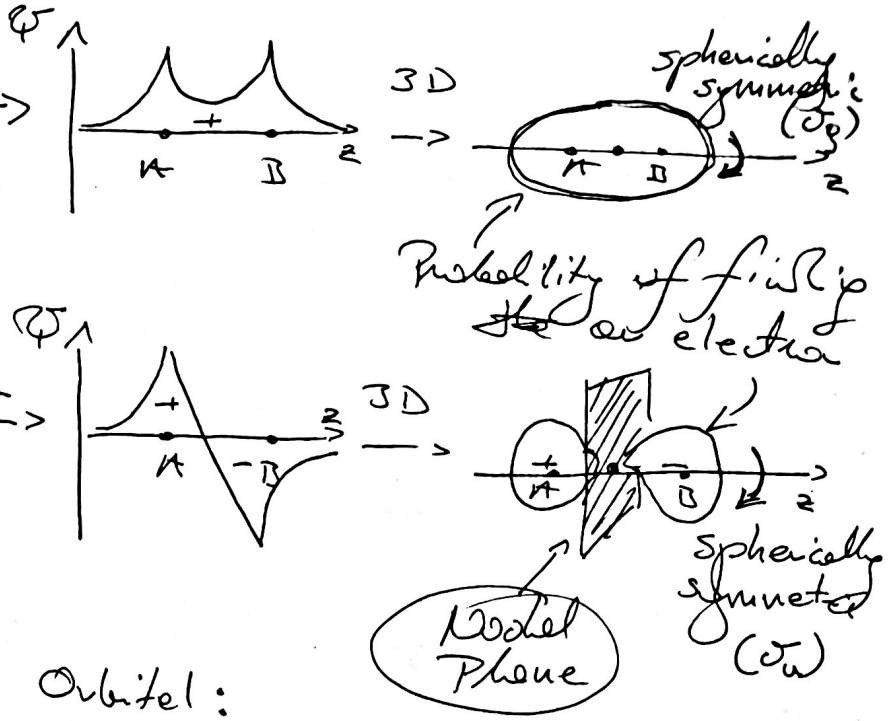
Diatomic Molecules - Molecular Orbitals (MOs)

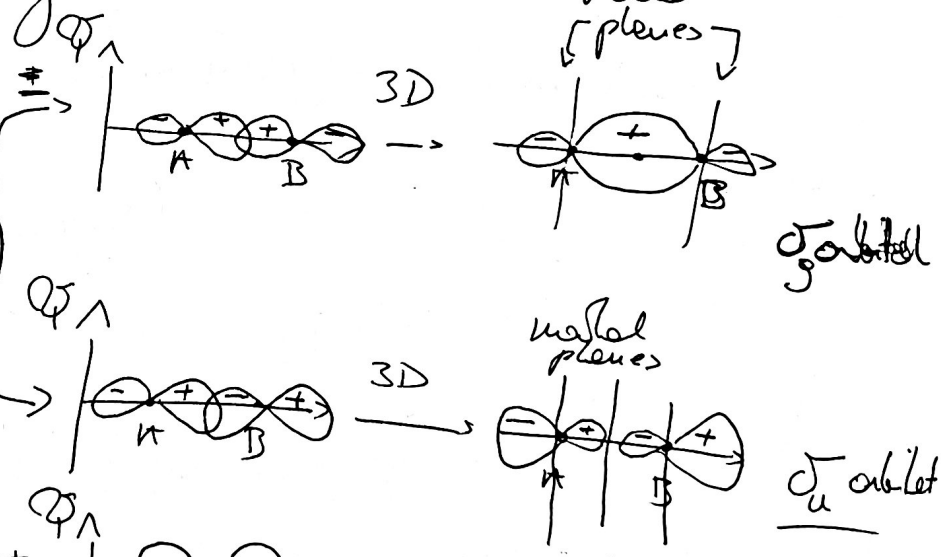
$\psi_{\pm} = 1s_A \pm 1s_B$



Bonding orbital:

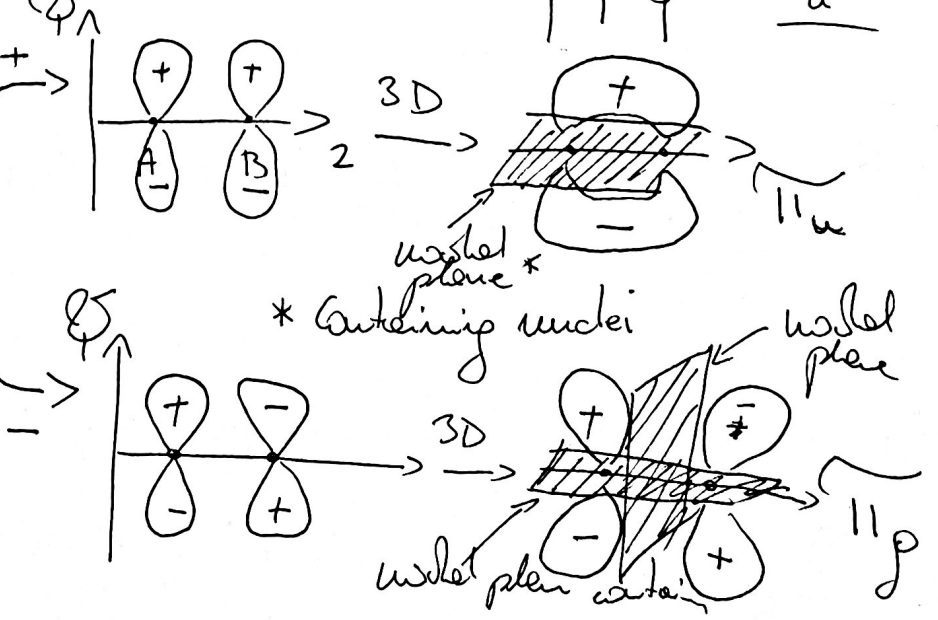
Antibonding orbital:

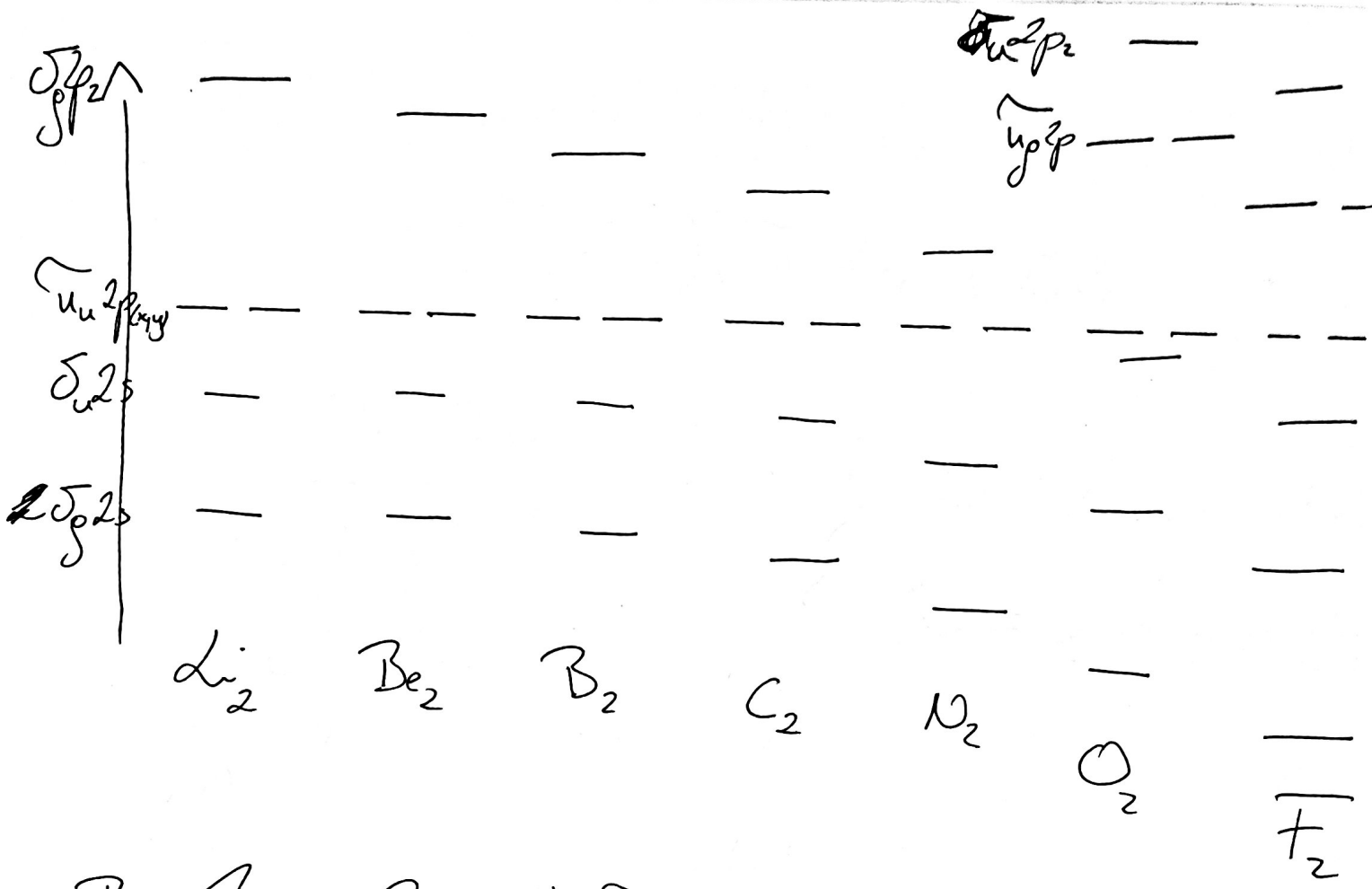
$\psi_{\pm} = 2p_{z,A} \pm 2p_{z,B}$



$\psi_{\pm} = 2p_{(x,y)A} \pm 2p_{(x,y)B}$

$(p_x + p_y \to 0)$





Bond order: $\frac{1}{2}[(e's \text{ in } B.O.s) - (e's \text{ in } A.O)]$

$H_2 \rightarrow B.O. = 1$

$He_2 \rightarrow B.O. = \frac{1}{2}(2-2) = 0$

$He_2^+ \rightarrow B.O. = \frac{1}{2}(2-1) = \frac{1}{2}$

$1\sigma_u$ —

$1\sigma_g$ —

B_2: $(KK)(\sigma_g 2s)(\sigma_u 2s)(\pi_u 2p_x)(\pi_u 2p_y)$
(10e)

- PARAMAGNETIC

C_2: $(KK)(\sigma_g 2s)(\sigma_u 2s)(\pi_u 2p_x)(\pi_u 2p_y)$

- DIAMAGNETIC

O_2 : $(KK)(\sigma_g 2s)(\sigma_u 2p)(\sigma_g 2p_z)(\pi_u 2p_x)(\pi_u 2p_y)$
16e's
$(\pi_g 2p_x)(\pi_g 2p_y)(\sigma_u 2p_z)$

O_2 : B.O =

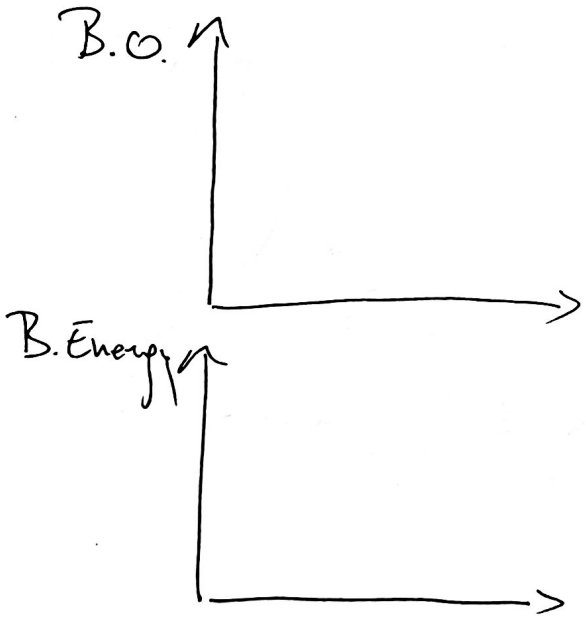
O_2^+ : B.O =

O_2^- : B.O =

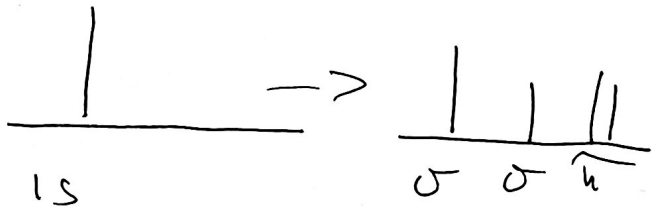
O_2^{2-} B.O. =

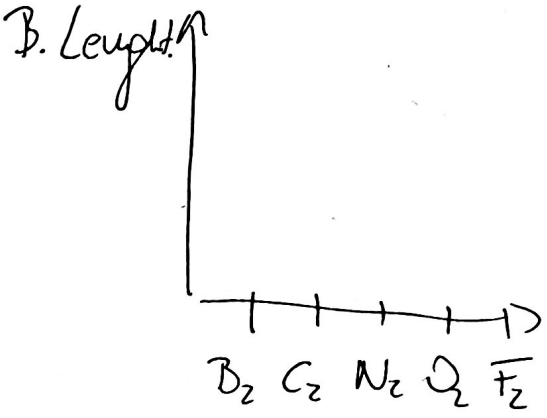
O_2 : Lewis structure

$\dot{O}=\dot{O}$ vs $|\dot{O}\equiv\dot{O}|$



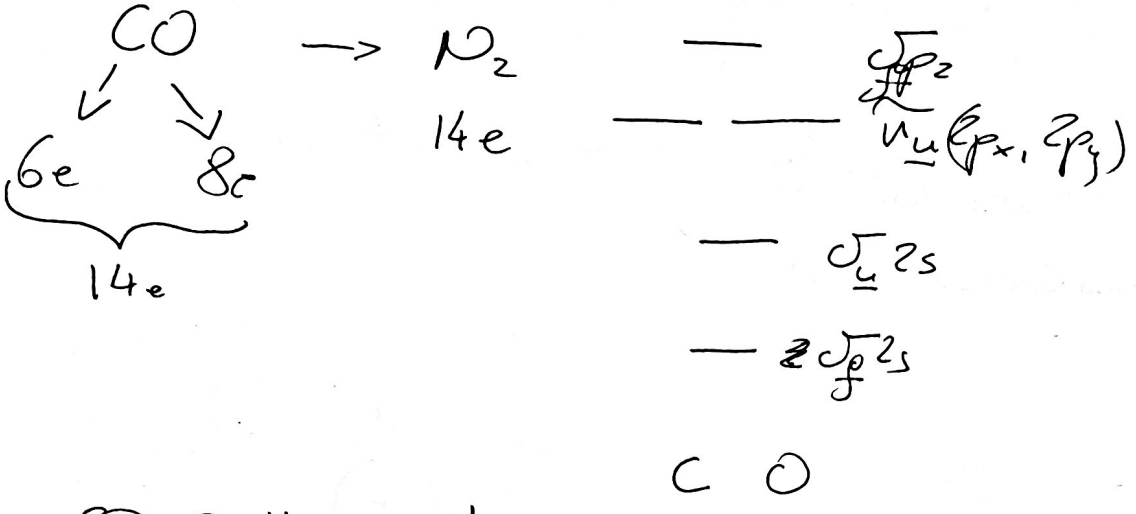
H emission vs Molecule Emission.



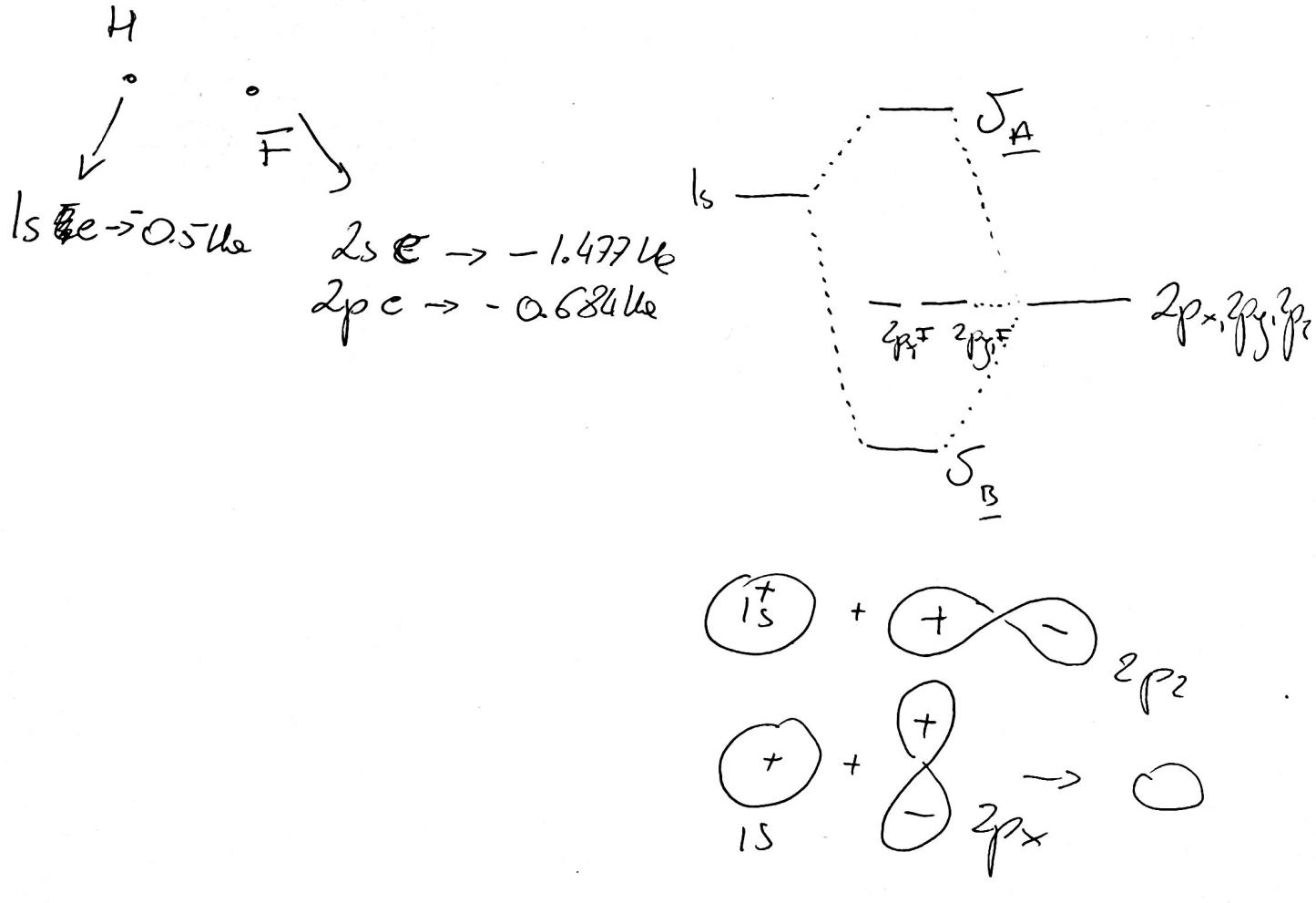


Heteronuclear Diatomic Molecules

① Similar ~~Atoms~~



② Different atoms



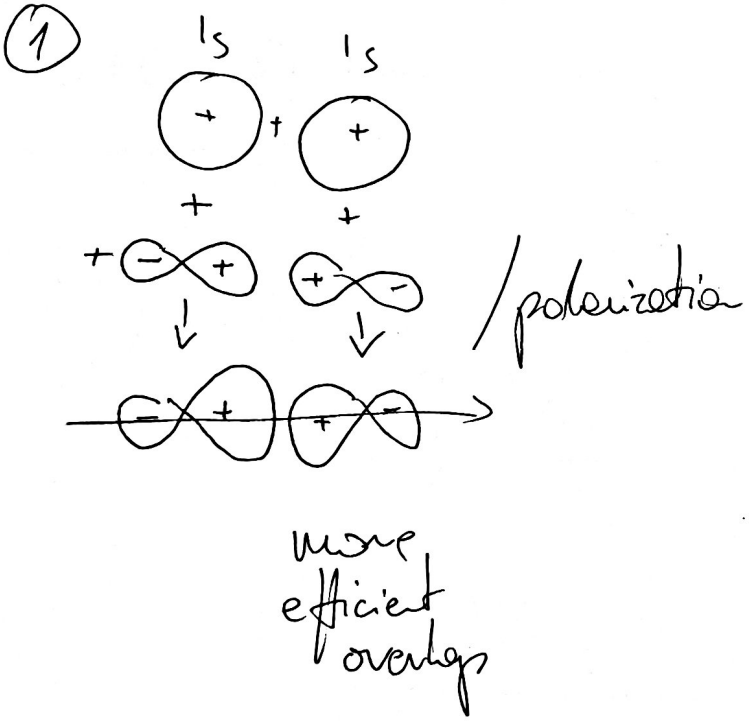
LCAO-MO

$$\Psi = (2s_A + 2s_B) + (2p_{x,A} + 2p_{x,B} + 2p_{y,A} + 2p_{y,B}) + (2p_{z,A} + 2p_{z,B})$$

each with a coeff.

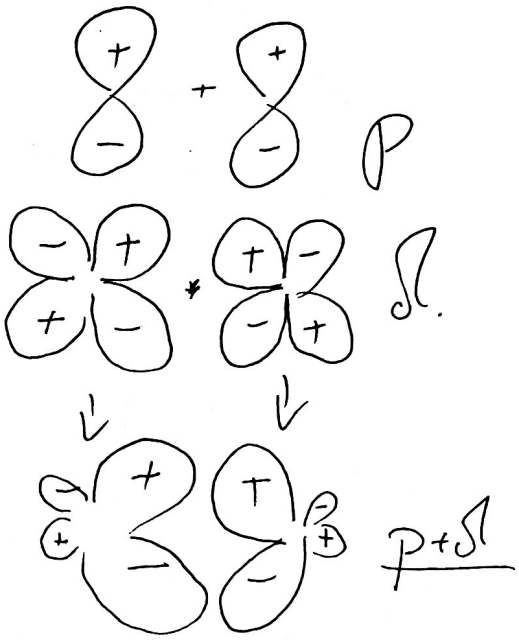
8 A.O. in $\rightarrow$ 8 M.O. out
(linear combination)

(1)



more efficient overlap

(2)



Molecular Term Symbols

$M_L = m_{l,1} + m_{l,2} + \dots$ — orbital angular momenta

M_L → total orbital angular momenta

$m_{l,i} = 0$ for σ
$m_l = \pm 1$ for π
$m_l = \pm 2$ for δ

multiplicity $2S+1$

$|M_L|$ → absolute value of total angular mo

$M_L = 0 \mapsto \Sigma$
$M_L = 1 \mapsto \Pi$
$M_L = 2 \mapsto \Delta$
$M_L = 3 \mapsto \Phi$

H_2 molecule:

$M_L = 0 + 0 = 0$
$M_S = +\frac{1}{2} - \frac{1}{2} = 0$
$\Big\} \; {}^1\Sigma$

He_2^+ $(\sigma_g 1s)^2 (\sigma_u 1s)^1$

$M_L = 0$
$M_S = \frac{1}{2}$ or $-\frac{1}{2} \mapsto S = \frac{1}{2}$
$\Big\} \; {}^2\Sigma$

B_2 molecule

$(KK)^4 (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\pi_u 2p_x)^1 (\pi_u 2p_y)^1$

M_L	M_S +1	0	−1
+2			
0			
−2			

O_2 molecule

$(KK)^4 (\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p_z)^2 (\pi_u 2p_x)^2 (\pi_u$
$(\pi_g 2p_x)^1 (\pi_g 2p_y)^1$

M_L	+1	0	−1
+2			
0			
−2			

H_2 molecule

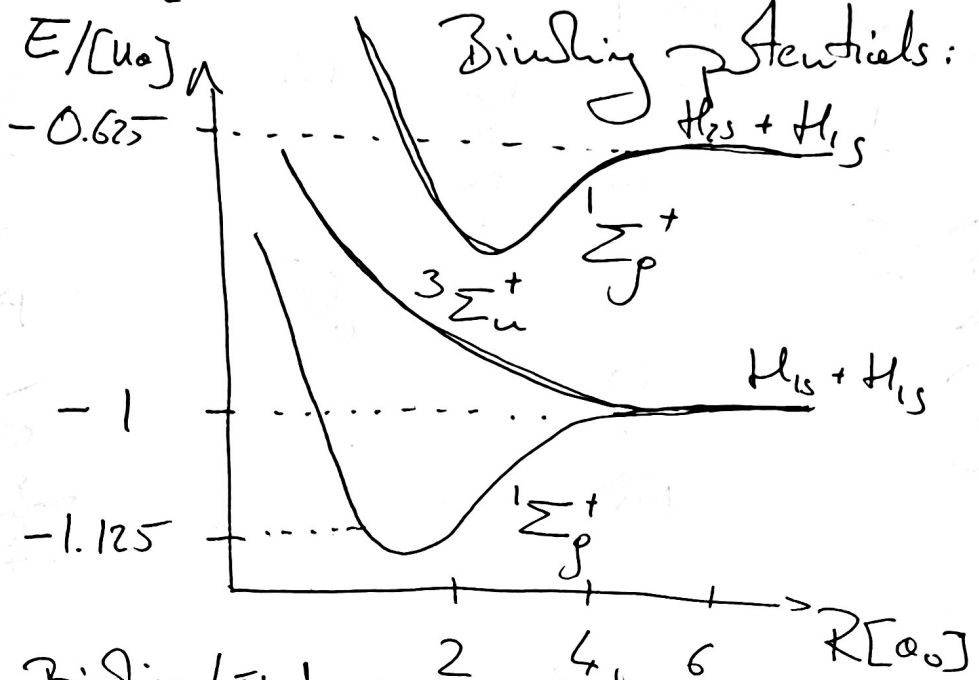
$H\cdot + H\cdot \rightarrow H_2$

$1s \quad 1s \rightarrow {}^1\Sigma_g^+ \; (1\sigma_g)^2$ or ${}^3\Sigma_u^+ \; (1\sigma_g)^1(1\sigma_u)^1$

${}^2S_{1/2} \quad {}^2S_{1/2}$ ${}^1\Sigma_u^+$

$1s + 2s \rightarrow {}^1\Sigma_g^+ \; (1\sigma_g)^1(2\sigma_g)^1$

${}^2S_{1/2} \quad {}^2S_{1/2}$



O_2 Binding / Electronic Excitations:

$((1\pi_{g,x})^2(1\pi_g)^2 \rightarrow {}^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+$ — $3\sigma_u$; — — $1\pi_u$

$((1\pi_{g,x})(1\pi_{g,y})(3\sigma_u)^1) \rightarrow {}^3\Pi_u, {}^1\Pi_u$ — $3\sigma_u$; — — $1\pi_u$