Bonding, Antibonding, + Molecular Orbitals

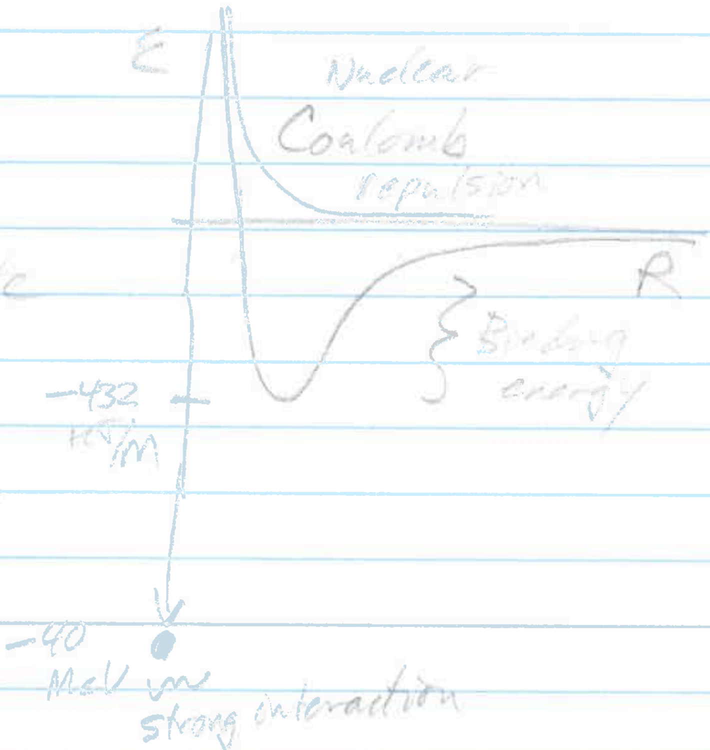
H_2 (D_2) molecule

$\times \frac{(\uparrow\downarrow - \downarrow\uparrow)}{\sqrt{2}}$

Far apart

Together = He

Bound State



strong interaction

$$\mathcal{H} = \underbrace{\frac{e^2}{R}}_{\text{proton repulsion}} - \frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)\psi(r_1, r_2)$$

$$+ \left[- \frac{e^2}{|r_1 - \frac{R}{2}\hat{z}|} - \frac{e^2}{|r_1 + \frac{R}{2}\hat{z}|} \right.$$

$$\left. - \frac{e^2}{|r_2 - \frac{R}{2}\hat{z}|} - \frac{e^2}{|r_2 + \frac{R}{2}\hat{z}|} \right] \psi$$

Perturbation

$$+ \frac{e^2}{|r_1 - r_2|}\psi$$

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_R + \overbrace{\underbrace{\frac{e^2}{R}}_{\text{Nuclear repulsion}} + \underbrace{\frac{e^2}{|r_L - r_R|}}_{\text{e-e repulsion}} \underbrace{- \frac{e^2}{|r_L + \frac{R}{2}\hat{z}|} - \frac{e^2}{|r_R - \frac{R}{2}\hat{z}|}}_{\text{interaction w/ other nucleus}}}^{\text{Perturbation } U_{int}}$$

φ = Hydrogen ground state WF

$|\psi_1\rangle = (|\varphi_R^{r}(r_2)\rangle\varphi_L^{\ell}(r_1)\rangle$ energy $E_0 = -2R_y = -2(13.6\,eV)$

$|\psi_2\rangle = |\varphi_R^{R}(r_2)\rangle\varphi_L^{\ell}(r_1)\rangle)/\sqrt{2}$

$$E = E_0 + \langle\psi_0|U|\psi_0\rangle + \sum \frac{|\langle\psi_0|U|\psi_1\rangle|^2}{E_0 - E_1}$$

except degenerate

$$\mathcal{H}^{2\times2}_{ij} = \langle\psi_i|U_{int}|\psi_j\rangle$$

$$= \begin{pmatrix} A & -J \\ -J & A \end{pmatrix}$$

$A = \int U_{int} |\varphi_R^R(r_1)|^2 |\varphi_L^{\ell}(r_2)|^2$

$$J = \underbrace{-\int U_{int}\, \varphi_R(r_1)\, \varphi_R^*(r_2)\, \varphi_L(r_2)\, \varphi_L^*(r_1)}_{\text{Exchange Integral}}$$

$$\psi_\pm(r_1, r_2) = [\varphi_R(r_1)\varphi_L(r_2) \pm \varphi_R(r_2)\varphi_L(r_1)]/\sqrt{2}$$

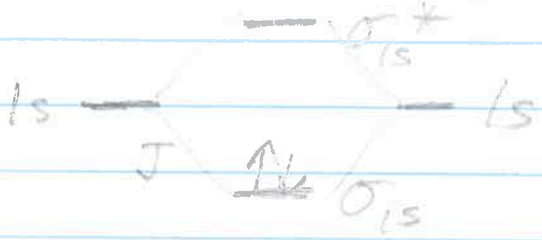
$$E_\pm = (A \mp J)$$

ψ_+ symmetric ⇔ Spin WF antisymmetric
Bonding
singlet $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$, $s=0$

ψ_- antisymmetric ⇔ Spin triplet, $s=1$.
(Antibonding)

~~Note~~ :

- J is binding energy
- Bond is σ_{1s} orbital



- Focus on spins ('integrate out' orbitals)

$(S_1+S_2)^2 = 0$ $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$ → energy $-J$

$(S_1+S_2)^2 = 2$ $(\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$, ↑↑, ↓↓ → energy $+J$

SAKURAI (3.5.30) Changes $S_z = \pm\hbar/2 \to S_z = \pm 1/2$!
Effective Hamiltonian $S = 1/2$

Spin ½
$S^2 = S(S+1) = 3/4$
singlet $(S_1+S_2)^2 = 0$
triplet $(S_1+S_2)^2 = 1(1+1) = 2$

$$\mathcal{H}_{spin} = A - \frac{1}{2}J\left(1 + \frac{4}{\hbar^2} S_1 \cdot S_2\right)$$

$$S_1 \cdot S_2 = \frac{1}{2}\left[(S_1+S_2)^2 - S_1^2 - S_2^2\right]$$

$$= \frac{1}{4}$$

$$\mathcal{H}_{spin} = A - J + 2J\frac{(S_1+S_2)^2}{2}$$

$$= A - J + J(\underbrace{S_1^2}_{3/4} + \underbrace{S_2^2}_{3/4} + 2 S_1 \cdot S_2)$$

$$= A + J\left(\tfrac{1}{2} + 2 S_1 \cdot S_2\right) = A + \tfrac{1}{2}J\left(1 + 4 S_1 \cdot S_2\right)$$

Heisenberg
An[illegible]

Shortcut! W/o spin-orbit splitting,
↑ & ↓ not connected by Hamiltonian
→ Treat ↑ & ↓ as two different kinds of particles

(~~"Two spin states per orbital"~~)
↑ spin part antisymmetric, ↓ ant symm. spin handles rest, theorem?

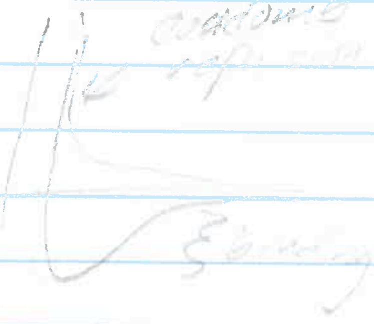
<u>Converse</u>: "Isospin" in nuclear physics. Treat p & n as isospin +½ -½.
Electromagnetism & quark mass difference "small" symmetry breaking

Later →

"Molecular orbital theory" — σ_{1s}^* antibonding (excited state)

$1s^A$ ↑ ↓ $1s^B$

⇅ σ_{1s} bonding } bonding energy



(3 kJ/m)

He_2 0.01 kJ/Mol 1993

H_2 432 kJ/m

σ-bonds
cylindrical symmetry

Li_2 bond
Be_2 "No" bond
B_2 $1s_2$ $2s_2$ 2p

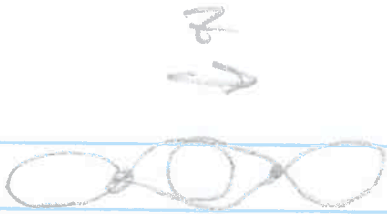
Nodal plane
⇒ π_{2px}

289 kJ/m

C_2 = double bond

599 kJ/m

σ_{2p_z}



N_2

— σ^*

— π_z

↑↓ σ_{2p_y}

↑↓ ↑↓ π_{2p_x} 2 π_{2p_y} 2

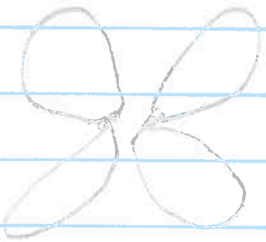
941 KJ/m

triple bond

O_2 ↑ ↑ π^*_{2px}, π^*_{2py}

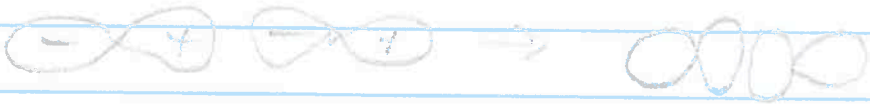
↑↓ ↑↓ π_{2px} π_{2py}

— σ_{2p_z}



3 bonds & 1 anti. bonds = Double bond

495 KJ/m



$\sigma^*_{2p_z}$