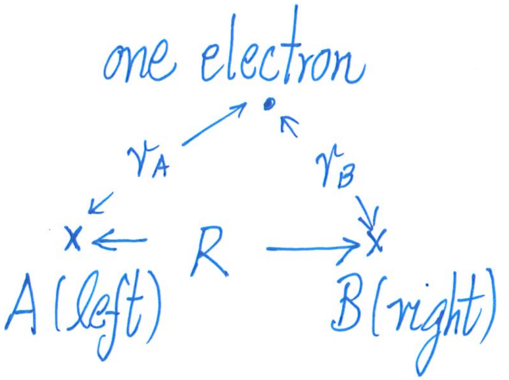
Appendix A : Quantum Nature of Bonding

- Electronic part of H_2^+ problem



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

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

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

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

- LCAO $\quad \psi = c_A \psi_A + c_B \psi_B$ 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, $H_{AA} = \int \psi_A^* \hat{H} \psi_A \, d^3r$; $H_{BB} = \int \psi_B^* \hat{H} \psi_B \, d^3r$

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

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

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

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

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

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

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

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

- $J(R)$ 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

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

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

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

- $K(R)$ 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

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

Non-trivial solutions require

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

to solve for E

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

$$\Rightarrow \boxed{E = \begin{cases} E_{1S} + \dfrac{J-K}{1-S} \equiv E_- = E_-(R) & \longleftarrow -C_A = C_B \text{ (anti-bonding)} \\[2ex] E_{1S} + \dfrac{J+K}{1+S} \equiv E_+ = E_+(R) & \longleftarrow C_A = C_B \text{ (bonding)} \end{cases}} \tag{A9}$$

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

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

$$= C_+^2\left[2 + 2S\right]$$

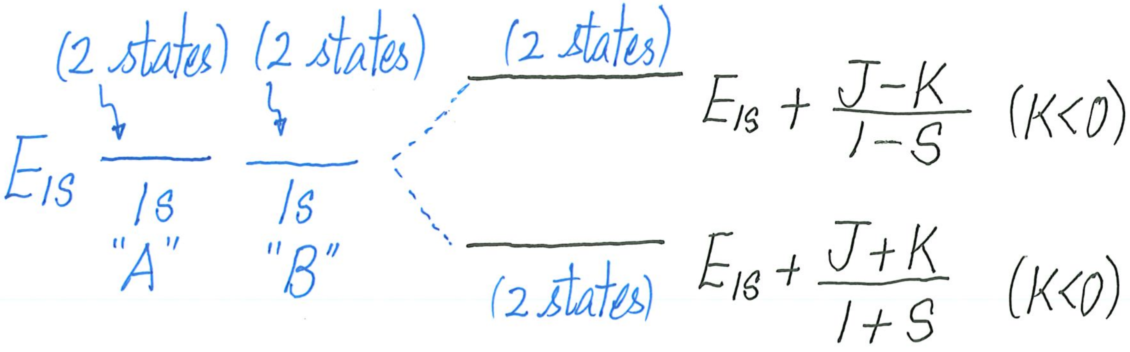
($\because$ Real "1s" $\psi_A(\vec{r})$ and $\psi_B(\vec{r})$)

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

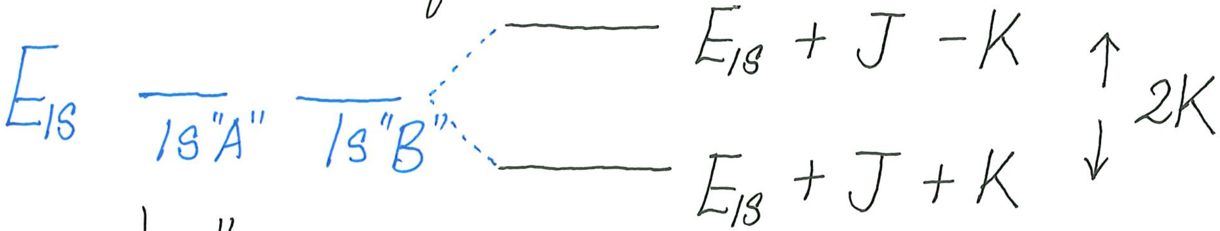
(formally, $\sim \frac{1}{\sqrt{2}}$ for $S \ll 1$)

- For H-atom 1s orbitals, $S(R) = \underbrace{e^{-R}}_{\text{drops rapidly with separation (so } S \approx 0 \text{ not bad)}}\left[1 + R + \frac{R^2}{3}\right]$ (atomic units)

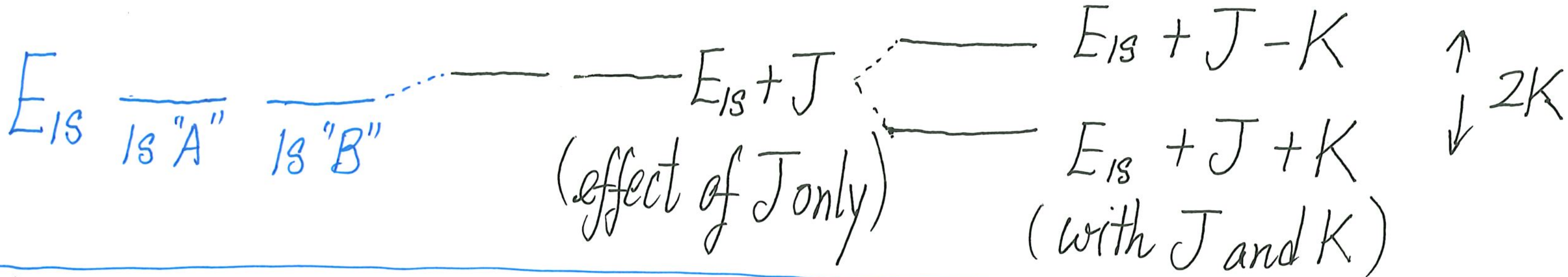
Back to Eq.(9)



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



OR in "slow motion"



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

(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 ⇒ $\underbrace{K(R)}_{\text{"Exchange integral"}}$ is entirely Quantum

  (c.f. helium atom excited states)

- Originated from $\psi_\pm \sim \left[\psi_{1s}(\vec{r}-\vec{R}_A) \underset{\uparrow}{\pm} \psi_{1s}(\vec{r}-\vec{R}_B)\right] \sim \left[\psi_A \pm \psi_B\right]$

  Superposition (a signature of QM)

∴ 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:

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

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

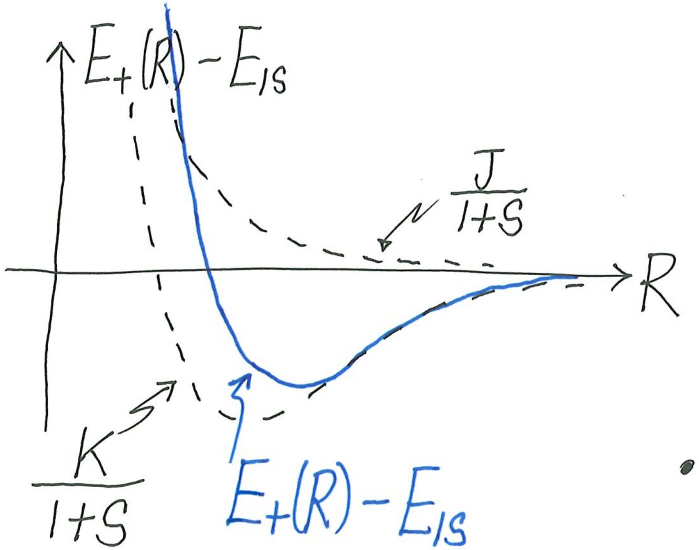
$$S(R) = e^{-R}\left[1+R+\frac{R^2}{3}\right]$$

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

Recall:

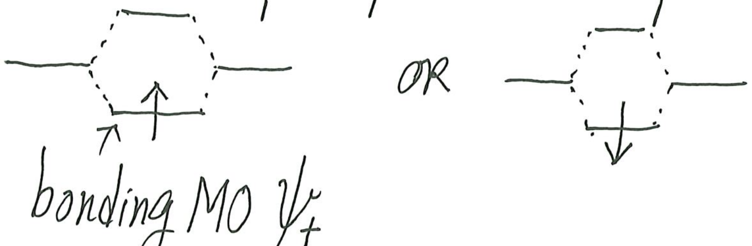
$$E_+(R) = E_{1S} + \frac{J}{1+S} + \frac{K}{1+S} \qquad \text{(bonding MO)}$$

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



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 $\underbrace{\text{Molecular Orbital Theory}}_{\text{single-electron states in molecule for filling in electrons}}$ (MO Theory)

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

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

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.

An interesting comment by Dirac in 1929 on physics and chemistry

P. A. M. Dirac, Proceedings of the Royal Society A 123, 714 (1929)
(p. 714 - 733)

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Should appreciate that up to now, work and progress continue to be made in how to perform QM calculations more accurately and efficiently for the understanding of molecules (many biology related)

Already before the arrival of quantum mechanics there existed a theory of atomic structure, based on Bohr's ideas of quantised orbits, which was fairly successful in a wide field. To get agreement with experiment it was found