent to $m_\ell = 0 \rightarrow \sigma$-state
 e^- attracted to both nuclei, far away looks like atom
σ - bonding → $\psi^*\psi$ increase between nuclei (e^- density)
σ* - anti-bond → $\psi^*\psi$ decrease between nuclei

<u>Reference state</u> – 2 atoms
(H_2^+ – atom and proton)
As atoms approach,
 their electrons
– attract other nucleus
– repel each other (not H_2^+)
-- always the nuclei repel



Balance n-n repuls, e-n attr.

Full Hamiltonian (need to know!!):

$$\boldsymbol{H} = -\sum_{\alpha=1}^{2} \hbar^2/2M_\alpha \nabla_\alpha^2 - \sum_{i=1}^{N} \hbar^2/2m_e \nabla_i^2 - \sum_i\sum_\alpha Z_\alpha e^2/r_{i\alpha} + \sum_{ij} e^2/r_{ij} + \sum_{\alpha,\beta} Z_\alpha Z_\beta e^2/R_{\alpha\beta}$$

n-KE e-KE n-e attr. e-e repul. n-n repul

Bonding balance: e – n attract with n – n repel

MO : For one electron, can drop sums on *i* and 4[th] term,
solution is a 1 e- wave fct. – i.e. orbital with 2 nuclei

Plot as fct of R (n-n separation) go from united to
separate atoms, or He→2H, with H_2 between

1-elctron plot:

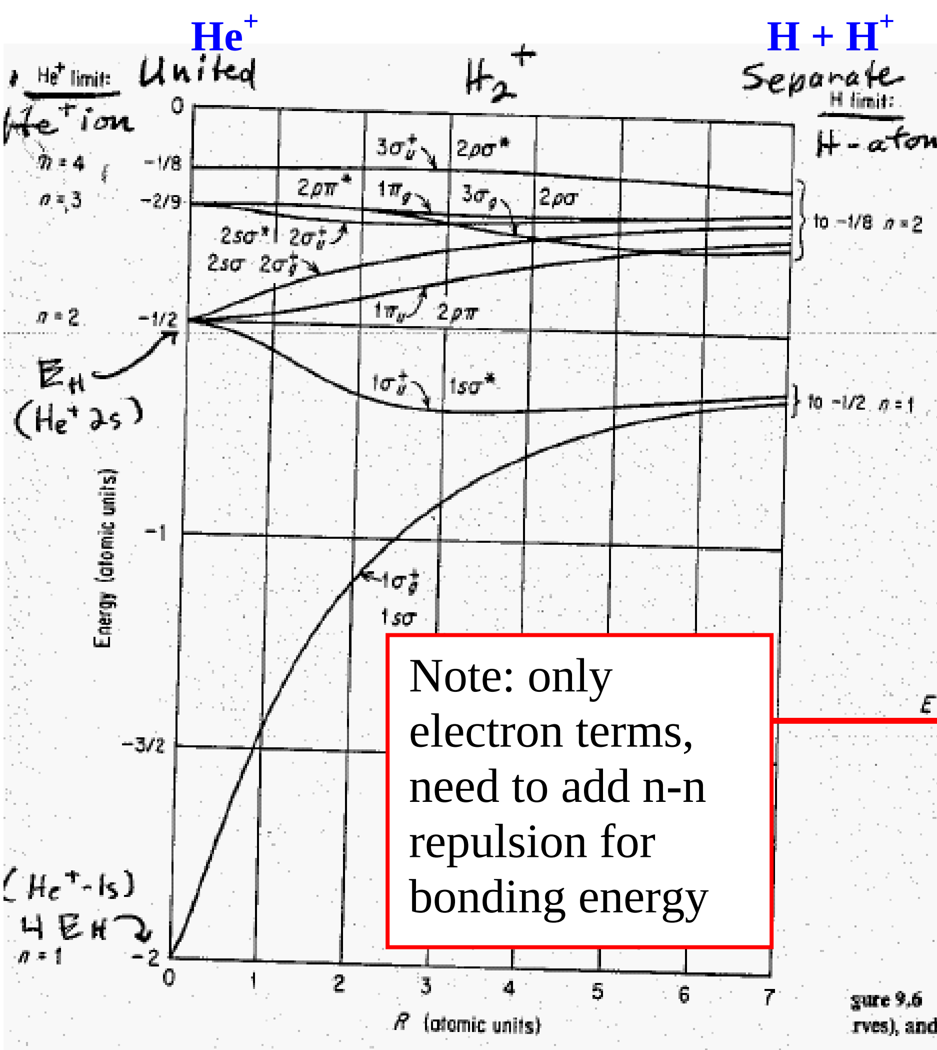
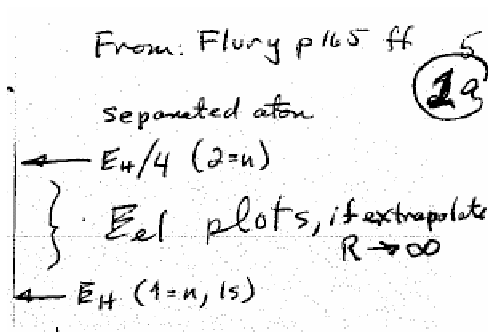
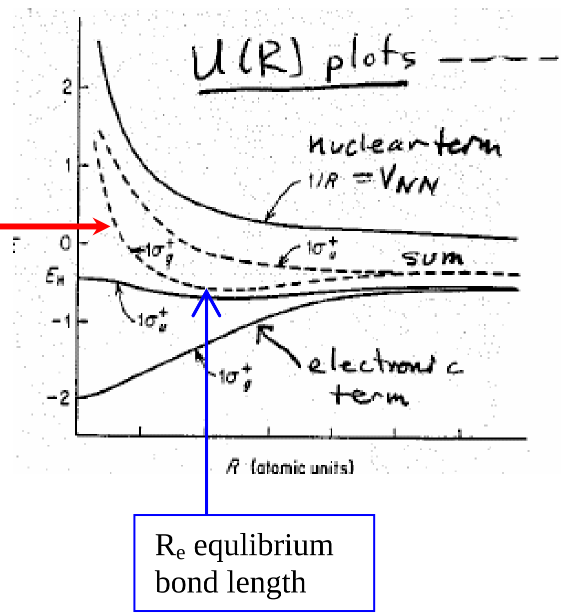


Figure 9.2 Several lowest electronic energy levels of H_2^+ as a function of internuclear distance. (Adapted from J. C. Slater, *Quantum Theory of Molecules and Solids*, Volume 1, McGraw-Hill Book Company, New York, 1963. By permission.)





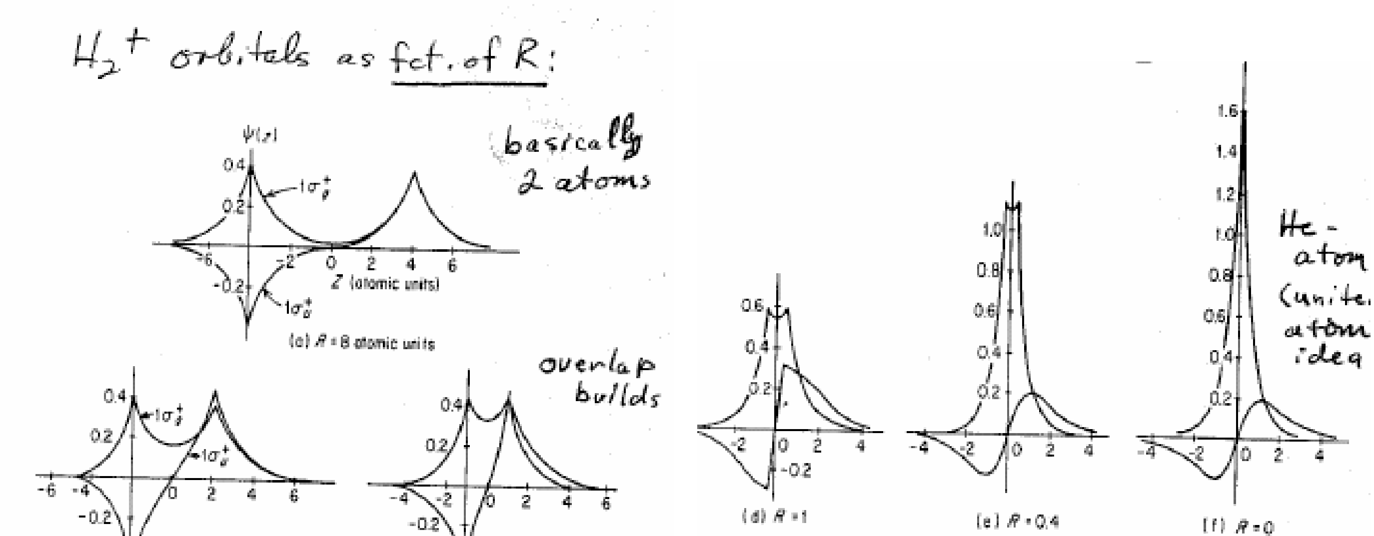


Figure 9.3 Normalized wave functions for the $1\sigma_g^+$ and $1\sigma_u^+$ states of H_2^+, along the internuclear axis, for various internuclear separations. (Adapted from Slater. By permission—see Fig. 9.1.)

LCAO-MO Linear Combination of Atomic Orbitals

MO theory-- Simpler more transparent method

AO's – form a basis—

i.e. describe all the functions possible for e^-

For molecule need MO –

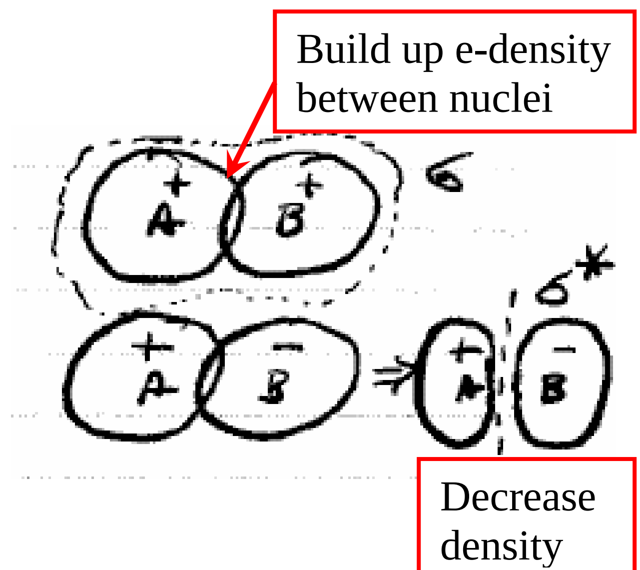
orbital ($1e^-$) delocalize over 1 ion several nuclei

Form linear combination AO's $\Rightarrow$ LCAO–MO

So if lowest E AO's for H_2^+ are 1s

Then $\sigma_b \sim (1s_A) + (1s_B)$

$\sigma^* \sim (1s_A) - (1s_B)$



Continue on this track:
more electrons – just put 2 in each MO (opposite spin)

$H_2^+ \rightarrow (\sigma_b)^1$ — weak bond (1/2)

$H_2 \rightarrow (\sigma_b)^2$ — strongly bound (1)

( ) = bond order

B.O. = (#e-bond - #e-antibond)/2

He_2^+ → $(\sigma_b)^2 (\sigma^*)^1$ — weaker (1/2)

He_2 → $(\sigma_b)^2 (\sigma^*)^2$ — no bond (0)

$[(\text{number})_b - (\text{number})^*]/2$

Can continue to 2nd row in same manner

$(2s_A) + (2s_B)$ → σ_b discriminate by $2\sigma_b$, $2\sigma^*$

$(2s_A) - (2s_B)$ → σ^* or $\sigma_b(2s)$, $\sigma^*(2s)$

$(2p_z)_A + (2p_z)_B$ → σ_b molec. axis → z

$(2p_z)_A - (2p_z)_B$ → σ^* symm. about z → σ

$(2p_{x,y})_A + (2p_{x,y})_B$ → π_b 2 possibilities x or y

$(2p_{x,y})_A - (2p_{x,y})_B$ → π^* degenerate, weaker overlap

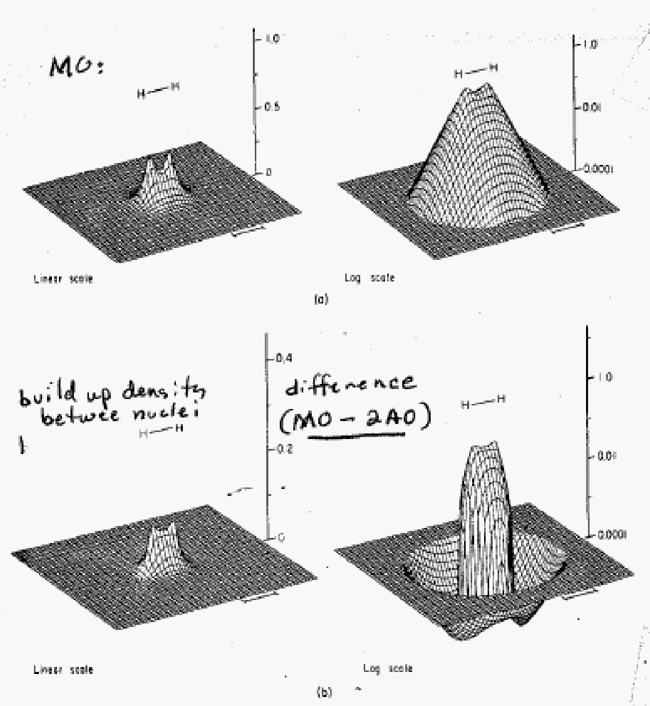


FIGURE 22.8 (a) Electron density in H_2 in the plane of the internuclear axis. The electron density is drawn on a vertical axis, in one case on a linear scale, and in the other case on a logarithmic scale. (b) Electron density difference plot. Here the electron density of the two H atoms has been subtracted from the electron density in H_2. These plots therefore show how the electron density changes as the result of formation of the H—H bond. [Reprinted with permission of Macmillan Publishing Co., Inc., from *Orbital and Electron Density Diagrams* by A. Streitwieser and P. H. Owens. © 1973 Macmillan Publishing Co., Inc.]

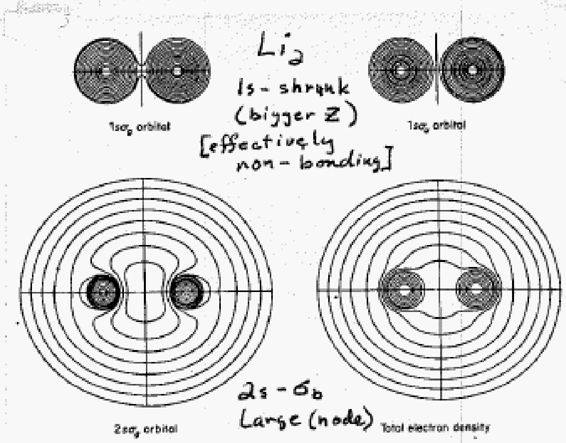
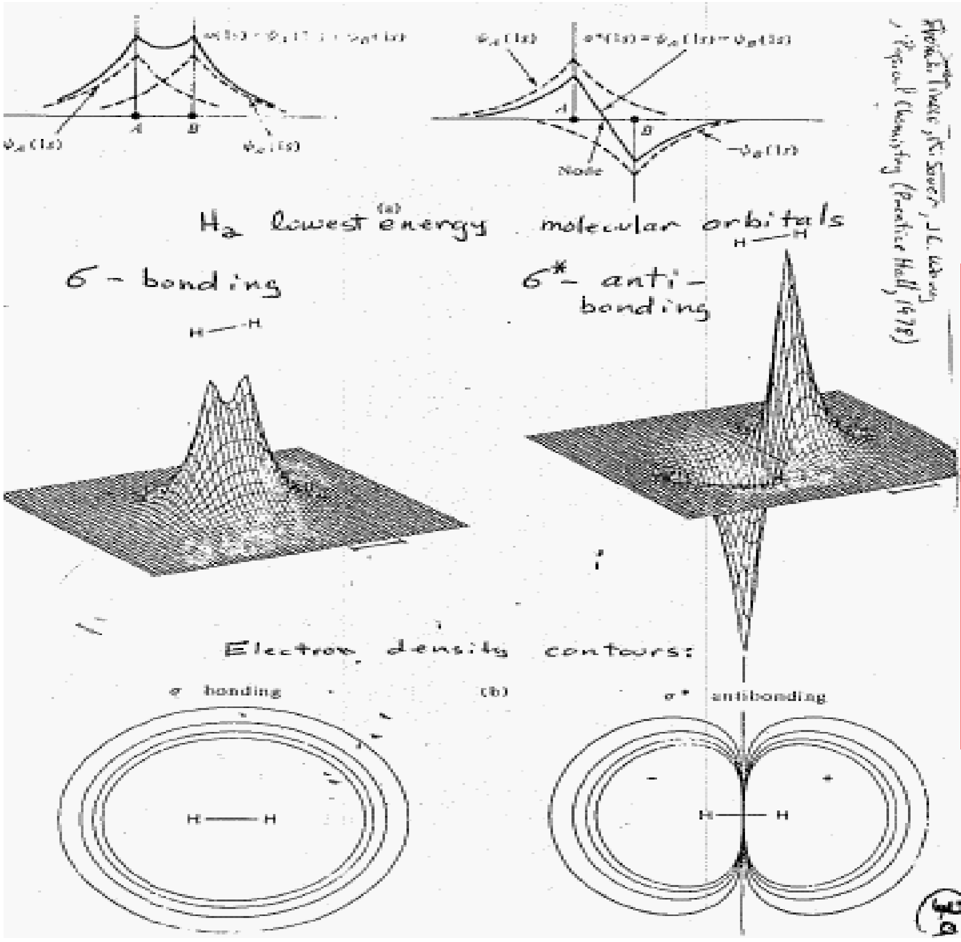
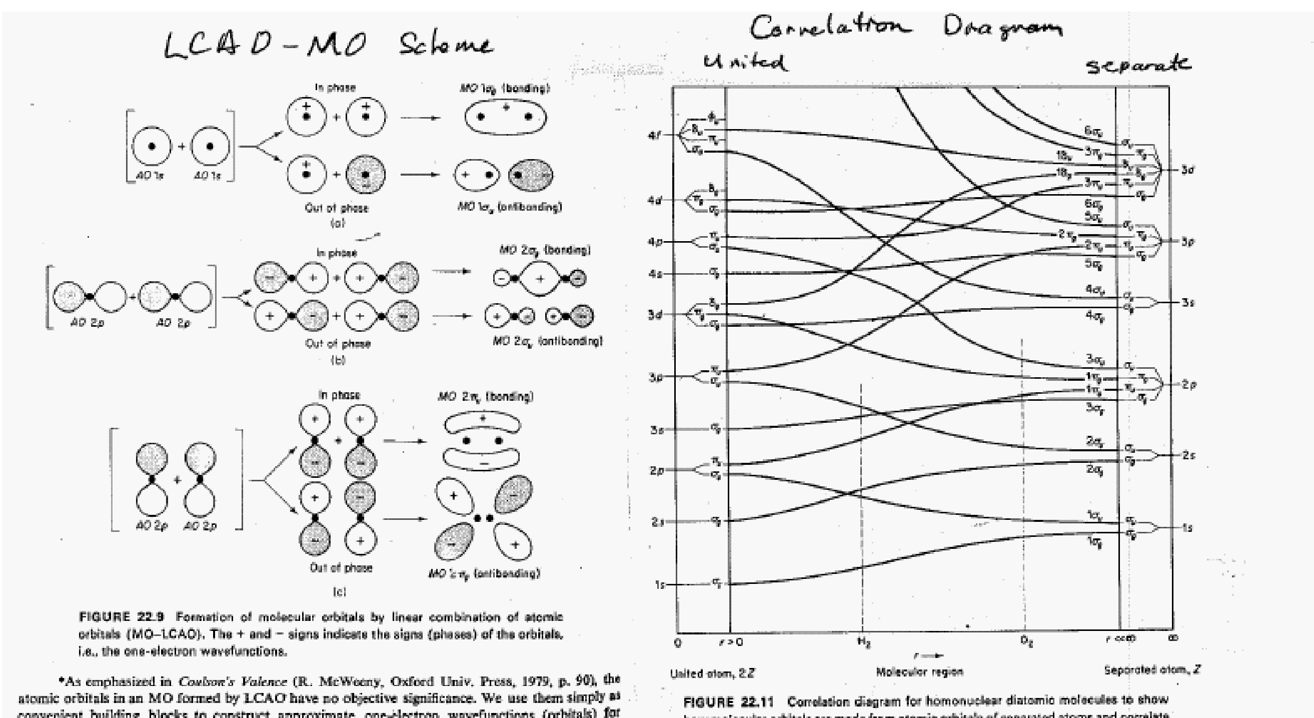


FIGURE 22.10 Contour maps of electron density in individual orbitals and of total electron density for Li_2 molecule. Adjacent contour lines differ by a factor of 2. The outermost contour is an electron density of 4.12×10^{-10} electrons pm^{-3}. The internuclear distance is the experimental value 267.2 pm. [A. C. Wahl, *Science* 151, 961 (1966). Copyright 1966 by the American Association for the Advancement of Science.]

Combination of 1s orbitals
– H_2 1s based σ, σ*
Compare to 2s -- Li_2 σ, σ*



Representations of bonding and anti-bonding, σ and σ*, molecular orbitals
Learn: recognize, interpret shapes



LCAO-MO Scheme diagram -- Correlation Diagram

Put this together again – approx. ***H*** as sum of 1-elect h_i

$$H_{el} = \sum_{i=1}^{N} \left(-\hbar^2/2m\ \nabla_i^2 + V(r_i)\right)$$ V(r_i) – elect. potential

part depend on r_i only [H–F typical method]

Summed ***H*** ⇒ product w/f: $\psi = \prod_{i=1}^{N} \phi_i (r_i)$

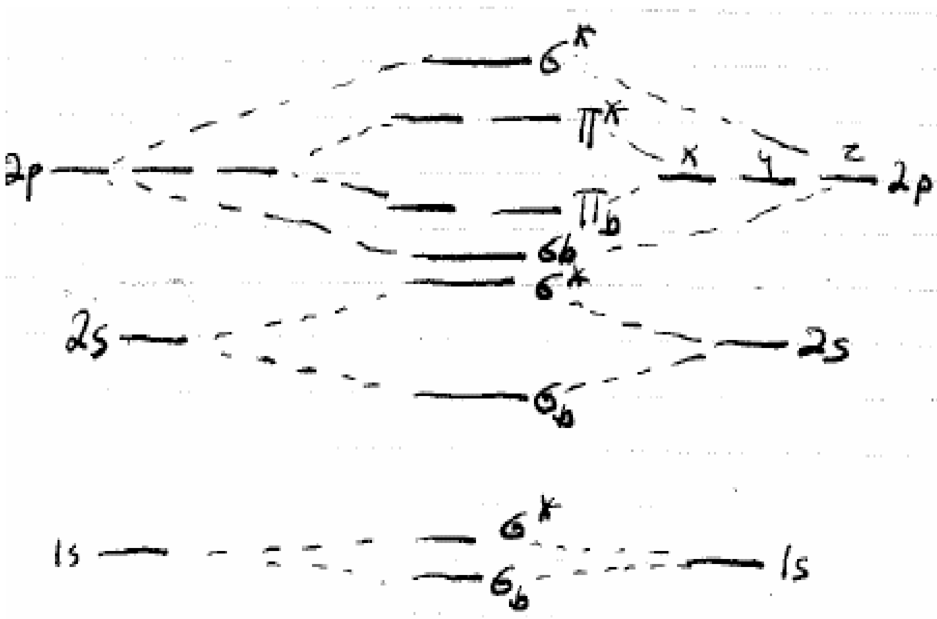
ϕ_i → MO = $1e^-$ w/f

Energy is sum of occupied orbital: $E = \sum_{i=1}^{N} \varepsilon_i$

Typical picture homo nuclear diatomic

Aufbau—fill in order of increase energy, 2 elect. each MO

1s interaction strong H_2, weak for 2nd row



This ordering changes as cross periodic table

interaction of 2s σ and 2p σ causes a shift

→ see handout (next page)

early in series – AO--less s-p separation, MO--$\pi_b < \sigma_b$

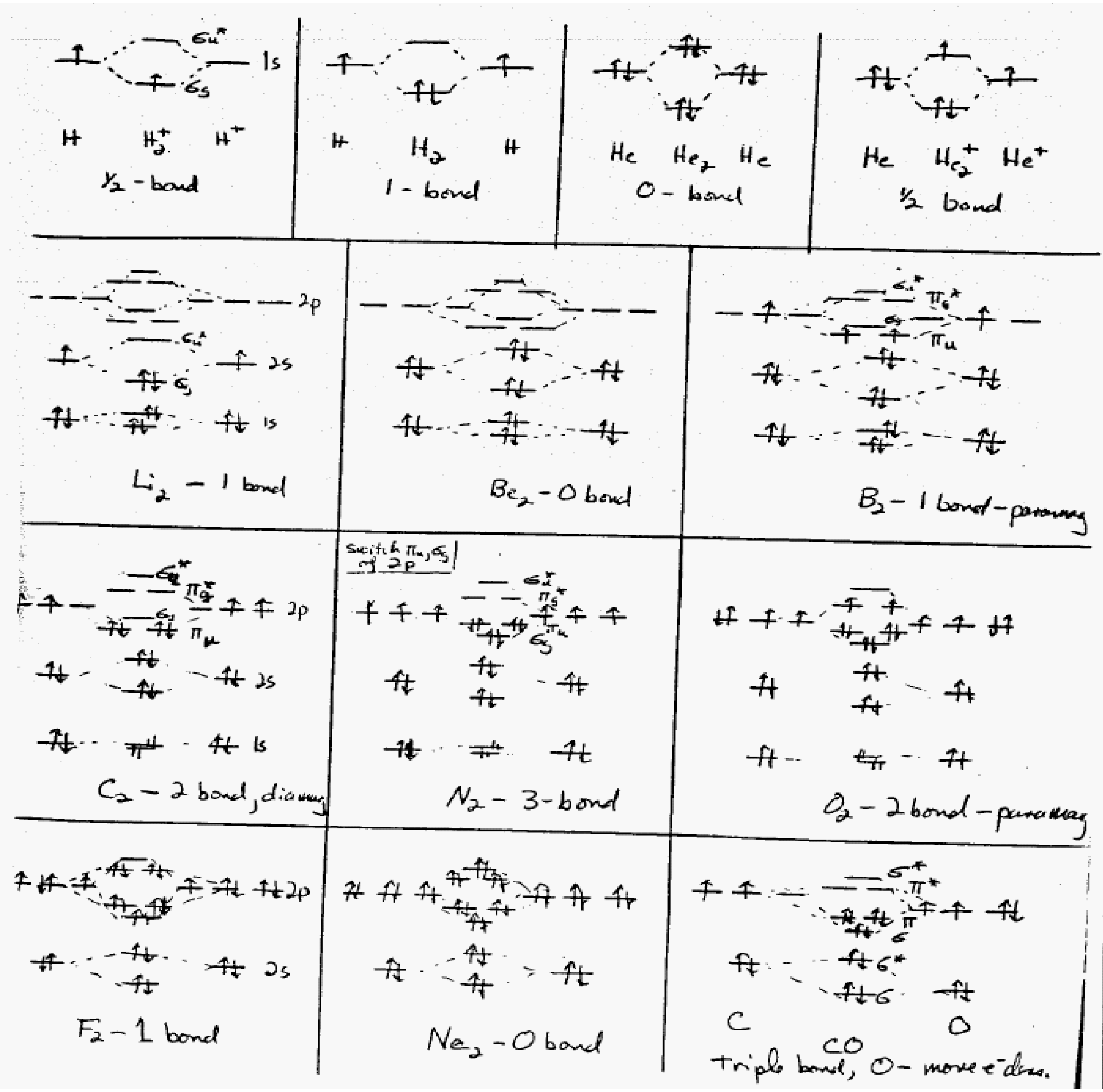
later – more shielding– AO - s-p separate, MO - $\sigma_b < \pi_b$

Express as <u>configuration</u> → $2e^-$ each σ, 4e each π:

$(1\sigma_b)^2\ (1\sigma^*)^2\ (2\sigma_b)^2\ (2\sigma^*)^2\ (3\sigma_b^{(2p)})^2\ (1\pi_b)^4\ (1\pi^*)^4\ (3\sigma^*)^2$

3rd row series – same idea – these will be shrunk

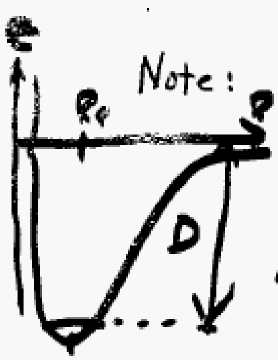
MO diagrams (LCAO approach)



Homo nuclear Diatomics

Ex... p48 (2e)

Molecule	De (eV)	Re (Å)	"bond order"	Configuration (lowest energy)	Ground Term	Comment
H_2^+	2.78	1.06	½	$(\sigma_g^{1s})^1$	$^2\Sigma_g^+$	
H_2	4.76	0.74	1	$(\sigma_g^{1s})^2$	$^1\Sigma_g^+$	
He_2	—	—	0	$(\sigma_g^{1s})^2(\sigma_u^{1s})^2$	$^1\Sigma_g$	ground state unbound
Li_2	1.1	2.67	1	$(\sigma_g^{1s})^2(\sigma_u^{1s})^2(\sigma_g^{2s})^2$	$^1\Sigma_g$	weak
Be_2	—	—	0	$[KK]^4(\sigma_g^{2s})^2(\sigma_u^{2s})^2$	$^1\Sigma_g$	ground state unbound
B_2	2.9	1.6	1	or $\{KK(\sigma_g^{2s})^2(\sigma_u^{2s})^2(\pi_u^{2p})^2$ / $KK(\sigma_g^{2s})^2(\sigma_u^{2s})^2(\pi_u^{2p})^2(\sigma_g^{2p})^1$	$^3\Sigma_g$	2 possible confi paramagnetic ground stat
C_2	6.4	1.24	2	$KK(\sigma_g)^2(\sigma_u^*)^2(\pi_u)^4$	$^1\Sigma_g$	
N_2	10.	1.12	3	$KK\sigma_g^2\sigma_u^{*2}\pi_u^4(\sigma_g^{2p})^2$	$^1\Sigma_g$	strongest bon
O_2	5.2	1.21	2	$KK\sigma_g^2\sigma_u^{*2}\pi_u^4\sigma_g^2(\pi_g^*)^2$	$^3\Sigma_g$	paramagnetic relative stab. of σ_g^{2p} + π_u^{2p} c
F_2	1.6	1.42	1	$KK\sigma_g^2\sigma_u^{*2}\sigma_g^2\pi_u^4(\pi_g^*)^4(\sigma_u^*)^0$	$^1\Sigma_g$	
Ne_2	—	—	0	$KK\sigma_g^2\sigma_u^{*2}\sigma_g^2\pi_u^4\pi_g^{*4}\sigma_u^{*2}$	$^1\Sigma_g$	unbound



Note:
a) "bond order" reflected in De, Re trends
b) He_2, Be_2, Ne_2 all possible as excited states (bound) — eg. He_2^* – $(\sigma_g)^2(\sigma_u^*)^1(\sigma_g^{2s})^1$ – ½
c) More than half-filled less well bound yet shorter bond than less than half-filled for same bond order
d) Open shells have more than one possible term $(\pi_u^2) \rightarrow {}^1\Delta_g, {}^3\Sigma_g, {}^1\Sigma_g$

Homonuclear Diatomics

Molc	D_e (eV)	R_e (Å)	bond order	Configuration (lowest energy)	Grd term	Comment
H_2^+	2.78	1.06	1/2	$(\sigma_g^{1s})^1$	$^2\Sigma_g^+$	
H_2	4.76	0.74	1	$(\sigma_g^{1s})^2$	$^1\Sigma_g^+$	
He_2	---	---	0	$(\sigma_g^{1s})^2(\sigma_u^{1s})^2$	$^1\Sigma_g$	ground state unbound
Li_2	1.1	2.67	1	$(\sigma_g^{1s})^2\ (\sigma_u^{1s})^2\ (\sigma_g^{2s})^2$	$^1\Sigma_g$	weak ground state
Be_2	---	---	0	$[KK]^4(\sigma_g^{2s})^2(\sigma_u^{2s})^2$	$^1\Sigma_g$	unbound
B_2	2.9	1.6	1	$KK(\sigma_g^{2s})^2(\sigma_u^{2s})^2(\pi_u^{2s})^2$ alt: $KK(\sigma_g^{2s})^2(\sigma_u^{2s})^2(\pi_u^{2s})^1(\sigma_g^{2p})^1$	$^3\Sigma_g$	2 possible configurations paramagnetic ground state
C_2	6.4	1.24	2	$KK\ (\sigma_g)^2\ (\sigma_u^*)^2\ (\pi_u)^4$	$^1\Sigma_g$	
N_2	10	1.12	3	$KK\ \sigma_g^2\ \sigma_u^{*2}\ \pi_u^4\ (\sigma_g^{2p})^2$	$^1\Sigma_g$	strongest bond
O_2	5.2	1.21	2	$KK\ \sigma_g^2\ \sigma_u^{*2}\ \pi_u^4\ \sigma_g^2\ (\pi_g^*)^2$	$^3\Sigma_g$	paramagnetic relative stability of σ_g^{2p} and π_u^{2p}
F_2	1.6	1.42	1	$KK\ \sigma_g^2\ \sigma_u^{*2}\ \sigma_g^2\ \pi_u^4\ (\pi_g^*)^4\ (\sigma_u^*)^0$	$^1\Sigma_g$	
Ne_2	---	---	0	$KK\ \sigma_g^2\ \sigma_u^{*2}\ \sigma_g^2\ \pi_u^4\ \pi_u^{*4}\ \sigma_u^{*2}$	$^1\Sigma_g$	unbound

Note: a) "bond order" reflected in D_e, R_e trends

b) He_2, Be_2, Ne_2 all possible as excited states (bound) – e.g. He_2^* – $(\sigma_g)^2(\sigma_u^*)^1(\sigma_g^{2s})^1$ – partial

c) More than half-fill less well bound yet shorter bond than less than half-fill for same bond order

d) Open shells have more than one possible term ($^{2S+1}\Lambda$, where $\Lambda = \Sigma_\iota m_{L\iota}$) $(\Pi_u^4) \rightarrow {}^1\Delta_g\ ,\ {}^3\Sigma_g\ ,\ {}^1\Sigma_g$