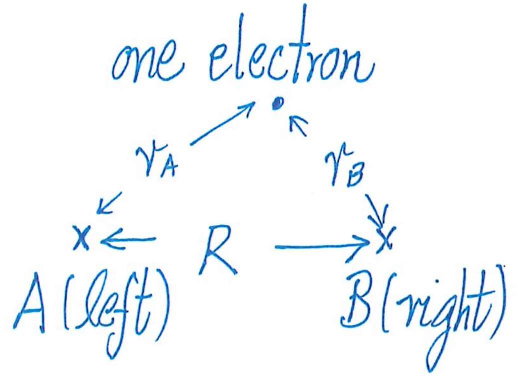
Appendix A : Quantum Nature of Bonding



- Electronic part of H_2^+ problem

$$\hat{H}_{electronic} = \hat{H} = \frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_A|} - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|} + \frac{e^2}{4\pi\varepsilon_0 R} \quad \text{(SI units)} \quad (A1)$$

save the subscript ($\hat{H}_{electronic}$); fixed ($\vec{R}_A$); fixed ($\vec{R}_B$); (see figure $|\vec{R}_A-\vec{R}_B|$) (R)

Task: $\underbrace{\text{Ground state}}_{\text{should involve hydrogen 1s atomic orbitals (left and right)}}$ (low-energy states)

centered at A →

$$\psi_{1s,A} = \psi_{1s}(\vec{r}-\vec{R}_A) \equiv \psi_A \quad ; \quad \psi_{1s,B} = \psi_{1s}(\vec{r}-\vec{R}_B) \equiv \psi_B$$

← centered at B

$$\hat{H}_{electronic} = \hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \quad (A2) \quad \text{(atomic units)}$$

- LCAO $\psi = c_A \psi_A + c_B \psi_B$ as trial wavefunction (A3)
- It follows from variational calculation using (A2) that

$$\boxed{\begin{pmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0 \quad (A4)}$$

to solve for E's and $\begin{pmatrix} c_A \\ c_B \end{pmatrix}$ for each E

Formally, $H_{AA} = \int \psi_A^* \hat{H} \psi_A \, d^3r$; $H_{BB} = \int \psi_B^* \hat{H} \psi_B \, d^3r$

$H_{AB} = \int \psi_A^* \hat{H} \psi_B \, d^3r$; $H_{BA} = \int \psi_B^* \hat{H} \psi_A \, d^3r = H_{AB}^*$

$S_{AA} = \int \psi_A^* \psi_A \, d^3r = 1 = S_{BB} = \int \psi_B^* \psi_B \, d^3r$ [normalized atomic orbitals]

$S_{AB} = \int \psi_A^* \psi_B \, d^3r = S_{BA}^* = S(R)$ [a function of R]

E.g. $H_{AB} = \int \psi_{1s}^*(\vec{r} - \vec{R}_A) \hat{H}(\vec{r}) \psi_{1s}(\vec{r} - \vec{R}_B) \, d^3r$; $S_{AB} = \int \psi_{1s}^*(\vec{r} - \vec{R}_A) \psi_{1s}(\vec{r} - \vec{R}_B) \, d^3r$ [long form]

- Look at H_{AA} and H_{BA}

$$H_{AA} = \int \psi^*_{1s}(\vec{r}-\vec{R}_A)\overbrace{\left[\frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_A|}\right]\psi_{1s}(\vec{r}-\vec{R}_A)}^{E_{1s}\,\psi_{1s}(\vec{r}-\vec{R}_A)\ \text{[c.f. TISE of atom at }\vec{R}_A\text{]}}\, d^3r$$

$$+ \underbrace{\int \psi^*_{1s}(\vec{r}-\vec{R}_A)\left[\frac{-e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|} + \frac{e^2}{4\pi\varepsilon_0 R}\right]\psi_{1s}(\vec{r}-\vec{R}_A)\, d^3r}_{J(R)\,\equiv\, J\ \text{(a function of } R\text{)}}$$

$$= \overbrace{E_{1s}}^{-13.6\text{eV}} + J = H_{BB}\ \text{(why?) [write it out]} \qquad \text{(A5)}$$

- $J(R)$ has classical interpretation (what is it?)
- For $\underbrace{\text{H-atom 1s}}_{\psi_{1s}(\vec{r}-\vec{R}_A)\,\sim\, e^{-\frac{|\vec{r}-\vec{R}_A|}{a_B}}}$, $J(R)$ can be evaluated analytically

$$H_{BA} = \int \psi^*_{1s}(\vec{r}-\vec{R}_B)\overbrace{\left[\frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_A|}\right]\psi_{1s}(\vec{r}-\vec{R}_A)}^{E_{1s}\,\psi_{1s}(\vec{r}-\vec{R}_A)}\,d^3r$$

$$+\underbrace{\int \underbrace{\psi^*_{1s}(\vec{r}-\vec{R}_B)}_{\text{atomic orbital centered at }\underline{\underline{\vec{R}_B}}}\left[\frac{-e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|} + \frac{e^2}{4\pi\varepsilon_0 R}\right]\underbrace{\psi_{1s}(\vec{r}-\vec{R}_A)}_{\text{atomic orbital centered at }\underline{\underline{\vec{R}_A}}}\,d^3r}_{K(R)\equiv K\ \ \text{(a function of } R\text{)}}$$

$$= E_{1s}\,S + K \qquad \text{(A6)} \qquad \left(\text{recall: } S(R) = \int \psi^*_{1s}(\vec{r}-\vec{R}_A)\,\psi_{1s}(\vec{r}-\vec{R}_B)\,d^3r\right)$$

- $K(R)$ does not have classical interpretation (entirely quantum)
- For H-atom 1s, $K(R)$ can be evaluated analytically
- K plays a key role in determining the bonding (and anti-bonding) MO

The 2x2 matrix equation (Eq. (A4)) becomes

$$\begin{pmatrix} E_{1S} + J - E & E_{1S}\cdot S + K - E\cdot S \\ E_{1S}\cdot S + K - E\cdot S & E_{1S} + J - E \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0 \qquad (A7)$$

Non-trivial solutions require

$$\begin{vmatrix} E_{1S} + J - E & E_{1S}\cdot S + K - E\cdot S \\ E_{1S}\cdot S + K - E\cdot S & E_{1S} + J - E \end{vmatrix} = 0 \qquad (A8) \quad \text{to solve for } E$$

$$\Rightarrow \quad E_{1S} + J - E = \pm \left(E_{1S} S + K - E\cdot S \right)$$

$$\Rightarrow \boxed{E = \begin{cases} E_{1S} + \dfrac{J-K}{1-S} \equiv E_- = E_-(R) \\ E_{1S} + \dfrac{J+K}{1+S} \equiv E_+ = E_+(R) \end{cases}} \quad \begin{matrix} \leftarrow -C_A = C_B \text{ (anti-bonding)} \\ (A9) \\ \leftarrow C_A = C_B \text{ (bonding)} \end{matrix}$$

Note: $K(R)$ could be negative

Aside: $S_{AB} = S(R) = \int \psi_A^*(\vec{r})\, \psi_B(\vec{r})\, d^3r$

- $S_{AB}(R) \neq 0$ in general ($\because$ $\psi_{1s}(\vec{r}-\vec{R}_A)$ and $\psi_{1s}(\vec{r}-\vec{R}_B)$ are centered at $\vec{R}_A, \vec{R}_B$)
- Atoms (Nuclei) very far away, $S(R) = 0$ ($\because$ no overlap)
- $S(R)$ enters in normalizing $\psi_+(\vec{r}) = C_+[\psi_A(\vec{r}) + \psi_B(\vec{r})]$

$$\int \psi_+^*(\vec{r})\, \psi_+(\vec{r})\, d^3r = 1 = C_+^2\left[1 + 1 + \int \psi_A^*(\vec{r})\psi_B(\vec{r})\,d^3r + \int \psi_B^*(\vec{r})\psi_A(\vec{r})\,d^3r\right]$$

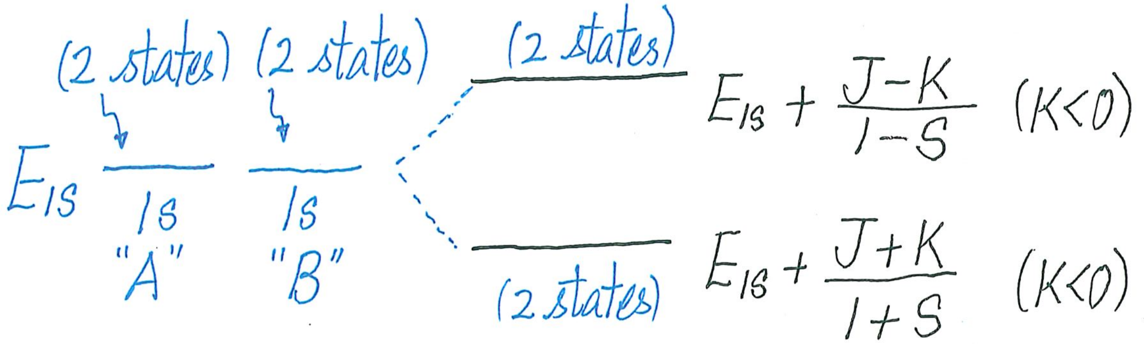
$$= C_+^2\,[2+2S] \quad (\because \text{ Real "1s" } \psi_A(\vec{r}) \text{ and } \psi_B(\vec{r}))$$

$$\Rightarrow C_+ = \frac{1}{\sqrt{2(1+S)}} \quad \left(\text{formally, } \sim \frac{1}{\sqrt{2}} \text{ for } S \ll 1\right)$$

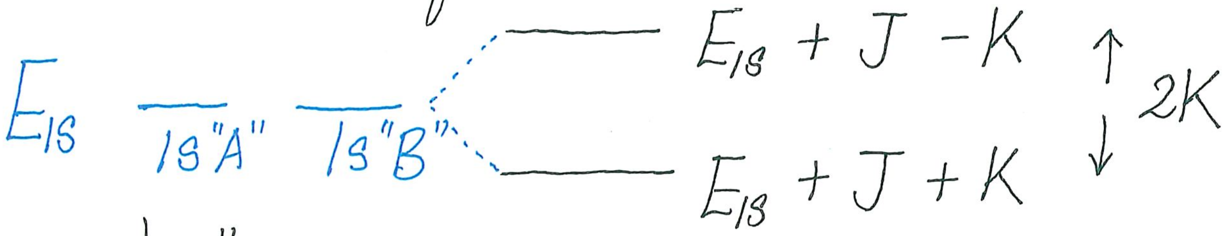
- For H-atom 1s orbitals, $S(R) = \underbrace{e^{-R}}_{\text{drops rapidly with separation}}\left[1 + R + \frac{R^2}{3}\right]$ (atomic units)

(so $S \approx 0$ not bad)

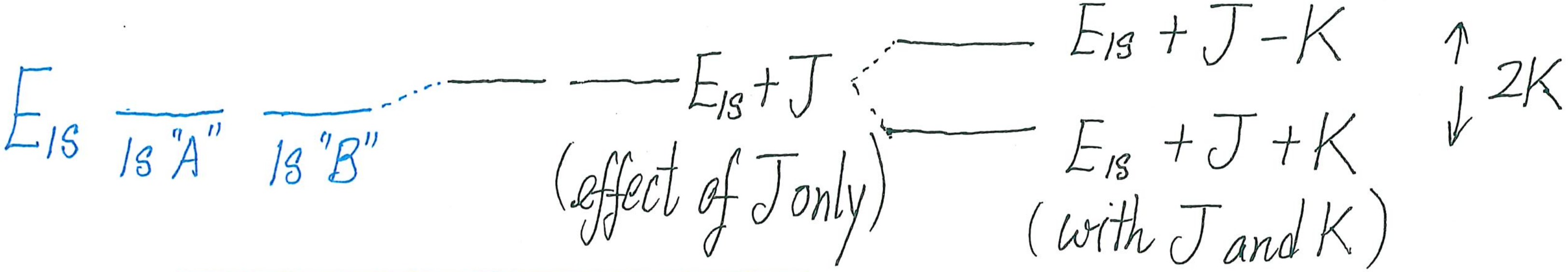
Back to Eq.(9)



Taking $S(R) \approx 0$ at H_2^+ equilibrium separation



OR in "slow motion"



∴ Integral K(R) plays a crucial role in giving the bonding MO and bonding.

(Key concept)

Bonding is Quantum Mechanical

$$K(R) = \int \underbrace{\psi^*_{1s}(\vec{r}-\vec{R}_B)}_{\text{centered at } \vec{R}_B} \left[\frac{-e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|}\right] \underbrace{\psi_{1s}(\vec{r}-\vec{R}_A)}_{\text{centered at } \vec{R}_A} d^3r + \frac{e^2}{4\pi\varepsilon_0 R} S(R) \quad \text{(see Eq. (A6))}$$

- No classical interpretation $\Rightarrow$ $\underbrace{K(R)}_{\text{"Exchange integral" (c.f. helium atom excited states)}}$ is entirely Quantum
- Originated from $\psi_\pm \sim [\psi_{1s}(\vec{r}-\vec{R}_A) \underset{\substack{\uparrow \\ \text{Superposition (a signature of QM)}}}{\pm} \psi_{1s}(\vec{r}-\vec{R}_B)] \sim [\psi_A \pm \psi_B]$

$\therefore$ Bonding $\underbrace{\text{(K(R) is crucial) is a Quantum effect}}$

This point should be appreciated. [This point is often missed in Chemistry courses.]

Should contrast with $J(R)$:

$$J(R) = \int \psi_{1s}^{*}(\vec{r}-\vec{R}_A)\left[\frac{-e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|}\right]\psi_{1s}(\vec{r}-\vec{R}_A)\,d^3r + \frac{e^2}{4\pi\varepsilon_0 R} \quad \text{(see Eq. (A5))}$$

$$= \int \frac{(+e)\cdot\left(-e\,|\psi_{1s}(\vec{r}-\vec{R}_A)|^2\right)}{4\pi\varepsilon_0|\vec{r}-\vec{R}_B|}\,d^3r \quad + \frac{e^2}{4\pi\varepsilon_0 R}$$

$-e\,|\psi_{1s}(\vec{r}-\vec{R}_A)|^2\,d^3r$ = bit of electron charge at $\vec{r}$ in 1s orbital centered at atom A in d^3r

1st Term: Electron residing in atom A's 1s orbital sees nucleus B (potential energy) (and vice versa)

⇒ $J(R)$ has classical EM interpretation (c.f. direct integral in helium atom)

This is the textbook explanation of bonding (covalent).

But we saw that $J(R)$ is not the crucial part for bonding.

For H-atom 1s atomic orbitals:

$$K(R) = -e^{-R}\left[1+R\right] + \frac{1}{R}S(R)$$

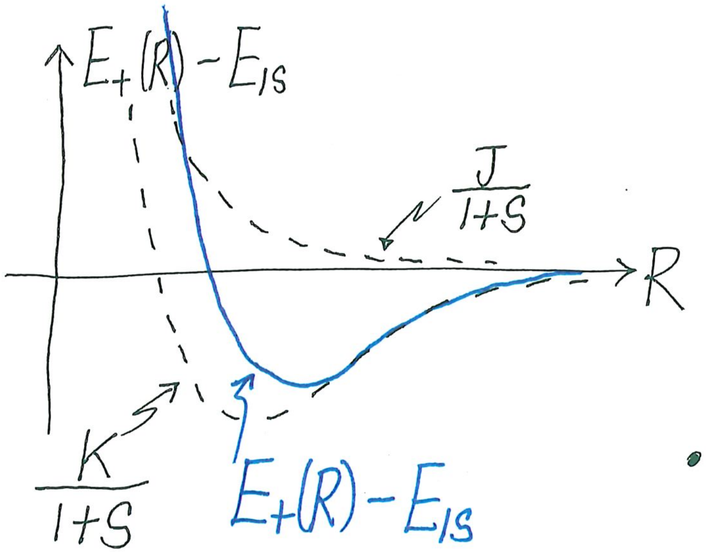
$$J(R) = e^{-2R}\left[1+\frac{1}{R}\right] \qquad \text{(A10)} \quad \text{[in atomic units]}$$

$$S(R) = e^{-R}\left[1+R+\frac{R^2}{3}\right]$$

[students are not expected to know how to evaluate K(R), J(R), S(R)]

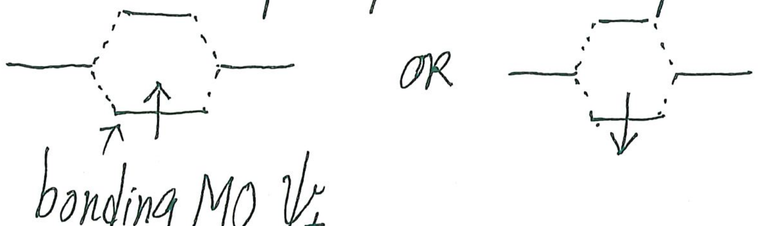
Recall: $E_+(R) = E_{1s} + \frac{J}{1+S} + \frac{K}{1+S}$ (bonding MO)

$E_-(R) = E_{1s} + \frac{J}{1-S} - \frac{K}{1-S}$ (anti-bonding MO)



This is the behavior of K(R) that leads to the stability of the bonding MO.

- Only one electron in H_2^+
- Ground state: $\psi_+(\vec{r})\cdot\underbrace{\alpha}_{\text{spin-up}}$ OR $\psi_+(\vec{r})\cdot\underbrace{\beta}_{\text{spin-down}}$



This is the basic idea of the $\underbrace{\underline{\text{Molecular Orbital Theory}}}_{\text{single-electron states in molecule for filling in electrons}}$ (MO Theory)

MPI-App-(A12)

Robert S. Mulliken and Friedrich Hund[+] developed Molecular Orbital Theory

- 1927 at Göttingen (worked in Born's group)
- Mulliken developed LCAO

1966 Nobel Chemistry Prize to Mulliken
"for his fundamental work concerning bonds and the electronic structure of molecules by the molecular orbital theory"

[Hund was left out, but Mulliken said he would have glady shared the Prize with Hund.]

Mulliken (left) and Hund

[+] Hund's contributions also included the Hund's rules.