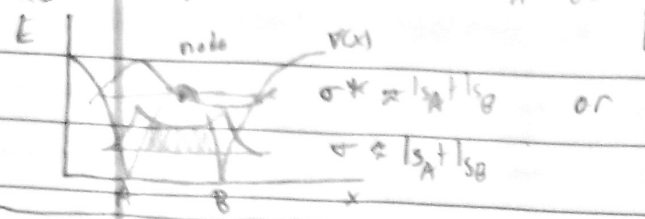
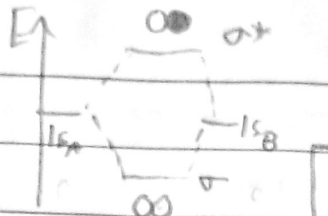
## Lecture 12 review:

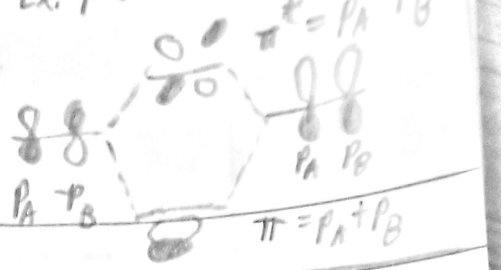
**Bonding**

- needs tunnelling
- needs quantum interference ($\psi_A \pm \psi_B$)

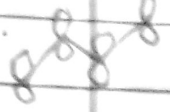


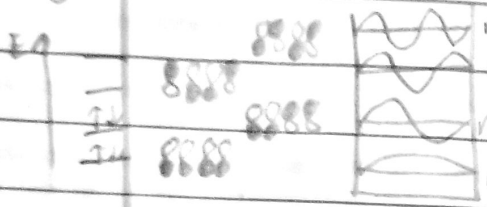

Ex. p orbitals




ex.



signs of p orbitals match ↘ ↙ wavefunctions (the order does, at least, $-+-+$ or $+-+-$ apply)




ex.


$\psi = \psi_\sigma(x_1, m_s = \frac{1}{2}) \cdot \psi_\sigma(x_2, m_s = -\frac{1}{2}) =$

$\psi = \sigma_{1+}\sigma_{2-} = \sigma^2$

(orbital type; which $e^-$; spin type)

- The function $\psi = \psi_1 \cdot \psi_2$ (ex. $\sigma_1 \sigma_2$) violates postulate 4.
- $\psi_{12} = \psi_1(x_1) \cdot \psi_2(x_2) \xrightarrow{\text{flip}} \psi_{21} = \psi_1(x_2) \cdot \psi_2(x_1)$
- $\psi_{12} = -\psi_{21}(x)$ for fermions, Not necessarily true for above statement.
- To Fix:

$\psi_{12}(x_1, x_2) \propto \psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)$

$\psi_{21}(x_2, x_1) \propto \psi_1(x_2)\psi_2(x_1) - \psi_1(x_1)\psi_2(x_2)$

$\propto -\psi_{12}(x_1, x_2)$

- By flipping $e^-$ & subtracting, satisfy Postulate 4.

## Lecture 13: Multi-$e^-$ molecules

- Wavefunction of $2e^-$:
- $e^-$ #1: $\hat{H}_1 \psi_1(x_1) = E_1 \psi_1(x_1)$
- $e^-$ #2: $\hat{H}_2 \psi_2(x_2) = E_2 \psi_2(x_2)$
- For now, assume for enough apart that $e^- e^-$ repulsion is ignorable
- Try $\psi(x_1, x_2) = \psi_1(x_1) \cdot \psi_2(x_2)$

$\hat{H}\psi = (\hat{H}_1 + \hat{H}_2)\psi$

$= (\hat{H}_1 + \hat{H}_2)\psi_1\psi_2$

$= \psi_2 \hat{H}_1 \psi_1 + \psi_1 \hat{H}_2 \psi_2$

$= \psi_2 E_1 \psi_1 + \psi_1 E_2 \psi_2$

$= E_1 \psi_1 \psi_2 + E_2 \psi_1 \psi_2$

$= (E_1 + E_2)\psi_1\psi_2$

$\hat{H}\psi = E\psi$ ← if $\psi = \psi_1\psi_2$, $E = E_1 + E_2$

- This holds for more than 2 $e^-$ as well.

- Shorthand notation for antisymmetric wavefunction: "Determinant"

$$\begin{vmatrix} a_1 & a_2 \\ b_1 & b_2 \end{vmatrix} = a_1 b_2 - a_2 b_1$$

$$\psi = \begin{vmatrix} \sigma_{1+} & \sigma_{1-} \\ \sigma_{2+} & \sigma_{2-} \end{vmatrix} = \sigma_{1+}\sigma_{2-} - \sigma_{1-}\sigma_{2+}$$