Multielectron atoms, and bonding in H2+

Note Title 12-11-2009

Final exam

Syllabus: Chemical potential, chemical and phase equilibrium, and all of quantum chemistry

Weightage: ~30% for thermo and rest quantum

He atom $\psi_{1s}(1)\ \psi_{1s}(2)$ — singlet

— $\psi_{1s}(1)\ \psi_{n\ell}(2)$ $\qquad$ $\psi_{n_1\ell_1}(1)\ \psi_{n_2\ell_2}(2)$

$n\ell$ = 2s

exchange degeneracy ⇕

— $\psi_{1s}(2)\ \psi_{n\ell}(1)$

$a = \pm b$ $\qquad$ $\psi = a\,\psi_{1s}(1)\,\psi_{n\ell}(2) + b\,\psi_{1s}(2)\,\psi_{n\ell}(1)$

Any property is independent of exchange of particle labels

$a = \pm b$

$$\Psi = \begin{cases} \text{singlet} \quad \Psi_+ = \frac{1}{\sqrt{2}} \left(\psi_{1s}(1)\,\psi_{n\ell}(2) + \psi_{1s}(2)\,\psi_{n\ell}(1) \right) \\ \text{triplet} \quad \Psi_- = \frac{1}{\sqrt{2}} \left(\psi_{1s}(1)\,\psi_{n\ell}(2) - \psi_{1s}(2)\,\psi_{n\ell}(1) \right) \end{cases}$$

If $r_1 = r_2$

$\Psi_- = 0 \Rightarrow$ electrons are anti-correlated

$\langle \hat{\mathcal{H}} \rangle = E_{\text{ionization}}$ $\quad \hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$

$$\langle E \rangle = \frac{\int \psi^* \hat{\mathcal{H}} \psi \, d\tau_1 \, d\tau_2}{\int \psi^* \psi \, d\tau_1 \, d\tau_2}$$

$$\psi_+ = \frac{1}{\sqrt{2}} \left(\varphi_{1s}(1) \, \varphi_{2s}(2) + \varphi_{1s}(2) \, \varphi_{2s}(1) \right)$$

$$\text{Denominator} = \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2}} \int \left(\varphi_{1s}^*(1) \, \varphi_{2s}^*(2) + \varphi_{1s}^*(2) \, \varphi_{2s}^*(1) \right)$$

$$= \frac{1}{2} \left\{ \int \overbrace{\varphi_{1s}^*(1)}^{1} \left(\varphi_{1s}(1) \, \varphi_{2s}(2) + \varphi_{1s}(2) \right) d\tau_1 \right.$$

$$\left. \int \overbrace{\varphi_{2s}^*(2)}^{1} \overbrace{\varphi_{2s}(1)}^{1} d\tau_2 \right.$$

$$\left. + \cdots \right.$$

$$\int \frac{1}{\sqrt{2}} \left(\varphi_{1s}(1)\ \varphi_{2s}(2) + \varphi_{1s}(2)\ \varphi_{2s}(1) \right) \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right\}$$

$$\frac{1}{\sqrt{2}} \left(\qquad \right)$$

$$\frac{1}{2}\int \varphi_{1s}(1)\left(-\frac{\hbar^2}{2m}\nabla_1^2\ \varphi_{1s}(1)\right) d\tau_1 \times \int \varphi_{2s}(2)\ \varphi_{2s}(2)\, d\tau_2$$

$$\int \frac{1}{\sqrt{2}} \Big(\underset{\rho(1)}{\varphi_{1s}(1)} \varphi_{2s}(2) \frac{e^2}{r_1} \varphi_{1s}(1) \Big) \underset{\rho_2}{\varphi_{2s}(2)}\, d\tau_1\, d\tau_2$$

Coulomb integral $= \int \left(e\,\varphi_{1s}(1)\ \varphi_{1s}(1) \right) \frac{1}{r_1} \left(e\,\varphi_{2s}(2)\ \varphi_{2s}(2) \right) d\tau_1\, d\tau_2$

$$J = \int \varphi_{1s}(1)\,\varphi_{1s}(1)\,\frac{e^2}{r_{12}}\,\varphi_{2s}(2)\,\varphi_{2s}(2)\,d\tau_1\,d\tau_2$$

$\varphi(1)$ interelectronic repulsion $\varphi(2)$

exchange integral

$$K = \int \varphi_{1s}(1)\,\varphi_{1s}(2)\,\frac{e2}{r_{12}}\,\varphi_{2s}(1)\,\varphi_{2s}(2)\,d\tau_1\,d\tau_2$$

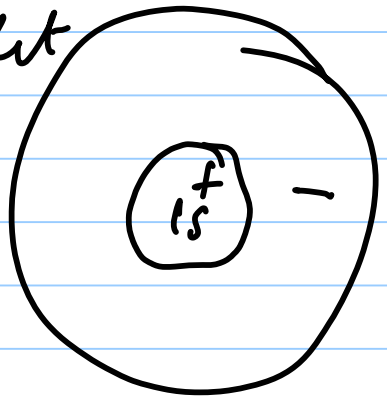
$E_0 + J + K$ → singlet

$E_0 + J - K$ positive

triplet

$E_0 + J$

E_0



Multielectron atom (general case)

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{i<j}\frac{e^2}{r_{ij}}$$

$\sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\nabla_i^2$: KE

$\frac{Ze^2}{r_i}$: nuclear attraction

$\sum_{i<j}\frac{e^2}{r_{ij}}$: interelectronic repulsion

$$\hat{\mathcal{H}} = \sum_i \mathcal{H}_i$$

$$\mathcal{H}_i = -\frac{\hbar^2}{2m_i}\nabla_i^2 + V_{CF}(r_i)$$

$V_{CF}(r_i)$: central field

$$E = E_1 + E_2 + \cdots$$

$$\psi = \psi_1, \psi_2 \cdots$$

Evaluate

$$V_{cf}(r_i) = ?$$

C $1s^2\ 2s^2\ 2p^2$

Hartree Self consistent field method "

$\psi_{n_1 l_1}(1)\ \psi_{n_2 l_2}(2)$

ψ_{1s}^{guess}

ψ_{2s}^{guess}

ψ_{2p}^{guess}

"self-consistency"

$$V_{eff}(1) = \int \psi^*_{n_2 l_2}(2) \frac{1}{r_{12}} \psi_{n_2 l_2}(2)\, d\tau_2 \qquad \hat{h}_i \psi_i = \epsilon_i \psi_i$$

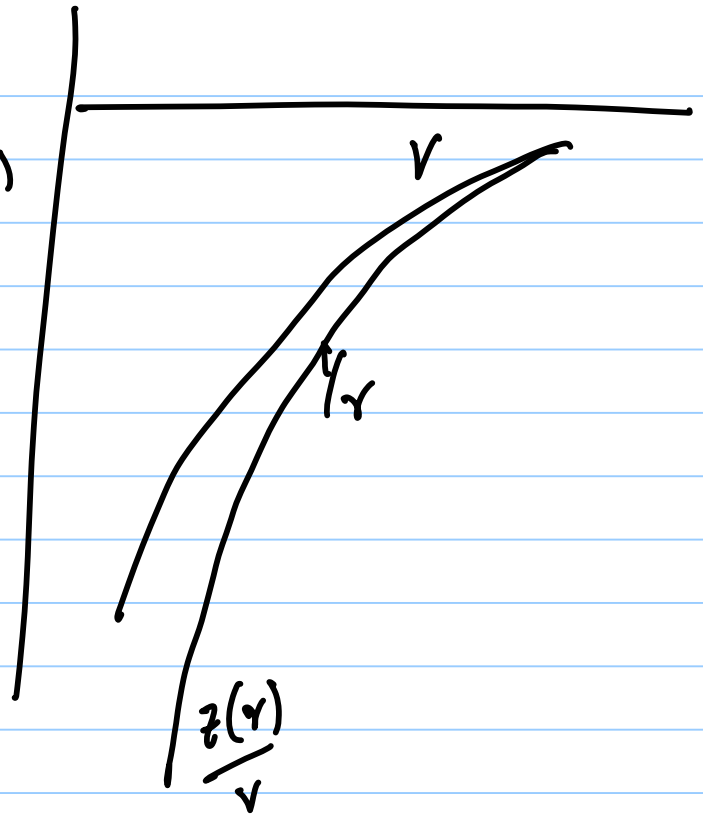
1) Guess some ψ based on intuition

2) Determine $V_{cf}(r_i)$

3) $\hat{h}\psi = E\psi$ and determine new ψ

$Z(r)$ is a function of r

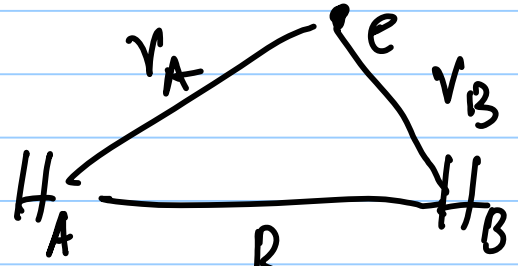
E becomes a function of l



Chemical bonding H_2^+

hybridization ← Valence bond theory – Heitler & London

Molecular Orbital theory – Mulliken & Hund



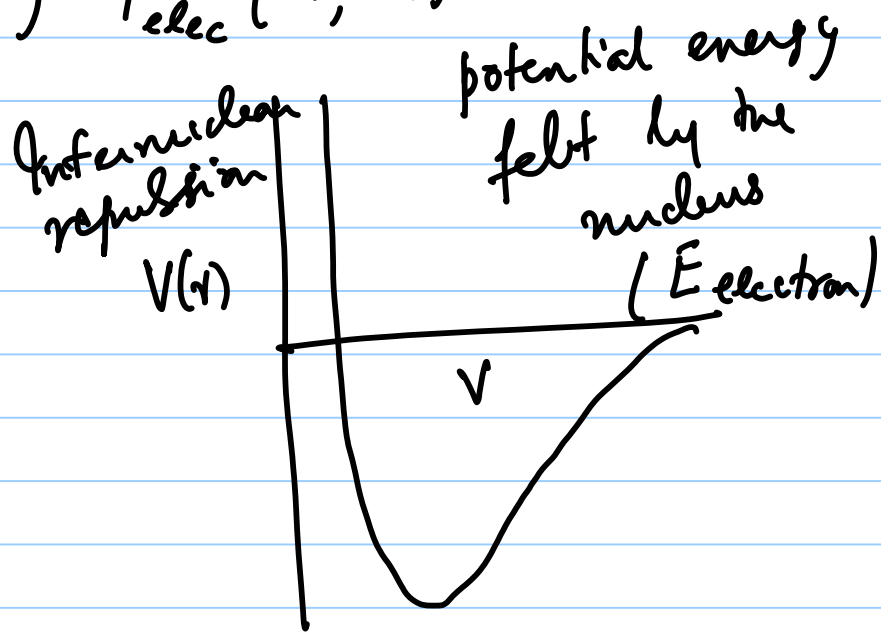
$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_A}\nabla_A^2}_{\text{nuclear energy}} \underbrace{-\frac{\hbar^2}{2m_B}\nabla_B^2}_{\text{kinetic } \hat{H}_{nucl}} \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}}_{\text{Helec}}$$

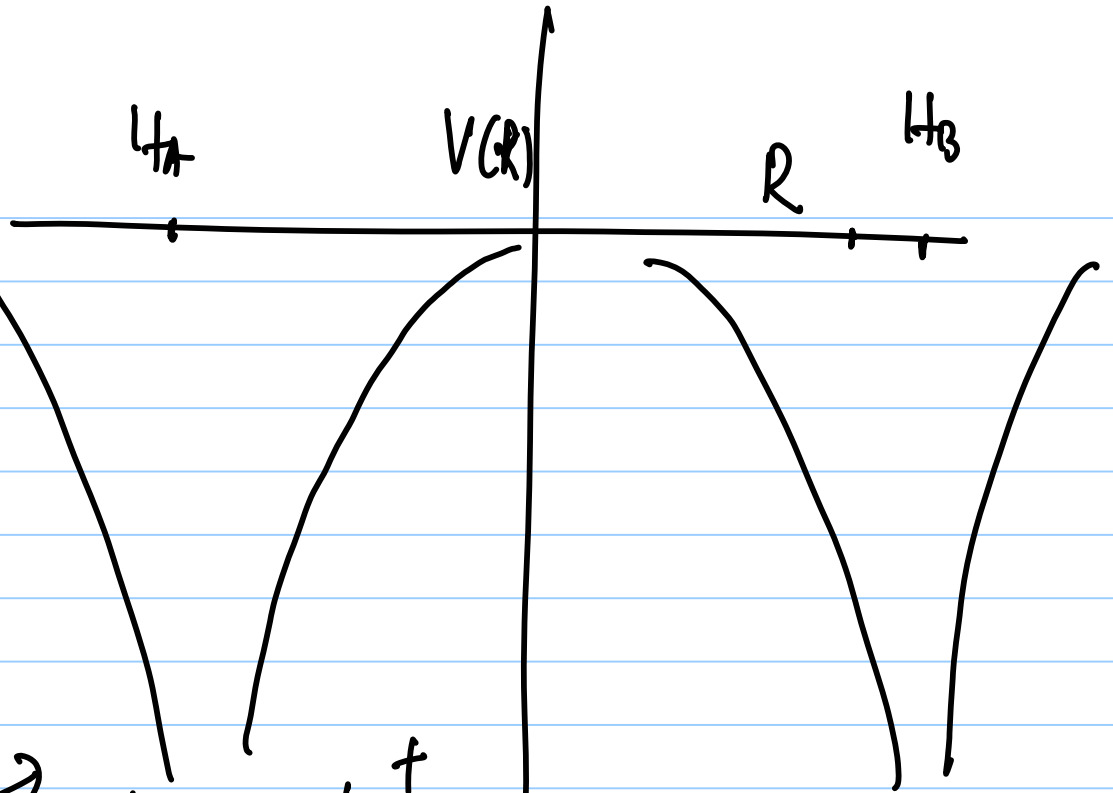
Given nuclear repulsion

$$\hat{H} = \hat{H}_{nucl} + \hat{H}_{elec}$$

Nucleus fixed (R) - Born - Oppenheimer approximation

$$\psi = \psi_{nucl}(R)\, \psi_{elec}(r; R)$$





$H_2^+ \rightarrow H_A + H_B^+ \rightarrow \varphi_{1s}(A)$

$\quad \hookrightarrow H_A^+ + H_B \rightarrow \varphi_{1s}(B)$

$a = \pm b$

$$a\,\varphi_{1s}(A) + b\,\varphi_{1s}(B)$$

$$\psi = a\left(\psi_{1s}(A) \pm \psi_{1s}(B)\right)$$

$$\langle E \rangle_{R=\infty} = \frac{\int \psi^* \mathcal{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$\text{Denominator} = \int \psi^* \psi \, d\tau$$

$$= a^2 \int \left(\psi_{1s}(A) + \psi_{1s}(B)\right)\left(\psi_{1s}(A) + \psi_{1s}(B)\right) d\tau_1 \, d\tau_2$$

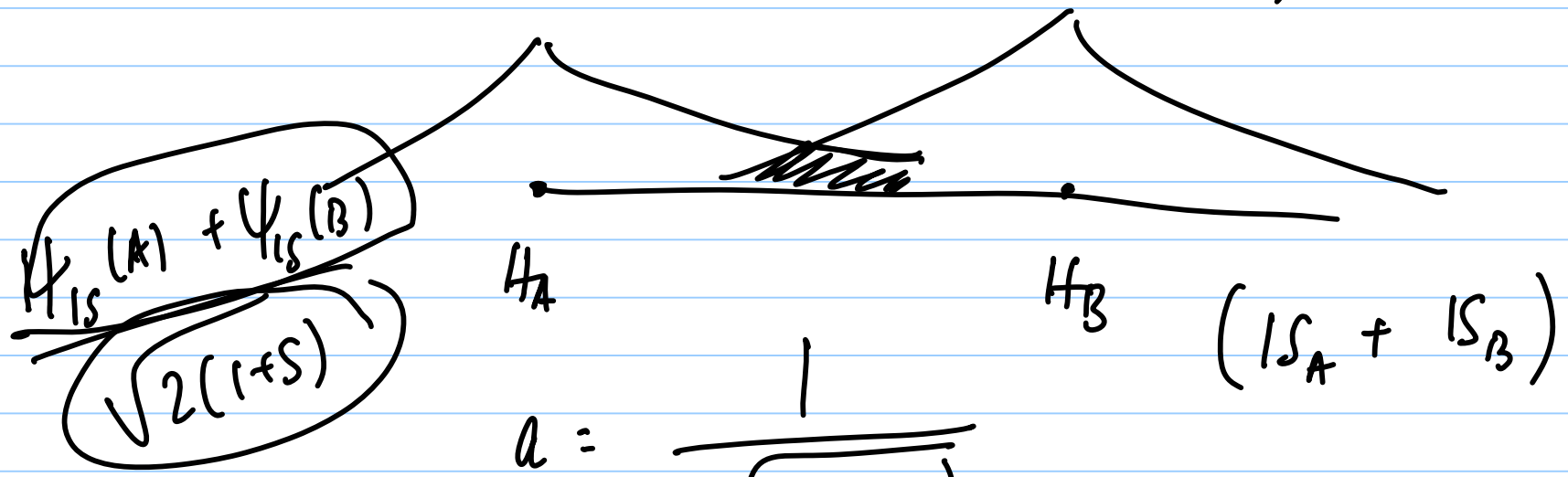
$$= a^2 \left\{ \int \psi_{1s}(A)\, \psi_{1s}(A)\, d\tau + \int \psi_{1s}(A)\, \psi_{1s}(B)\, d\tau \right.$$

$$\left. \int \psi_{1s}(B)\, \psi_{1s}(B)\, d\tau + \int \psi_{1s}(B)\, \psi_{1s}(A)\, d\tau \right\}$$

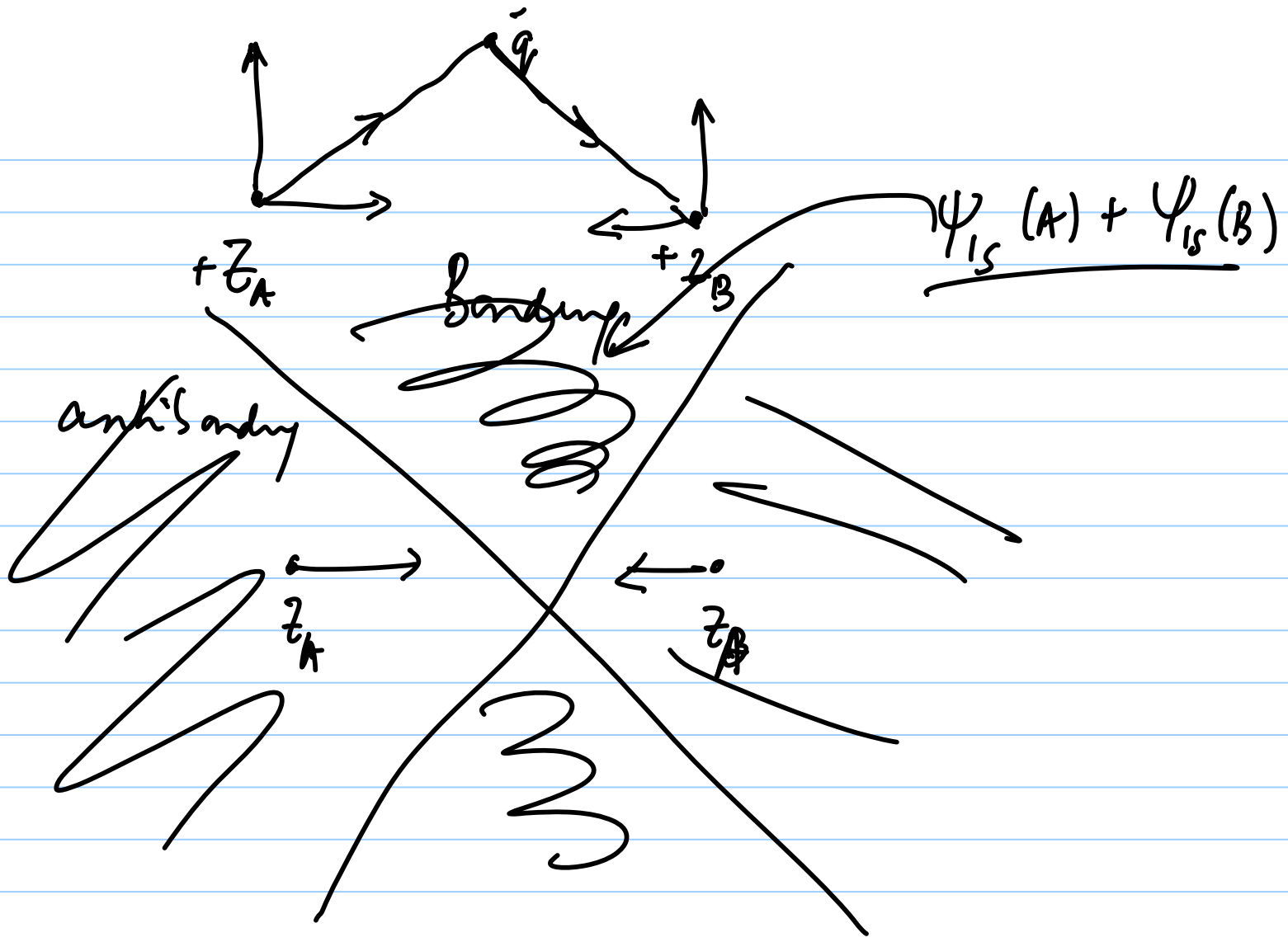
$$a = \frac{1}{\sqrt{2}}$$

$$S = \int 1s(A)\ 1s(B)\, dz$$

overlap of the functions



$$a = \frac{1}{\sqrt{2(1+S)}}$$


$\bar{q}$
$+z_A$
$+z_B$
$\psi_{1s}(A) + \psi_{1s}(B)$
bonding
antibonding
z_A
z_B

$$\langle E \rangle = \int \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right) \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)$$

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)$$

$$H\text{-atom} \quad \left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)$$

$$\int 1s_A \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A}\right) 1s_A + E_{H_{1s}(A)}$$

$$\int \left(1s_A \left(-\frac{1}{2}\nabla^2\right) 1s_B\right)$$

$$\int 1s_A \left(-\frac{1}{r_B}\right) 1s_A + \int 1s_A \frac{1}{R} 1s_A$$

$$+ \int 1s_A \left(-\frac{1}{r_A}\right) 1s_B + \int 1s_A \frac{1}{R} 1s_B$$