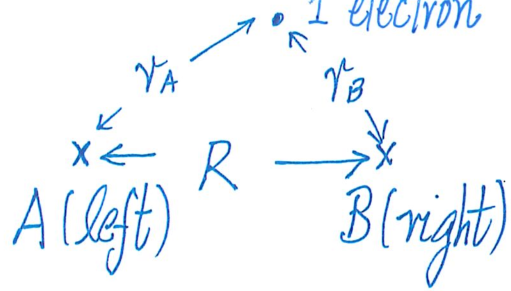
Appendix A: Quantum Nature of Bonding (Quantitative)

- Electronic part of H_2^+ problem



$$\underset{\substack{\uparrow\\ \text{save the subscript}}}{\hat{H}_{\text{electronic}}} = \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\underset{\substack{\uparrow\\ \text{fixed}}}{\vec{R}_A}|} - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\underset{\substack{\uparrow\\ \text{fixed}}}{\vec{R}_B}|} + \frac{e^2}{4\pi\varepsilon_0 \underset{\substack{\uparrow\\ (\text{see figure } |\vec{R}_A-\vec{R}_B|)}}{R}} \quad \text{(SI units)} \quad (A1)$$

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

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

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

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

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

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

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

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

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

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

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

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

$$H_{AA} = \int \psi_{1s}^*(\vec{r}-\vec{R}_A)\overbrace{\left[\frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0|\vec{r}-\vec{R}_A|}\right]\psi_{1s}(\vec{r}-\vec{R}_A)}^{\overset{-13.6\,\text{eV}}{\overbrace{E_{1s}}}\,\psi_{1s}(\vec{r}-\vec{R}_A)\ \text{[c.f. TISE of atom at } \vec{R}_A\text{]}}\, d^3r$$

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

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

- $J(R)$ has classical interpretation (what is it?) (see $|\psi_{1s}(\vec{r}-\vec{R}_A)|^2$)
- 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

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

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

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

- $K(R)$ does <u>not</u> 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

$$\begin{vmatrix} E_{1s}+J-E & E_{1s}\cdot S+K-E\cdot S \\ E_{1s}\cdot S+K-E\cdot S & E_{1s}+J-E \end{vmatrix} = 0 \qquad (A8)$$

to solve for E

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

$$\Rightarrow \quad E = \begin{cases} E_{1s} + \dfrac{J-K}{1-S} \equiv E_{-} = E_{-}(R) \\[2ex] E_{1s} + \dfrac{J+K}{1+S} \equiv E_{+} = E_{+}(R) \end{cases} \qquad (A9)$$

$-C_A = C_B$ (anti-bonding)

$C_A = C_B$ (bonding)

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 $\psi_+(\vec{r}) = C_+\left[\psi_A(\vec{r}) + \psi_B(\vec{r})\right]$

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

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

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

- 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)

Therefore, the bonding combination is

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}\left(\psi_{1s}(\vec{r}-\vec{R}_A) + \psi_{1s}(\vec{r}-\vec{R}_B)\right) = \frac{1}{\sqrt{2(1+S)}}(\psi_A + \psi_B)$$

(properly normalized)

Only when $S \approx 0$, then $\psi_+ \cong \frac{1}{\sqrt{2}}(\psi_A + \psi_B)$

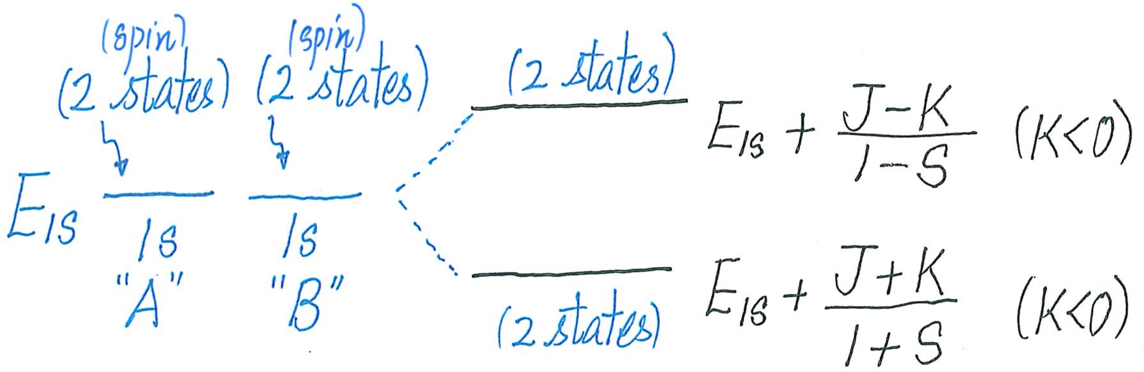
$E_+(R)$ can be obtained from ψ_+ by $\langle \psi_+ | \hat{H} | \psi_+ \rangle$

Similarly, $\psi_- = \frac{1}{\sqrt{2(1-S)}}(\psi_A - \psi_B)$ (properly normalized)

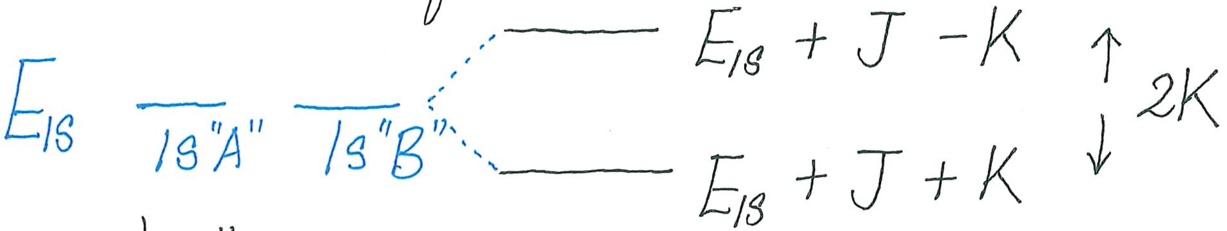
Only when $S \approx 0$, then $\psi_- \cong \frac{1}{\sqrt{2}}(\psi_A - \psi_B)$

$E_-(R)$ can be obtained from ψ_- by $\langle \psi_- | \hat{H} | \psi_- \rangle$

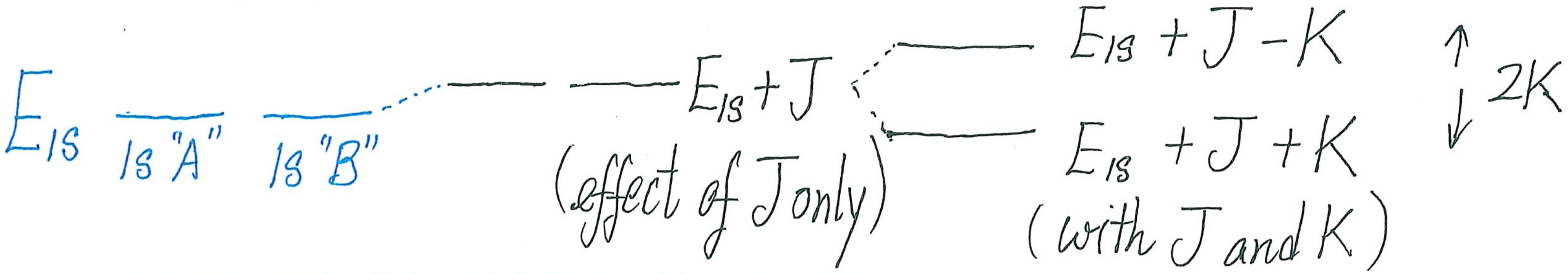
Back to Eq. (A9)



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



OR in "slow motion"



$\boxed{\because \text{ Integral } K(R) \text{ plays a crucial role in giving the bonding MO and bonding}}$

c.f. Exchange term

(Key concept)

"J(R)" integral is NOT crucial!

Bonding is Quantum Mechanical

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

- No classical interpretation ⇒ $\underbrace{K(R)}_{\text{"Exchange integral"}}$ is entirely Quantum

  "Exchange integral" (c.f. helium atom excited states)

- Originated from $\psi_\pm \sim [\psi_{1s}(\vec{r}-\vec{R}_A) \underset{\substack{\uparrow \\ \text{Superposition (a signature of QM)}}}{\pm} \psi_{1s}(\vec{r}-\vec{R}_B)] \sim [\psi_A \pm \psi_B]$

∴ 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 $J(R)$:

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

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

$-e|\psi_{1s}(\vec{r}-\vec{R}_A)|^2 d^3r$ = 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), J(R), S(R) have closed forms[+]:

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

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

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

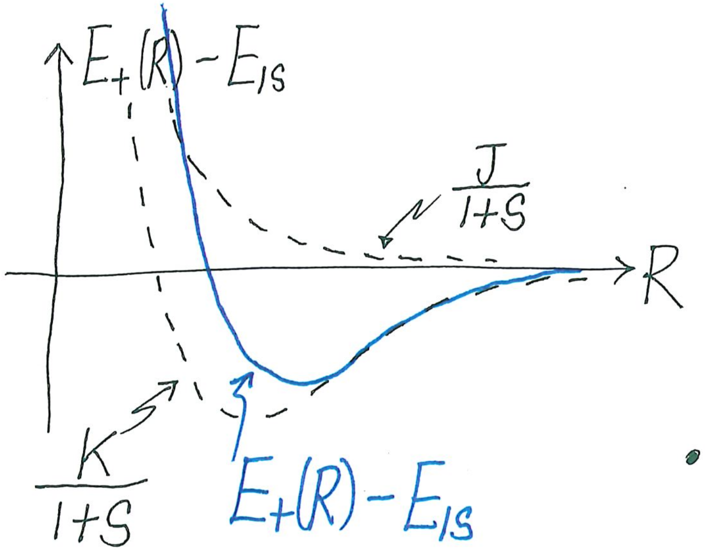
[students are <u>not</u> expected to know how to evaluate K(R), J(R), S(R)]

Recall:

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

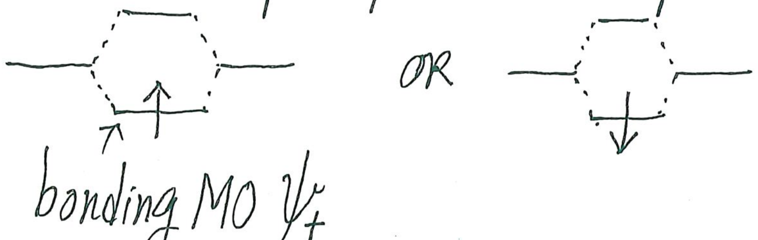
$$E_-(R) = E_{1s} + \frac{J}{1-S} - \frac{K}{1-S} \qquad \text{(anti-bonding MO)}$$

[+] Students are not supposed to know how to derive the closed forms.



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

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



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

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

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

Mulliken (left) and Hund

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.]

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