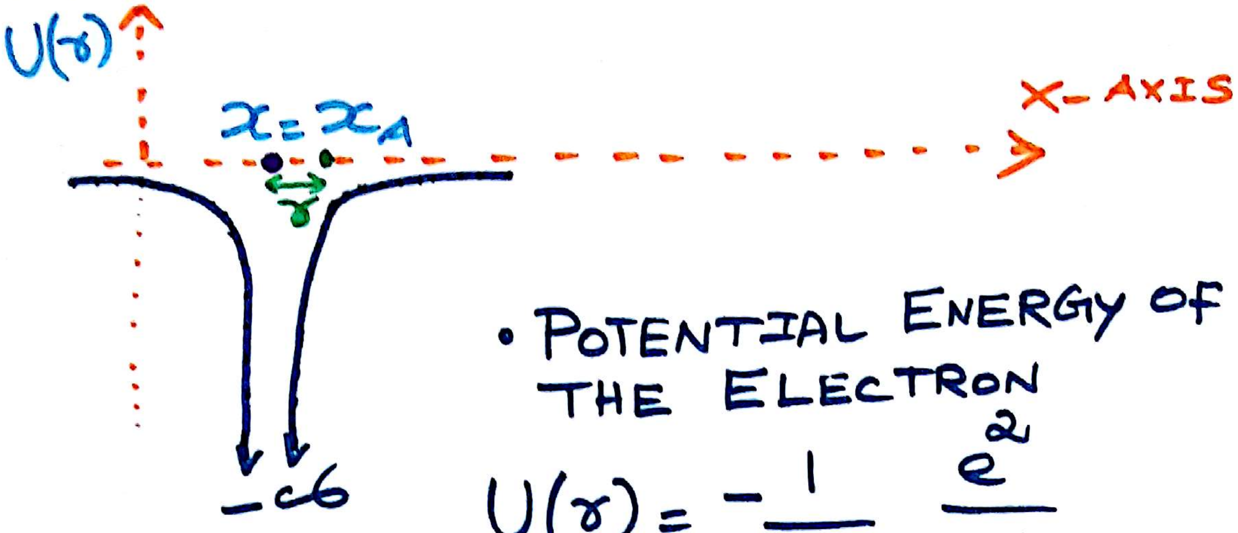
ATOM → MOLECULE → SOLID

- HYDROGEN ATOM



- POTENTIAL ENERGY OF THE ELECTRON

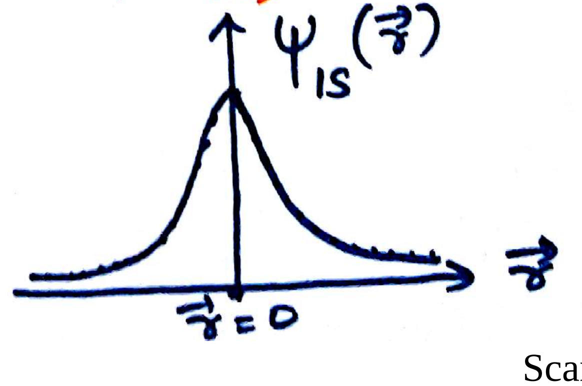
$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

- $U(r)$ IS LESS THAN OR EQUAL TO ZERO ALWAYS (ATTRACTIVE FORCE)
- AS $r \to 0$, $U(r) \to -\infty$
- VISUALIZE THIS ENERGY IN 3D SPACE
- GROUND STATE WAVE FUNCTION

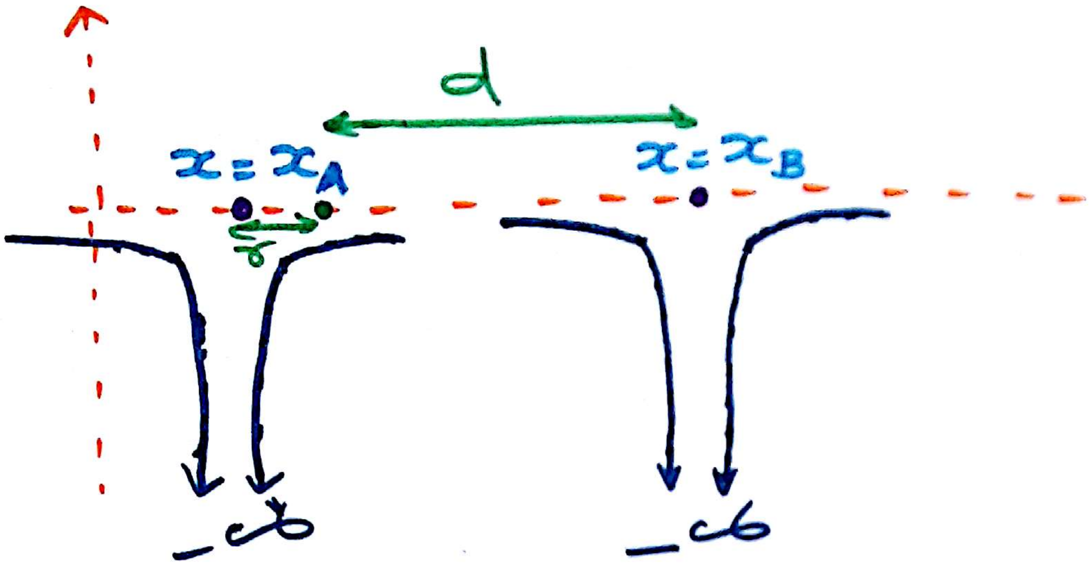
ASSUME $x_A = 0$ →

$$\psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

↳ ALWAYS POSITIVE REGARDLESS OF X, Y, Z VALUES

- 

- AN ELECTRON BETWEEN TWO ATOMS



- POTENTIAL ENERGY OF THE ELECTRON

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} + \Delta U(d)$$

PERTURBATION DUE TO THE ~~INTERNAL~~ INTERACTION OF THE ELECTRON WITH THE NEIGHBORING ATOM

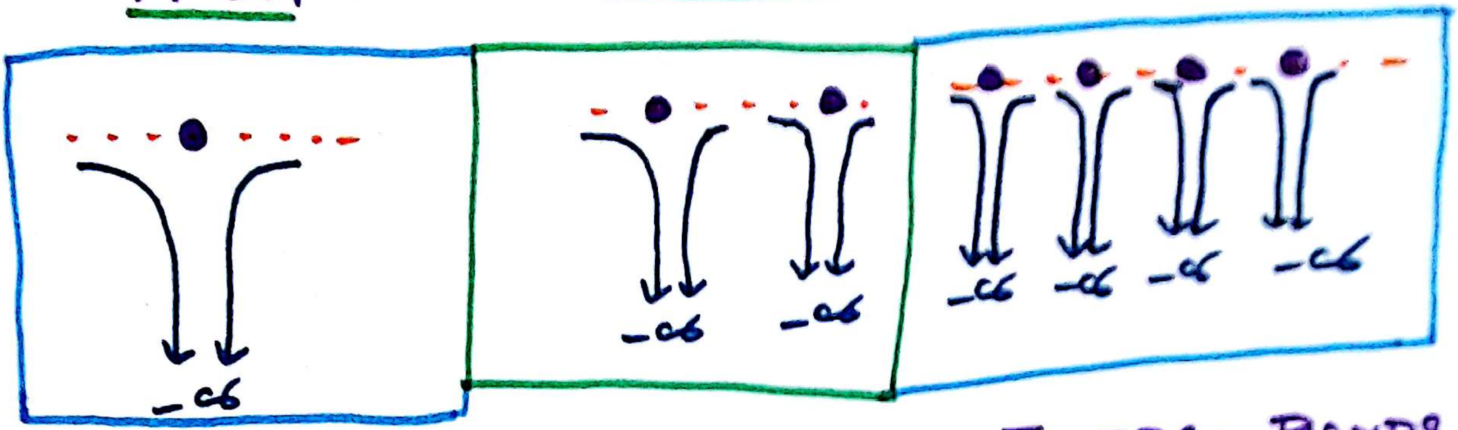
ELECTRON – ELECTRON
ELECTRON – NUCLEUS

WE KNOW:

- $\Delta U(d) = 0$ WHEN d IS LARGE
- WHEN $d \to 0$ OR WHEN d IS SMALL, INTER-ATOMIC INTERACTIONS BECOME IMPORTANT
- $\Delta U(d) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{d}$ (ELECTRON – ELECTRON REPULSION IGNORED)
- AS YOU DECREASE d, THE BARRIER BETWEEN THE ATOMS DECREASES.

$$\boxed{\text{PLOT } U(x) = -\frac{1}{4\pi\epsilon_0} e^2\left[\frac{1}{|x|} + \frac{1}{|x+d|}\right]}$$

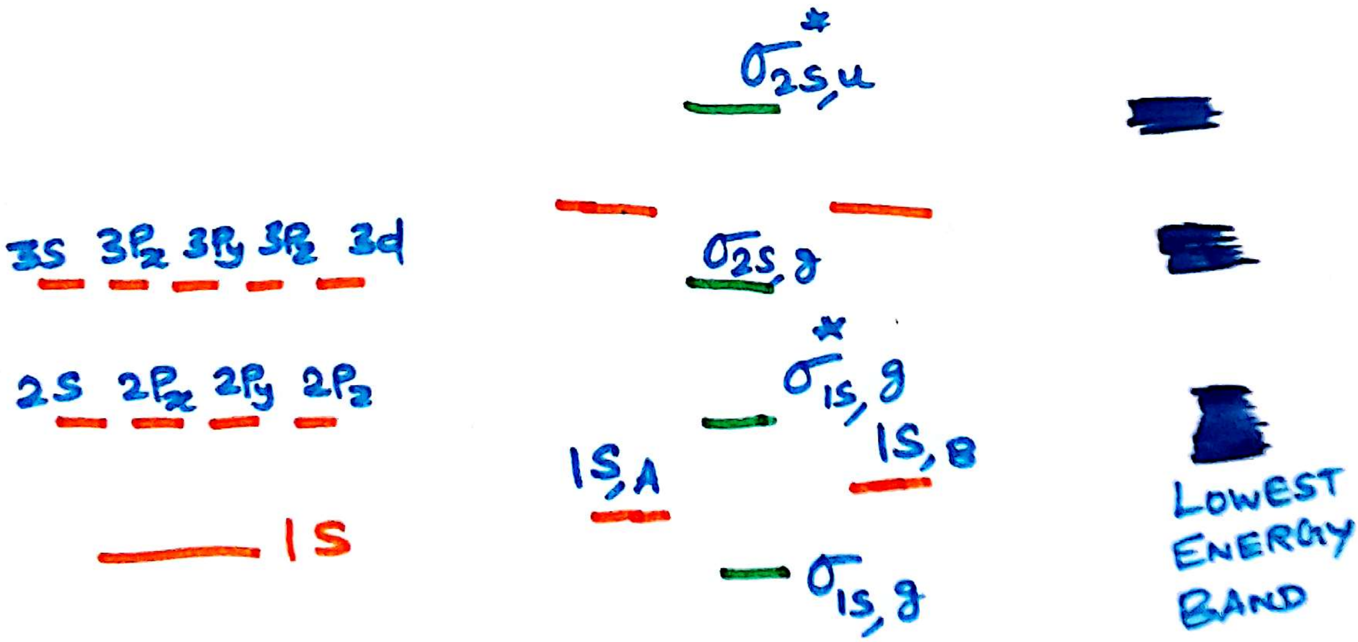
ATOM | MOLECULE | SOLID



- ATOMIC ORBITALS
- ENERG LEVELS

- MOLECULAR ORBITALS
- ENERGY LEVELS

- ENERGY BANDS
- ENERGY LEVELS



HYDROGEN MOLECULE

- LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

- $$\psi_M(\vec{r}) = \underbrace{C_A}_{\text{CONSTANT}} \underbrace{\psi_A(\vec{r})}_{\text{ATOMIC ORBITAL OF ATOM A}} + \overbrace{C_B}^{\text{CONSTANT}} \underbrace{\psi_B(\vec{r})}_{\text{ATOMIC ORBITAL OF ATOM B}}$$

- HAMILTONIAN

$$\hat{H} \equiv \underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + U_A(\vec{r})\right)}_{\hat{H}_{0,A}} + \underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + U_B(\vec{r})\right)}_{\hat{H}_{0,B}} + \Delta U(d)$$

$$\hat{H}_{0,A}\psi_A(\vec{r}) = E_{1s,A}\psi_A(\vec{r})$$
$$\hat{H}_{0,B}\psi_B(\vec{r}) = E_{1s,B}\psi_B(\vec{r})$$

$$\hat{H} \equiv \underbrace{\hat{H}_{0,A}}_{\text{HAMILTONIAN OF ISOLATED A}} + \underbrace{\hat{H}_{0,B}}_{\text{HAMILTONIAN OF ISOLATED B}} + \underbrace{\Delta U(d)}_{\text{PERTURBATION}}$$

- $$\hat{H}\psi_M(\vec{r}) = E_M\psi_M(\vec{r})$$

$$\hat{H}\left(C_A\psi_A(\vec{r}) + C_B\psi_B(\vec{r})\right) = E_M\psi_M(\vec{r})$$

$\times\ \psi_A^*(\vec{r})$ AND INTEGRATE ON BOTH SIDES AND USE THE FOLLOWING

$$\int_{\vec{r}} \psi_A^*(\vec{r})\, \hat{H}\, \psi_A(\vec{r})\, d\vec{r} \simeq E_{1s,A}$$

$$\int_{\vec{r}} \psi_A^*(\vec{r})\, \hat{H}\, \psi_B(\vec{r})\, d\vec{r} \simeq -V$$

$$\Rightarrow \quad \boxed{C_A E_{1s,A} - C_B V = E_M C_A}$$

$|||^{ly}$ $\quad \times\ \psi_B^*(\vec{r})$ AND INTEGRATE

$$\boxed{-V C_A + E_{1s,B} C_B = E_M C_B}$$

$$(E_{1s,A} - E_M) C_A - V C_B = 0$$

$$-V C_A + (E_{1s,B} - E_M) C_B = 0$$

SOLUTION :

$$\begin{vmatrix} E_{1s,A} - E_M & -V \\ -V & E_{1s,B} - E_M \end{vmatrix} = 0$$

$$\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

ANTI-BOND

$$\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

BOND

$$\Rightarrow \quad \boxed{E_M = E_{1s} \pm V}$$

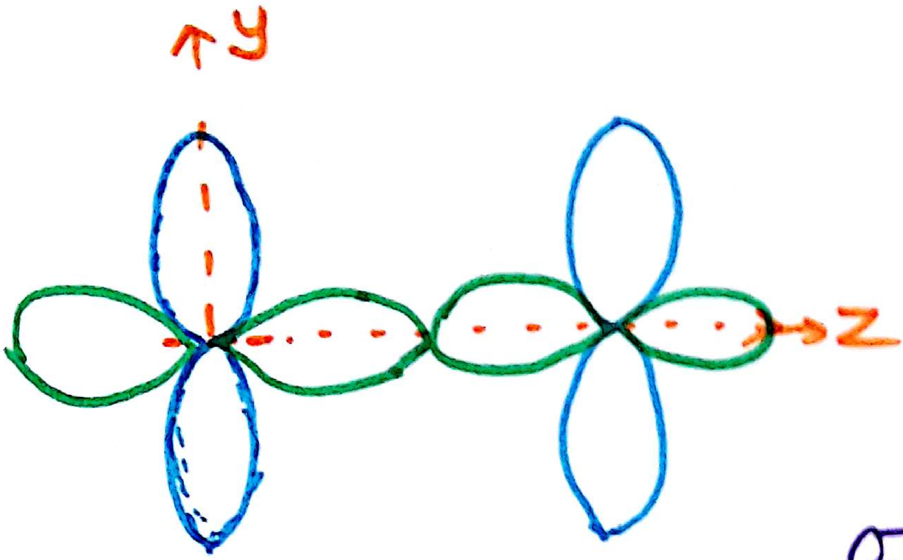
ANTI BONDING

$$E_M = E_{1s} + V$$

$$E_M = E_{1s} - V$$

BONDING

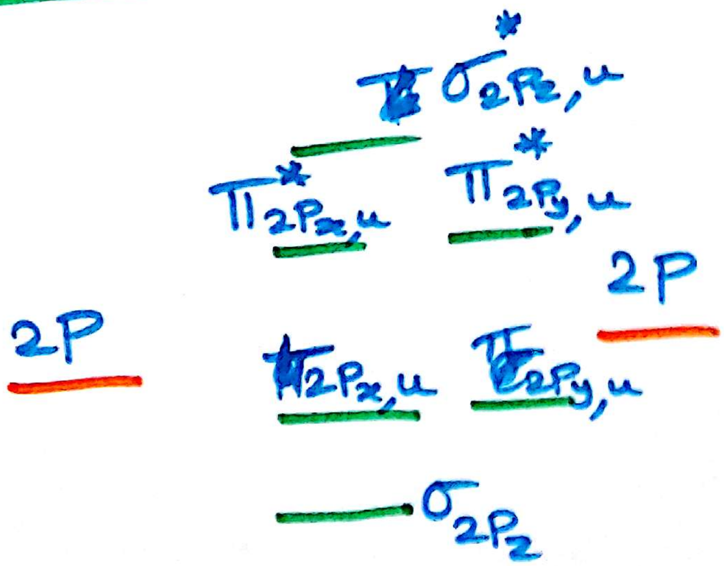
- OVERLAP OF P ORBITALS



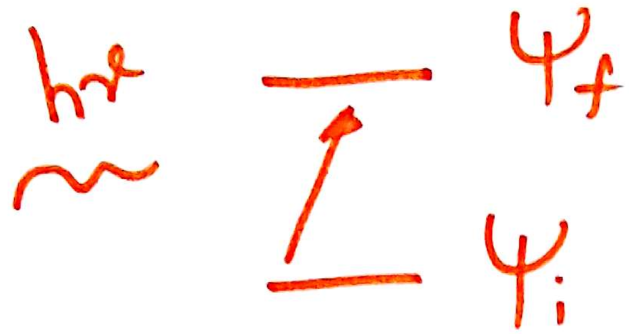
$$2P_{z,A} \oplus 2P_{z,B} \rightarrow \sigma^*_{2p,u},\ \sigma_{2p,g}$$

$$2P_{y,A} \oplus 2P_{y,B} \rightarrow \pi^*_{2p,g},\ \pi_{2p,u}$$

$$\boxed{E_{\sigma_{2p_z}} < E_{\pi_{2p,x}} = E_{\pi_{2p,y}} < E_{\pi^*_{2p,x}} = E_{\pi^*_{2p,y}} < E_{\sigma^*_{2p_z}}}$$



TRANSITION PROBABILITY



$\hat{V}(\vec{r}, t) \Rightarrow$ TIME-DEPENDENT PERTURBATION

TRANSITION PROBABILITY

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} \left| \langle \Psi_f | \underbrace{\hat{V}}_{\vec{\mu}\cdot\vec{E}} | \Psi_i \rangle \right|^2 \rho(E_f)$$

$$\Gamma_{i\to f} \propto \left| \langle \Psi_f | \hat{\mu} | \Psi_i \rangle \right|^2$$

TRANSITION DIPOLE MOMENT INTEGRAL

$\Gamma_{i\to f} = 0$: TRANSITION IS FORBIDDEN

$\Gamma_{i\to f} \neq 0$: TRANSITION IS ALLOWED

$\boxed{\text{SELECTION RULES}}$