Chapter 17

Molecular Bonding

Molecular Schrödinger equation

r - nuclei
s - electrons

$$\sum_{j=1}^{r}\frac{1}{M_j}\nabla_j^2\psi+\frac{1}{m_0}\sum_{i=1}^{s}\nabla_i^2\psi+\frac{2}{\hbar^2}\left(W-V\right)\psi=0$$

M_j = mass of j^{th} nucleus
m_0 = mass of electron
∇_j^2 = Laplace operator for nuclei
∇_i^2 = Laplace operator for electrons

$$V=\sum_{i,i'}\frac{e^2}{4\pi\varepsilon_0 r_{ii'}}+\sum_{j,j'}\frac{Z_jZ_{j'}e^2}{4\pi\varepsilon_0 r_{jj'}}-\sum_{i,j}\frac{Z_je^2}{4\pi\varepsilon_0 r_{ij}}$$

Coulomb potential

electron-electron repulsion

nuclear-nuclear repulsion

electron-nuclear attraction

Born-Oppenheimer Approximation

Electrons very light relative to nuclei ⟶ they move very fast.

In the time it takes nuclei to change position a significant amount,
electrons have "traveled their full paths."

Therefore,
Fix nuclei - calculate electronic eigenfunctions and energy for fixed nuclear positions.
Then move nuclei, and do it again.

The resulting curve is the energy as a function of internuclear separation.
If there is a minimum – bond formation.

Born-Oppenheimer Approximation

Separation of total Schrödinger equation into an

electronic equation and a

nuclear equation

is obtained by expanding the total Schrödinger equation in powers of $\left(m_0/M\right)^{1/4}$

M – average nuclear mass, m_0 - electron mass.

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1) **Not exact**
2) **Good approximation for many problems**
3) **Many important effects are due to the "break down" of the Born-Oppenheimer approximation.**

Born-Oppenheimer Approximate wavefunction

$$\psi_{n\nu}\left(x,\gamma\right)=\psi_{n}\left(x,\gamma\right)\psi_{n\nu}\left(\gamma\right)$$

electronic coordinates

nuclear coordinates

electronic wavefunction depends on electronic quantum number, *n*

nuclear wavefunction depends on electronic quantum number, *n* and nuclear (vibrational) quantum number, ν

Electronic wavefunction

$\psi_n(x,\gamma)$ depends on fixed nuclear coordinates, γ.

Obtained by solving "electronic Schrödinger equation"
for fixed nuclear positions, γ.

No nuclear kinetic energy term.

$$\sum_i^S \nabla_i^2 \psi_n(x,\gamma) + \frac{2M_0}{\hbar^2}\left[U_n(\gamma) - V(x,\gamma)\right]\psi_n(x,\gamma) = 0$$

The energy

$U_n(\gamma)$

depends on the nuclear coordinates and the electronic quantum number.

The potential function

$V(x,\gamma)$

complete potential function for fixed nuclear coordinates.

Solve, change nuclear coordinates, solve again.

Solve electronic wave equation

Nuclear Schrödinger equation becomes

$$\sum_{j=1}^{r} \frac{1}{M_j} \nabla_j^2 \psi_{n\nu}(\gamma) + \frac{2}{\hbar^2}\left[E_{n,\nu} - U_n(\gamma) \right] \psi_{n\nu}(\gamma) = 0$$

$U_n(\gamma)$ - **the electronic energy as a function of nuclear coordinates, γ, acts as the potential function.**

Before examining the hydrogen molecule ion and the hydrogen molecule need to discuss matrix diagonalization with non-orthogonal basis set.

Two states $\left|A\right\rangle$ and $\left|B\right\rangle$ orthonormal

No interaction

$$\underline{H}^{0}\left|A\right\rangle = E_A\left|A\right\rangle$$

$$\underline{H}^{0}\left|B\right\rangle = E_B\left|B\right\rangle$$

States have same energy:

$$E_A = E_B = E_0$$

Degenerate

With interaction of magnitude γ

$$\underline{H}\left|A\right\rangle = E_0\left|A\right\rangle + \gamma\left|B\right\rangle$$

$$\underline{H}\left|B\right\rangle = E_0\left|B\right\rangle + \gamma\left|A\right\rangle$$

The matrix elements are

$$\left\langle A\middle|\underline{H}\middle|A\right\rangle = E_0 \qquad H_{AA}$$

$$\left\langle B\middle|\underline{H}\middle|A\right\rangle = \gamma \qquad H_{BA}$$

$$\left\langle A\middle|\underline{H}\middle|B\right\rangle = \gamma \qquad H_{AB}$$

$$\left\langle B\middle|\underline{H}\middle|B\right\rangle = E_0 \qquad H_{BB}$$

Hamiltonian Matrix

$$\underline{\underline{H}} = \begin{array}{c|cc} & |A\rangle & |B\rangle \\ \hline \langle A| & E_0 & \gamma \\ \langle B| & \gamma & E_0 \end{array} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

Matrix diagonalization -
form secular determinant

$$\begin{vmatrix} E_0 - \lambda & \gamma \\ \gamma & E_0 - \lambda \end{vmatrix} = 0$$

Energy Eigenvalues

$$\lambda_+ = E_0 + \gamma$$

$$\lambda_- = E_0 - \gamma$$

Eigenvectors

$$|+\rangle = \frac{1}{\sqrt{2}}|A\rangle + \frac{1}{\sqrt{2}}|B\rangle \qquad |-\rangle = \frac{1}{\sqrt{2}}|A\rangle - \frac{1}{\sqrt{2}}|B\rangle$$

Matrix Formulation - Orthonormal Basis Set

eigenvalues

$$\sum_{j=1}^{N}\left(a_{ij}-\alpha\,\delta_{ij}\right)u_j=0 \qquad \left(i=1,2\cdots N\right)$$

vector representative of eigenvector

This represents a system of equations

$$\left(a_{11}-\alpha\right)u_1+a_{12}u_2+a_{13}u_3+\cdots \quad =0$$

$$a_{21}u_1+\left(a_{22}-\alpha\right)u_2+a_{23}u_3+\cdots \quad =0$$

$$a_{31}u_1+a_{32}u_2+\left(a_{33}-\alpha\right)u_3+\cdots \quad =0$$

only has solution if

$$\begin{vmatrix} (a_{11}-\alpha) & a_{12} & a_{13} & \cdot & \cdot & \cdot \\ a_{21} & (a_{22}-\alpha) & a_{23} & \cdot & \cdot & \cdot \\ a_{31} & a_{32} & (a_{33}-\alpha) & & & \\ \cdot & & & \cdot & & \\ \cdot & & & & \cdot & \\ \cdot & & & & & \cdot \end{vmatrix}=0$$

Basis Set Not Orthogonal but Normalized

overlap

Basis vectors not orthogonal $\langle i | j \rangle = \Delta_{ij} \neq 0$ Equals 1 if $i = j$.

In Schrödinger representation $\Delta_{ij} = \int \psi_i^* \psi_j \, d\tau \neq 0$

$$\sum_{j=1}^{N} \left(a_{ij} - \alpha \Delta_{ij} \right) u_j = 0 \qquad \left(i = 1, 2 \cdots N \right)$$

system of equations

↓ only has solution if

$$\begin{vmatrix} (a_{11}-\alpha) & (a_{12}-\Delta_{12}\alpha) & (a_{13}-\Delta_{13}\alpha) & \cdot & \cdot & \cdot \\ (a_{21}-\Delta_{21}\alpha) & (a_{22}-\alpha) & (a_{23}-\Delta_{23}\alpha) & \cdot & \cdot & \cdot \\ (a_{31}-\Delta_{31}\alpha) & (a_{32}-\Delta_{32}\alpha) & (a_{33}-\alpha) & & & \\ \cdot & & & \cdot & & \\ \cdot & & & & \cdot & \\ \cdot & & & & & \cdot \end{vmatrix} = 0$$

For a 2×2 matrix with non-orthogonal basis set

$$\begin{vmatrix} H_{AA} - E & H_{AB} - \Delta \cdot E \\ H_{BA} - \Delta \cdot E & H_{BB} - E \end{vmatrix} = 0$$

$E \longrightarrow$ eigenvalues

$\Delta \longrightarrow$ overlap integral

$\Delta \longrightarrow 0$, recover standard 2×2 determinant for orthogonal basis.

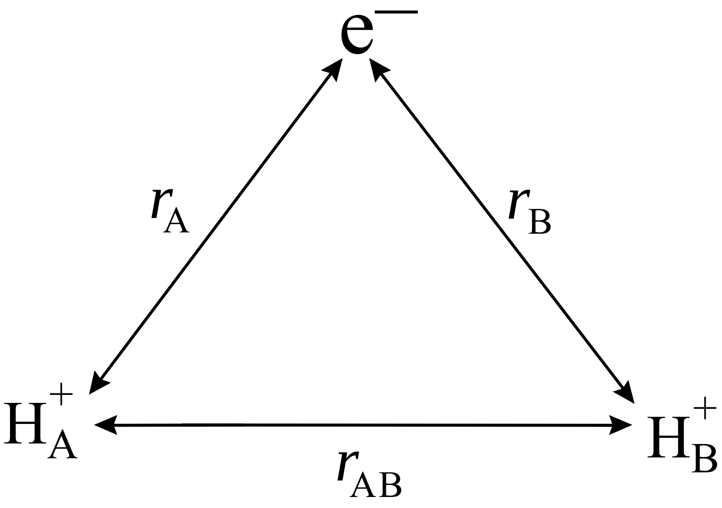
$$E_S = \frac{H_{AA} + H_{AB}}{1 + \Delta}$$

$$E_A = \frac{H_{AA} - H_{AB}}{1 - \Delta}$$

$$\psi_S = \frac{1}{\sqrt{2 + 2\Delta}} \left(|A\rangle + |B\rangle \right)$$

$$\psi_A = \frac{1}{\sqrt{2 - 2\Delta}} \left(|A\rangle - |B\rangle \right)$$

Hydrogen Molecule Ion - Ground State
A simple treatment



Born-Oppenheimer Approximation electronic Schrödinger equation

$$\nabla^2\psi + \frac{2m_0}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r_A} + \frac{e^2}{4\pi\varepsilon_0 r_B} - \frac{e^2}{4\pi\varepsilon_0 r_{AB}}\right)\psi = 0$$

∇^2 - refers to
electron coordinates
electron kinetic energy

Have multiplied through by $-\frac{2m_0}{\hbar^2}$

Large nuclear separations

$r_{\mathrm{AB}} \longrightarrow \infty$ System looks like H atom and H^+ ion

Energy

$$E = E_H = -Rhc = -13.6 \text{ eV}$$

Ground state wavefunctions

U_{1s_A} U_{1s_B}

Either H atom at A in 1s state with H^+ at B or
H atom at B in 1s state with H^+ at A

U_{1s_A} and U_{1s_B} degenerate

Suggests simple treatment involving

$$U_{1s_A} \quad \text{and} \quad U_{1s_B}$$

as basis functions ⟶ not orthogonal

Form 2×2 Hamiltonian matrix and corresponding secular determinant.

$$\begin{vmatrix} H_{AA} - E & H_{AB} - \Delta \cdot E \\ H_{BA} - \Delta \cdot E & H_{BB} - E \end{vmatrix} = 0$$

$E \longrightarrow$ eigenvalues

$\Delta \longrightarrow$ overlap integral

$$H_{AA} = \int U_{1s_A}^{*} \underline{H}\, U_{1s_A} d\tau \qquad H_{AA} = H_{BB}$$

$$H_{BA} = \int U_{1s_B}^{*} \underline{H}\, U_{1s_A} d\tau \qquad H_{AB} = H_{BA}$$

$$\Delta = \int U_{1s_A}^{*} U_{1s_B} d\tau$$

Energies and Eigenfunctions

$$E_S = \frac{H_{AA} + H_{AB}}{1 + \Delta}$$

$$E_A = \frac{H_{AA} - H_{AB}}{1 - \Delta}$$

$$\psi_S = \frac{1}{\sqrt{2 + 2\Delta}}\left(U_{1s_A} + U_{1s_B}\right)$$

$$\psi_A = \frac{1}{\sqrt{2 - 2\Delta}}\left(U_{1s_A} - U_{1s_B}\right)$$

S **- symmetric (+ sign)** ***A*** **- antisymmetric (- sign)**

(Not really symmetric and antisymmetric because only one electron.)

Evaluation of Matrix Elements

Need H_{AA}, H_{AB}, and Δ

$$H_{AA} = \int U^{*}_{1s_A} \underline{H} \, U_{1s_A} d\tau$$

$$\underline{H} = -\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}$$

Part of $\underline{H}$ looks like Hydrogen atom Hamiltonian

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right) U_{1s_A} = E_H U_{1s_A}$$

These terms operating on U_{1s_A} can be set equal to $E_H U_{1s_A}$,
E_H - energy of 1s state of H atom.

Then

$$H_{AA}=\int U_{1s_A}^{*}\left(E_H-\frac{e^2}{4\pi\varepsilon_0 r_B}+\frac{e^2}{4\pi\varepsilon_0 r_{AB}}\right)U_{1s_A}\,d\tau$$

$$H_{AA}=E_H+J+\frac{e^2}{4\pi\varepsilon_0 a_0 D}$$

$$J=\int U_{1s_A}^{*}\left(-\frac{e^2}{4\pi\varepsilon_0 r_B}\right)U_{1s_A}\,d\tau$$ (Coulomb Integral)

$$J=\frac{e^2}{4\pi\varepsilon_0 a_0}\left[-\frac{1}{D}+e^{-2D}\left(1+\frac{1}{D}\right)\right]$$

$$D=\frac{r_{AB}}{a_0}$$ distance in units of the Bohr radius

$$a_0=\frac{\varepsilon_0 h^2}{\pi\mu e^2}$$

$$H_{BA} = \int U_{1s_B}^{*}\left(E_H - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}\right)U_{1s_A}\,d\tau$$

(Again collecting terms equal to the H atom Hamiltonian.)

$$= \Delta E_H + K + \frac{\Delta e^2}{4\pi\varepsilon_0 a_0 D}$$

$$K = \int U_{1s_B}^{*}\left(-\frac{e^2}{4\pi\varepsilon_0 r_B}\right)U_{1s_A}\,d\tau$$

(Exchange integral)

$$K = -\frac{e^2}{4\pi\varepsilon_0 a_0}e^{-D}\left(1+D\right)$$

(*K* is a negative number)

$$\Delta = e^{-D}\left(1 + D + \frac{1}{3}D^2\right)$$

***J* - Coulomb integral - interaction of electron in 1s orbital around A with a proton at B.**

K - Exchange integral – exchange (resonance) of electron between the two nuclei.

These results yield

$$E_S = E_H + \frac{e^2}{4\pi\varepsilon_0 a_0 D} + \frac{J+K}{1+\Delta}$$

(K is a negative number)

$$E_A = E_H + \frac{e^2}{4\pi\varepsilon_0 a_0 D} + \frac{J-K}{1-\Delta}$$

The essential difference between these is the sign of the exchange integral, K.

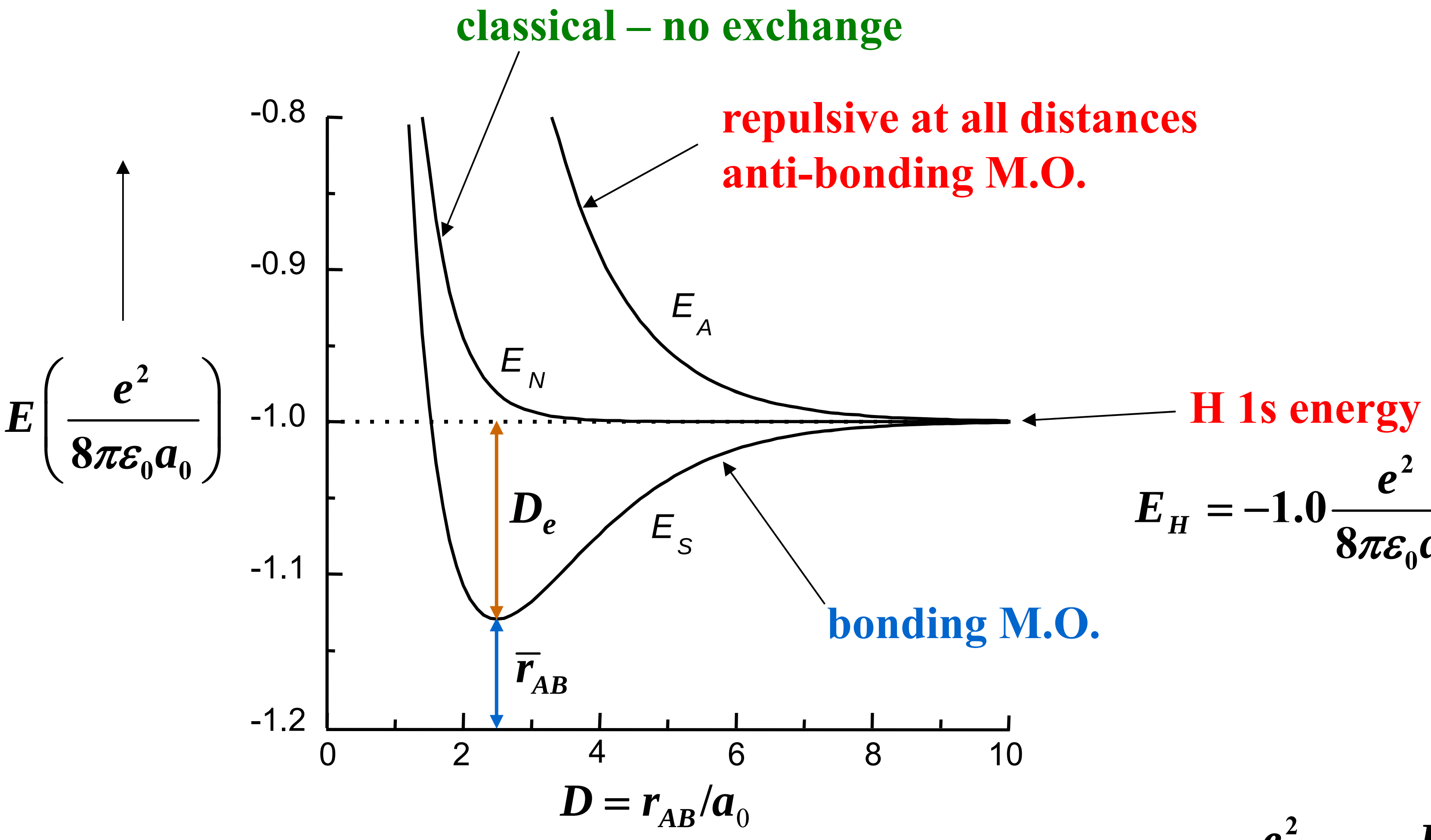
Also consider

$$E_N = H_{AA} = E_H + \frac{e^2}{4\pi\varepsilon_0 a_0} e^{-2D}\left(1 + \frac{1}{D}\right)$$

Classical - no exchange

Interaction of hydrogen 1s electron charge distribution at A with a proton (point charge) at B.

Electron fixed on A.



$$E_H = -1.0\frac{e^2}{8\pi\varepsilon_0 a_0}$$

$$E_S = E_H + \frac{e^2}{4\pi\varepsilon_0 a_0 D} + \frac{J+K}{1+\Delta}$$

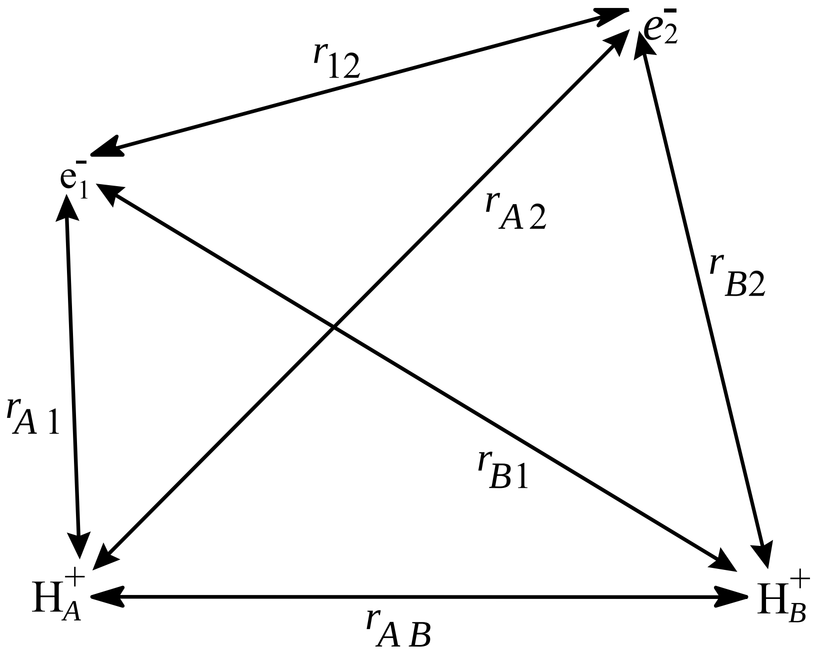
$$E_A = E_H + \frac{e^2}{4\pi\varepsilon_0 a_0 D} + \frac{J-K}{1-\Delta}$$

$\bar{r}_{AB}$ - equilibrium bond length

D_e - dissociation energy

	Dissociation Energy D_e	**Equilibrium Distance** $\overline{r_{AB}}$
This Calc.	**1.77 eV (36%)**	**1.32 Å (25%)**
Exp.	**2.78 eV**	**1.06 Å**
Variation in *Z'*	**2.25 eV (19%)**	**1.06 Å (0%)**

Hydrogen Molecule



In Born-Oppenheimer Approximation the electronic Schrödinger equation is

$$\nabla_1^2\psi + \nabla_2^2\psi + \frac{2m_0}{\hbar^2}\left[E + \frac{e^2}{4\pi\varepsilon_0 r_{A1}} + \frac{e^2}{4\pi\varepsilon_0 r_{B1}} + \frac{e^2}{4\pi\varepsilon_0 r_{A2}} + \frac{e^2}{4\pi\varepsilon_0 r_{B2}} - \frac{e^2}{4\pi\varepsilon_0 r_{12}} - \frac{e^2}{4\pi\varepsilon_0 r_{AB}}\right]\psi = 0$$

$r_{AB} \to \infty$, system goes to 2 hydrogen atoms

Use product wavefunction as basis functions

$\psi_I = U_{1s_A}(1)U_{1s_B}(2)$ Electron 1 around A electron 2 around B.

$\psi_{II} = U_{1s_A}(2)U_{1s_B}(1)$ Electron 2 around A electron 1 around B.

These are degenerate.

Form Hamiltonian Matrix ⟶ secular determinant

$$\underline{\underline{H}} = \begin{pmatrix} H_{I\,I} & H_{I\,II} \\ H_{II\,I} & H_{II\,II} \end{pmatrix}$$

$$\begin{vmatrix} H_{I\,I} - E & H_{I\,II} - \Delta^2 E \\ H_{II\,I} - \Delta^2 E & H_{II\,II} - E \end{vmatrix} = 0$$

$$H_{I\,I} = \iint \psi_I^* \, \underline{H} \, \psi_I \, d\tau_1 d\tau_2 \qquad H_{I\,I} = H_{II\,II}$$

$$H_{I\,II} = \iint \psi_I^* \, \underline{H} \, \psi_{II} \, d\tau_1 d\tau_2 \qquad H_{I\,II} = H_{II\,I}$$

$$\Delta^2 = \iint \psi_I^* \psi_{II} \, d\tau_1 d\tau_2$$

Diagonalization yields

$$E_S = \frac{H_{I\,I} + H_{I\,II}}{1+\Delta^2}$$

$$E_A = \frac{H_{I\,I} - H_{I\,II}}{1-\Delta^2}$$

$$\psi_S = \frac{1}{\sqrt{2+2\Delta^2}}\left[U_{1s_A}(1)\,U_{1s_B}(2) + U_{1s_B}(1)\,U_{1s_A}(2)\right]$$

$$\psi_A = \frac{1}{\sqrt{2-2\Delta^2}}\left[U_{1s_A}(1)\,U_{1s_B}(2) - U_{1s_B}(1)\,U_{1s_A}(2)\right]$$

S - symmetric orbital wavefunction
A - antisymmetric orbital wavefunction

Evaluating

attraction to nuclei

$$H_{II} = \int U_{1s_A}^*(1)U_{1s_B}^*(2)\left(2E_H - \frac{e^2}{4\pi\varepsilon_0 r_{B1}} - \frac{e^2}{4\pi\varepsilon_0 r_{A2}}\right.$$

nuclear-nuclear repulsion

Two kinetic energy terms and two electron-nuclear attraction terms comprise 2 H atom Hamiltonians.

$$\left. + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}\right) U_{1s_A}(1)U_{1s_B}(2)d\tau_1 d\tau_2$$

electron-electron repulsion

$$H_{II} = 2E_H + 2J + J' + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}$$

J same as before.

$$J' = \frac{e^2}{4\pi\varepsilon_0}\iint \frac{\left[U_{1s_A}(1)\, U_{1s_B}(2)\right]^2}{r_{12}}\, d\tau_1 d\tau_2$$

$$J' = \frac{e^2}{4\pi\varepsilon_0 a_0}\left[\frac{1}{D} - e^{-2D}\left(\frac{1}{D} + \frac{11}{8} + \frac{3}{4}D + \frac{1}{6}D^2\right)\right] \qquad D = r_{AB}/a_0$$

$$H_{I\,II} = \int U^*_{1s_A}(1)U^*_{1s_B}(2)\left(2E_H - \frac{e^2}{4\pi\varepsilon_0 r_{B1}} - \frac{e^2}{4\pi\varepsilon_0 r_{A2}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}\right)U_{1s_A}(2)U_{1s_B}(1)d\tau_1 d\tau_2$$

$$H_{I\,II} = 2\Delta^2 E_H + 2\Delta K + K' + \Delta^2\frac{e^2}{4\pi\varepsilon_0 r_{AB}}$$

K **and** Δ **same as before.**

$$K' = \frac{e^2}{4\pi\varepsilon_0}\iint\frac{\left[U_{1s_A}(1)\,U_{1s_B}(2)\right]\left[U_{1s_A}(2)\,U_{1s_B}(1)\right]}{r_{12}}d\tau_1 d\tau_2$$

$$D = r_{AB}/a_0$$

$$K' = \frac{e^2}{20\pi\varepsilon_0 a_0}\left[-e^{-2D}\left(-\frac{25}{8}+\frac{23}{4}D+3D^2+\frac{1}{3}D^3\right) + \frac{6}{D}\left[\Delta^2(\gamma+\ln D)+\Delta'^2 Ei(-4D)-2\Delta\Delta' Ei(-2D)\right]\right]$$

$\gamma = 0.5772\cdots$

(Euler's constant)

$$\Delta' = e^D\left(1-D+\frac{1}{3}D^2\right)$$

Ei **- integral logarithm**

math tables, approx., see book.

J and *K* - same physical meaning as before.

J - Coulomb integral. Attraction of electron around one nucleus for the other nucleus.

K - Corresponding exchange integral.

J' - Coulomb integral. Interaction of electron in 1s orbital on nucleus A with electron in 1s orbital on nucleus B.

K' - Corresponding exchange or resonance integral.

Putting the pieces together

$$E_S = 2E_H + \frac{e^2}{4\pi\varepsilon_0 r_{AB}} + \frac{2J + J' + 2\Delta K + K'}{1+\Delta^2}$$

$$E_A = 2E_H + \frac{e^2}{4\pi\varepsilon_0 r_{AB}} + \frac{2J + J' - 2\Delta K - K'}{1-\Delta^2}$$

K' is negative.

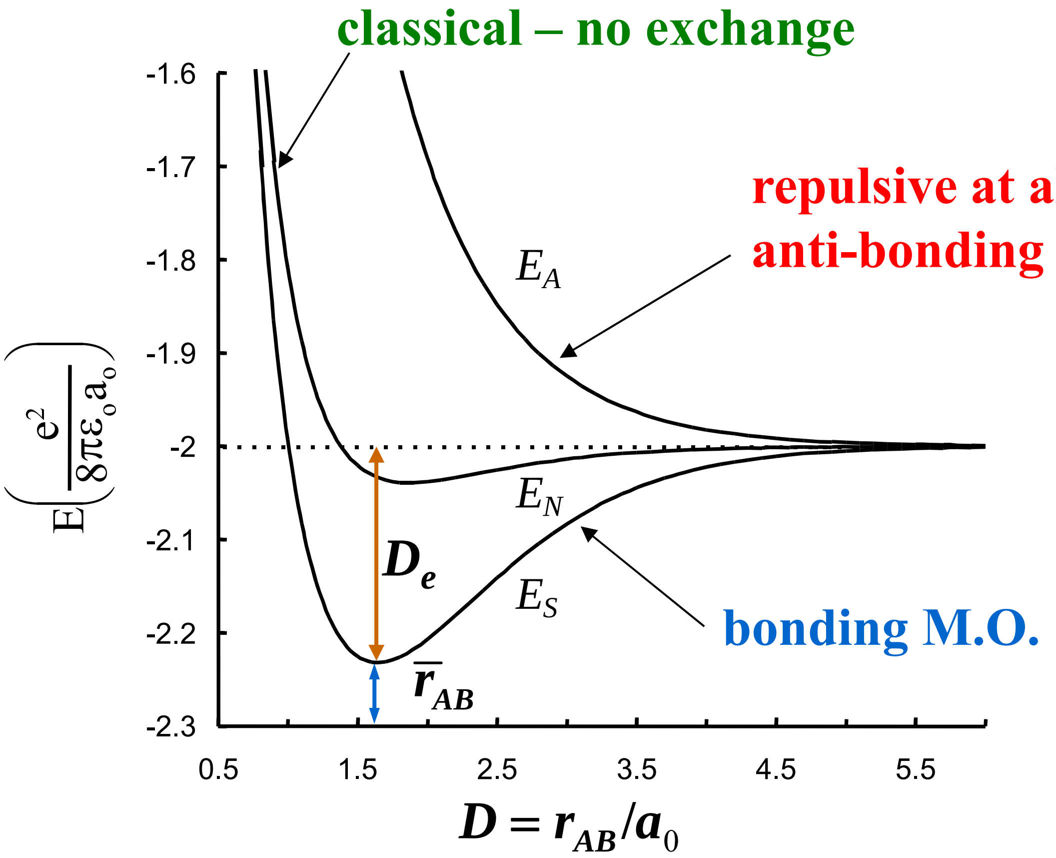
The essential difference between these is the sign of the K' term.

$$E_N = H_{II} = 2E_H + 2J + J' + \frac{e^2}{4\pi\varepsilon_0 r_{AB}} \longrightarrow$$

Energy of

$$\psi_I = U_{1s_A}(1)\,U_{1s_B}(2)$$

No exchange.
Classical interaction of spherical H atom charge distributions.
Charge distribution about H atoms A and B.
Electron 1 stays on A.
Electron 2 stays on B.



classical – no exchange

repulsive at all distances
anti-bonding M.O.

bonding M.O.

2 × H 1s energy

$$E_H = -1.0\frac{e^2}{8\pi\varepsilon_0 a_0}$$

	Dissociation Energy D_e	**Equilibrium Distance $\overline{r}_{AB}$**
This Calc.	**3.14 eV (33%)**	**0.80 Å (8%)**
Exp.	**4.72 eV**	**0.74 Å**
Variation in Z'	**3.76 eV (19%)**	**0.76 Å (3%)**

Vibrational Frequency - fit to parabola, 3400 cm^{-1}; exp, 4318 cm^{-1}