Homonuclear Diatomic Molecule

Energy Diagram

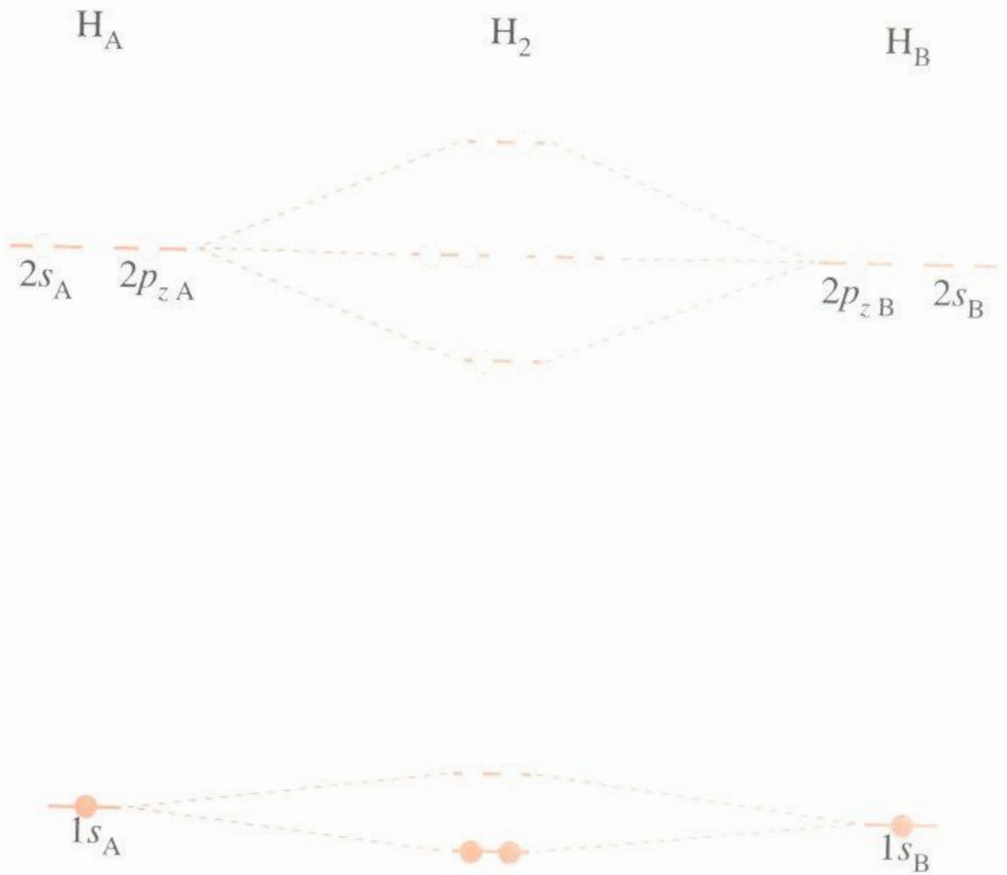
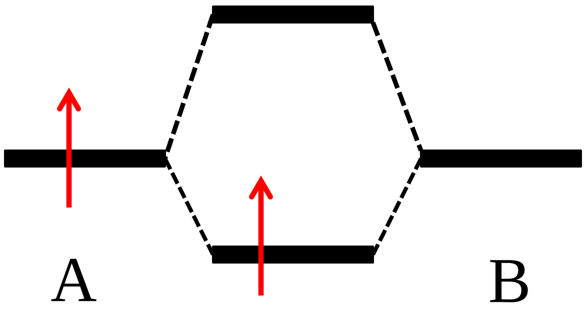
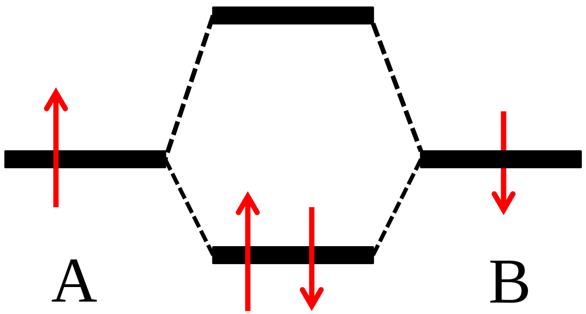


FIGURE 10.28
The six spatial molecular orbitals that are obtained when the LCAO-MO is a linear combination of six atomic orbitals, as in Equation 10.55. Only the molecular orbital of the lowest energy is occupied in the ground electronic state of H_2. The five unoccupied orbitals are called virtual orbitals.

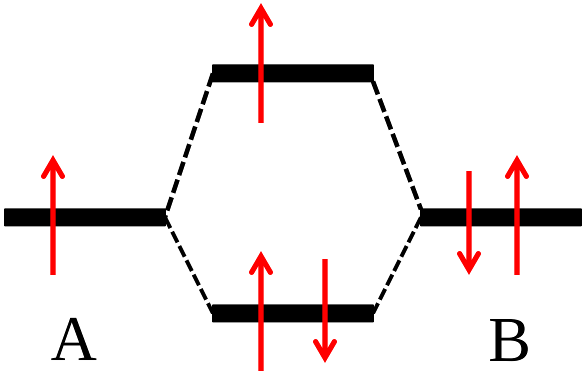
H_2^+, H_2, He_2^+, He_2



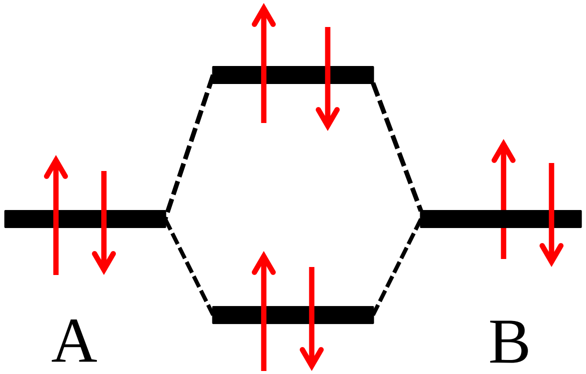
H_2^+ R_{eq}=1.06 Angstrom
Binding Energy 61 kcal/mol



H_2 R_{eq}=0.74 Angstrom
Binding Energy 105 kcal/mol

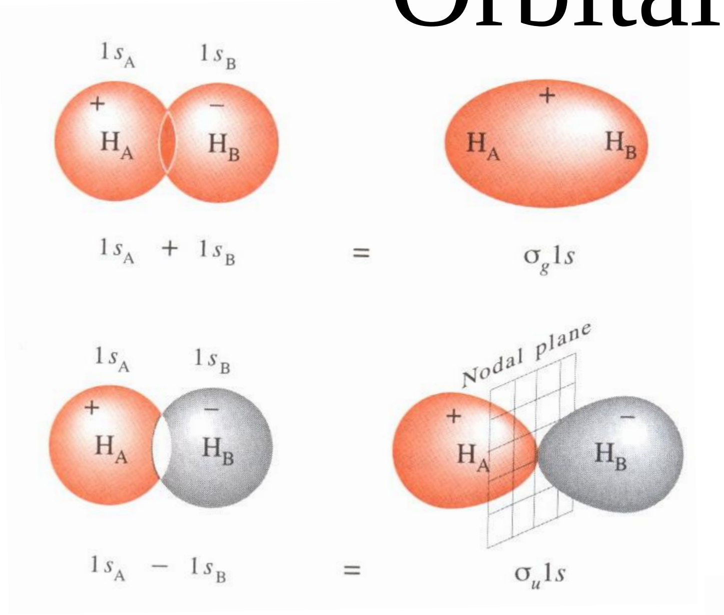


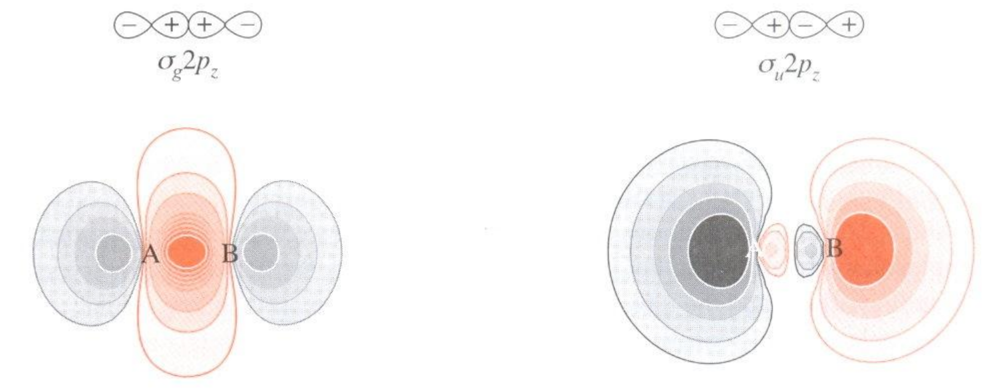
He_2^+ R_{eq}=1.08 Angstrom
Binding Energy 50 kcal/mol

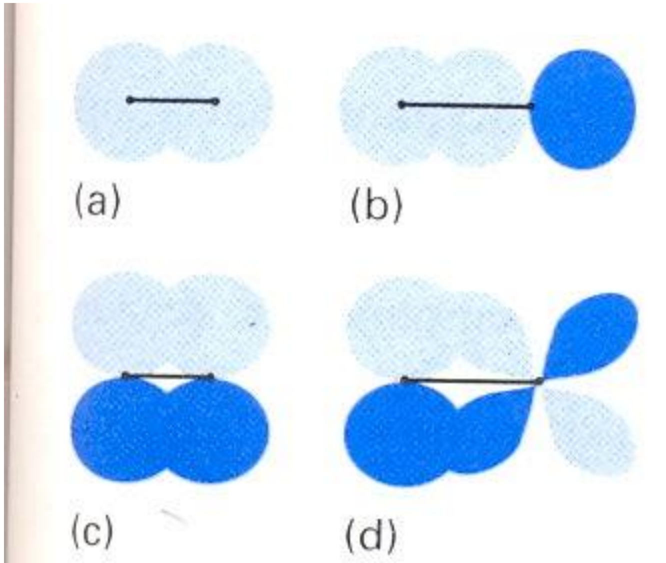


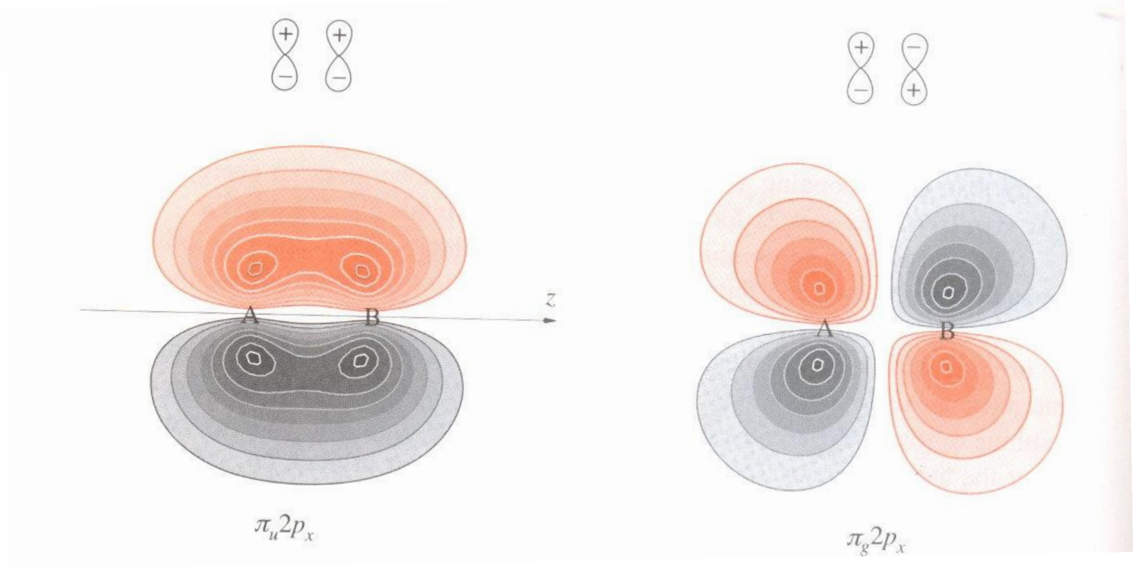
He_2 R_{eq}= Infinity not bound
Binding Energy 0 Kcal mol

Molecular Orbitals: Sum of Atomic Orbitals Sigma and Pi



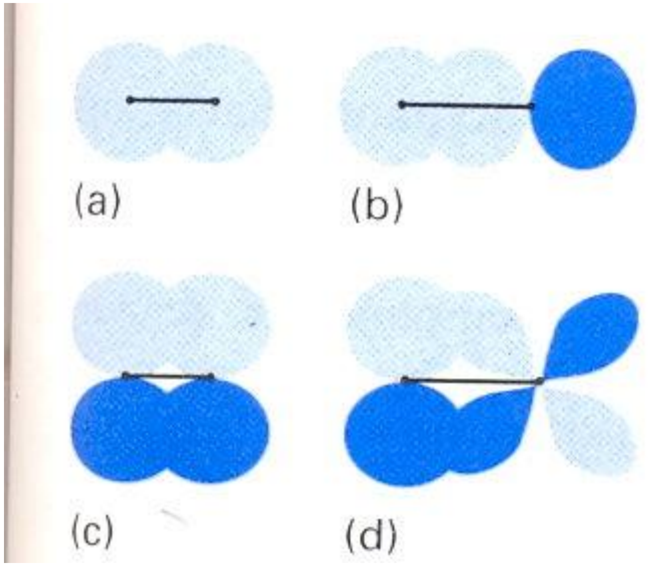






Symmetry of Orbitals Important

Allowed Combinations



Not Allowed Combinations: S=0, H_{AB}=0

Binding Energy: Orbital Interaction

- Binding depends on overlap of atomic orbitals:
  - too much overlap repulsion
  - too little overlap no bonding interaction
- Energies of atomic orbital closer the better

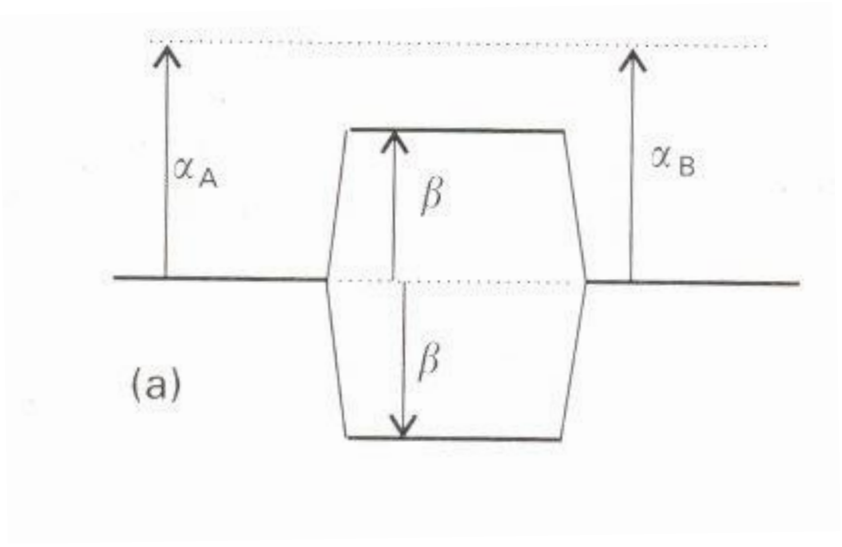
Consider the interaction of Orbital of atom A and B at E_A and E_B

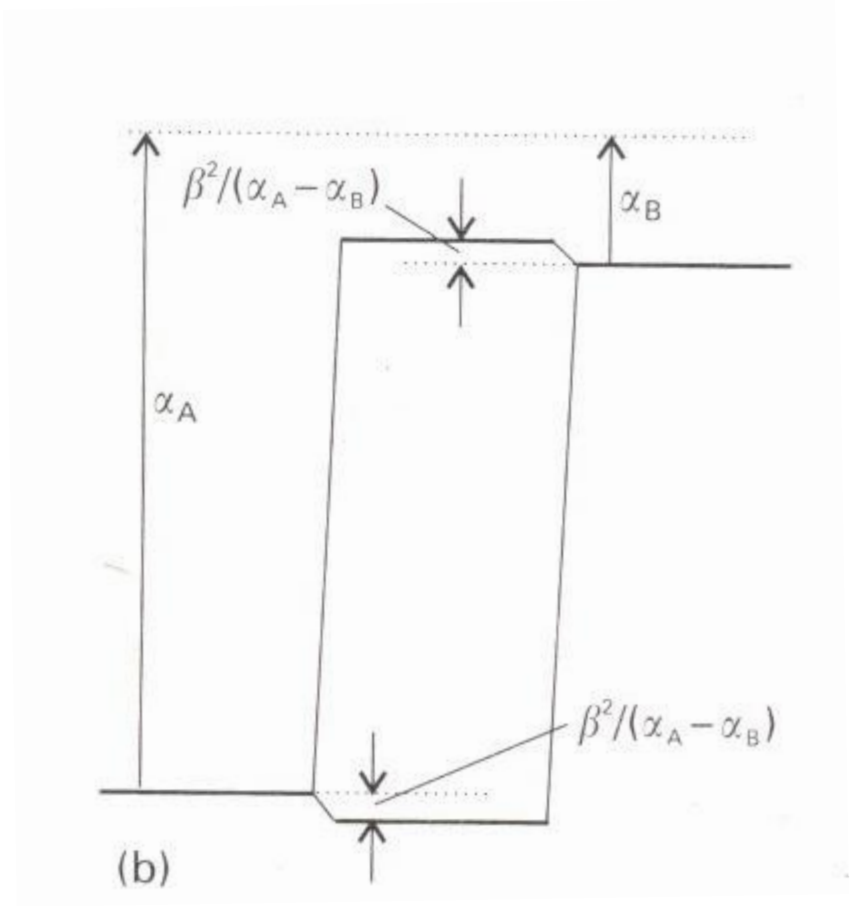
$$\begin{vmatrix} H_{AA}-E & H_{AB}-ES \\ H_{BA}-ES & H_{BB}-E \end{vmatrix} = \begin{vmatrix} \alpha_A-E & \beta-ES \\ \beta-ES & \alpha_B-E \end{vmatrix} = 0$$

Assume S=0 and $|\alpha_A-\alpha_B| >> \beta$

$$E_- = \alpha_A - \frac{\beta^2}{\alpha_B-\alpha_A}; \qquad E_+ = \alpha_B + \frac{\beta^2}{\alpha_B-\alpha_A}$$

Homo/Heteronuclear Diatomic Molecules

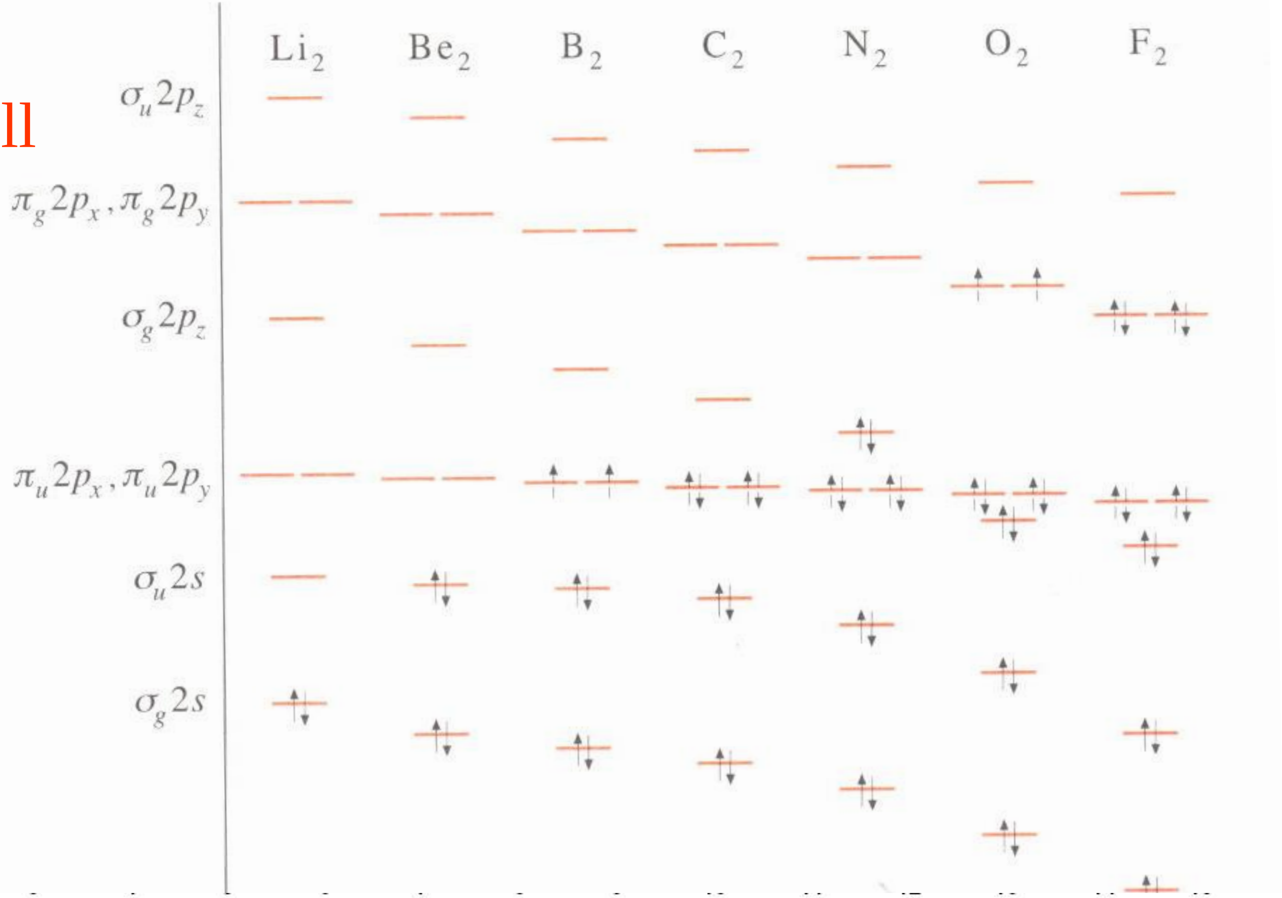




Bonding orbital localized on one nuclei

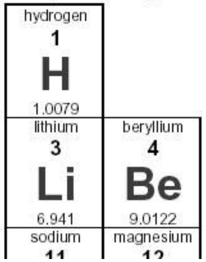
Second Row Homonuclear diatomic Molecules

Ignore
1S interaction
Since too small

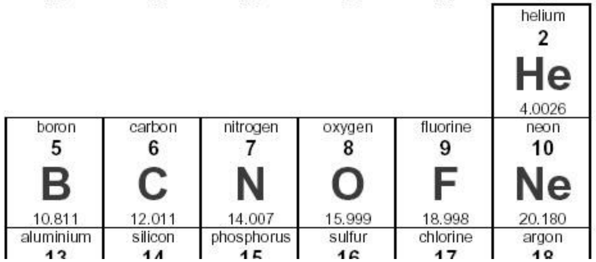


Valance
Orbitals are
considered

HOMO LUMO Gap ↔ Band Gap



hydrogen 1 **H** 1.0079	
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122
sodium	magnesium



					helium 2 **He** 4.0026
boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
aluminium	silicon	phosphorus	sulfur	chlorine	argon

CO Molecule: Orbitals

In heterodiatomic molecules electronegativity of the atoms determine the shape of the orbital

$$\Psi = C_A \psi_A + C_B \psi_B$$

C_A and C_B define the density on A and B

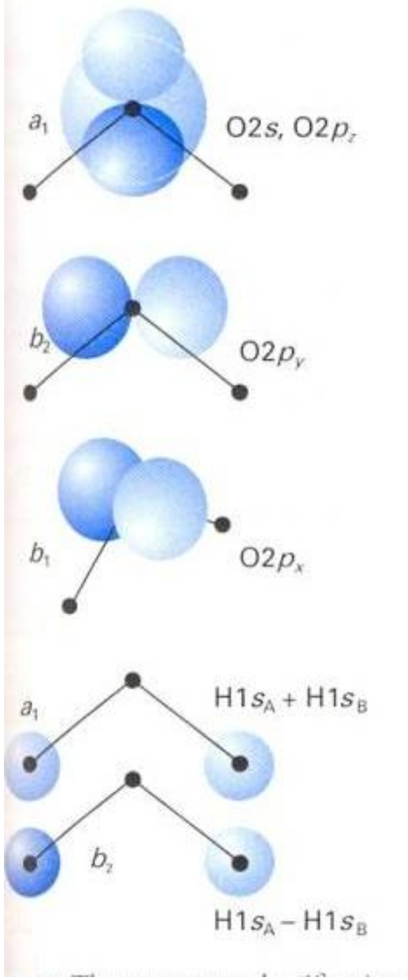
If A is more electronegative:

$|C_A| > |C_B|$ in bonding orbital

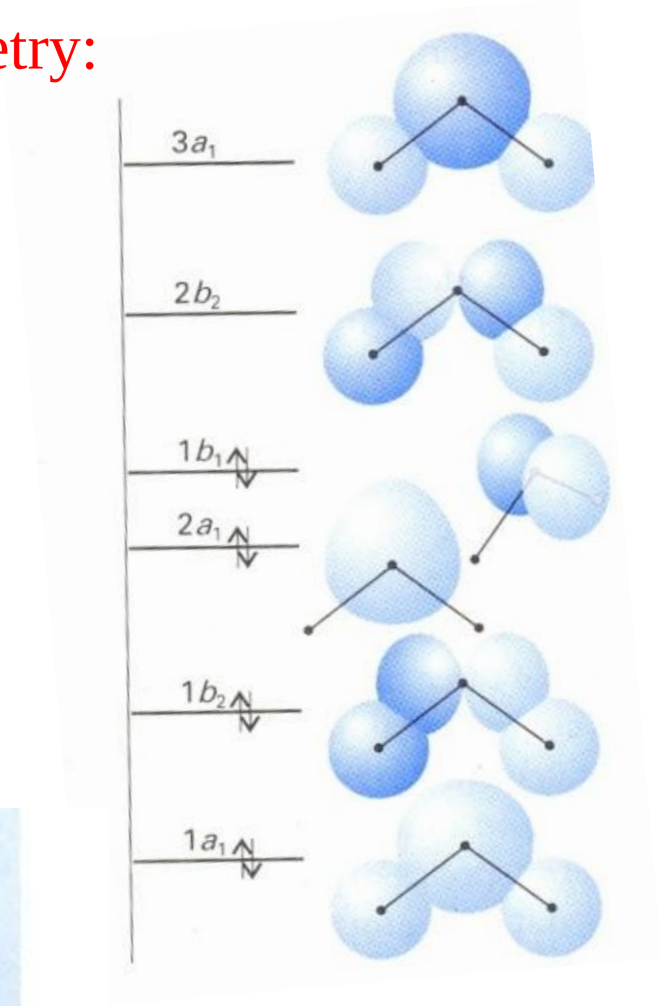
$|C_A| < |C_B|$ in antibonding orbital

Polyatomic Molecules

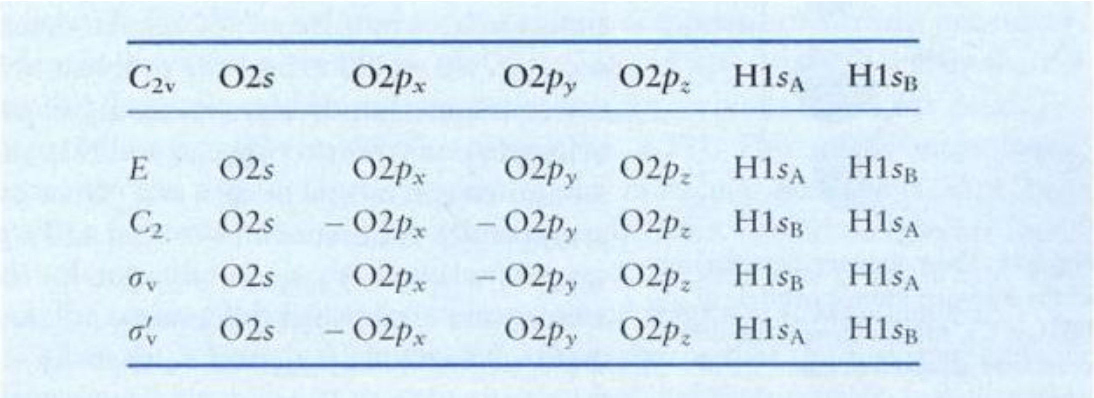
Water H_2O



You must think of symmetry:
Rotation of bisecter axis
Mirror at the water plane
Mirror at the middle



Hydrogens make linear combination: plus and minus pair like bonding and antibonding orbital



C_{2v}	O2s	O2p_x	O2p_y	O2p_z	H1s_A	H1s_B
E	O2s	O2p_x	O2p_y	O2p_z	H1s_A	H1s_B
C_2	O2s	−O2p_x	−O2p_y	O2p_z	H1s_B	H1s_A
σ_v	O2s	O2p_x	−O2p_y	O2p_z	H1s_B	H1s_A
σ'_v	O2s	−O2p_x	O2p_y	O2p_z	H1s_A	H1s_B

Hartree-Fock Roothaan Equation Electronic Structure

Kaito Takahashi

Born-Oppenheimer Approximation

Solve for the electron at a fixed nuclear geometry

$$\hat{H}^{0}(\mathbf{r};\mathbf{R})\Psi_{n}^{el}(\mathbf{r};\mathbf{R})=\left[-\frac{1}{2}\sum_{i=1}^{n}\nabla_{i}^{2}+V(\mathbf{r},\mathbf{R})\right]\Psi_{n}^{el}(\mathbf{r};\mathbf{R})=E_{n}(\mathbf{R})\Psi_{n}^{el}(\mathbf{r};\mathbf{R})$$

Calculate many nuclear geometries to obtain the potential energy surface

$$\hat{H}_{NU}(\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R})=E_{el,NU}\,\chi_{n,v_n}^{NU}(\mathbf{R})$$

$$\hat{H}_{NU}(\mathbf{R})=\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_{I}^{2}+V(\mathbf{R})\right)$$

Problem To Solve

$$\hat{H}^0(\mathbf{r};\mathbf{R})\Psi_n^{el}(\mathbf{r};\mathbf{R})$$

$$=\left[-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2+\sum_{I=1}^{N}\sum_{J\neq I}^{N}\frac{Z_I Z_J}{\left|\mathbf{R}_I-\mathbf{R}_J\right|}-\sum_{I=1}^{N}\sum_{i=1}^{n}\frac{Z_I}{\left|\mathbf{R}_I-\mathbf{r}_i\right|}+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right]\Psi_n^{el}(\mathbf{r};\mathbf{R})$$

$$=E_n(\mathbf{R})\Psi_n^{el}(\mathbf{r};\mathbf{R})$$

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_n)=\frac{1}{\sqrt{n!}}\begin{vmatrix}\psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_k(\mathbf{x}_1)\\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_k(\mathbf{x}_2)\\ \ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots\\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \ldots\ldots\ldots\ldots\ldots\ldots & \psi_k(\mathbf{x}_n)\end{vmatrix}$$

Operators and Matrix Elements

Hamiltonian is a sum of one and two electron operators

For example hydrogen molecule

$$\left[-\frac{1}{2}\nabla_1^2-\frac{1}{|\mathbf{r}_{1A}|}-\frac{1}{|\mathbf{r}_{1B}|}-\frac{1}{2}\nabla_2^2-\frac{1}{|\mathbf{r}_{2A}|}-\frac{1}{|\mathbf{r}_{2B}|}+\left[\frac{1}{|\mathbf{R}|}+\frac{1}{|\mathbf{r}_{12}|}\right]\right]$$

$$=\left[h_1+h_2+\frac{1}{|\mathbf{R}|}+\frac{1}{|\mathbf{r}_{12}|}\right]$$

h_1, h_2 : one electron operator

$\frac{1}{|\mathbf{r}_{12}|}$: two electron operator

$$\Psi_0(\mathbf{x}_1,\mathbf{x}_2)=\frac{1}{\sqrt{2}}\left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)-\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)$$

One Electron Operator Matrix Element

$$
\begin{aligned}
\langle 0|h_1|0\rangle = 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 &\left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)-\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)^* \\
&\times h(\mathbf{r}_1)\left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)-\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right) \\
&= 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 \Big[\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)h(\mathbf{r}_1)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) \\
&+\psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)h(\mathbf{r}_1)\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2) \\
&-\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)h(\mathbf{r}_1)\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2) \\
&-\psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)h(\mathbf{r}_1)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\Big]
\end{aligned}
$$

Due to orthonormality of the spin orbitals last two are zero with integration with respect to $\mathbf{x}_2$

One Electron Operator 2

$$\begin{aligned}
\left\langle 0 \middle| h_1 \middle| 0 \right\rangle &= 2^{-1} \iint d\mathbf{x}_1 d\mathbf{x}_2 \Big[\psi_i^{\,*}(\mathbf{x}_1)\psi_j^{\,*}(\mathbf{x}_2) h(\mathbf{r}_1) \psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) \\
&\qquad + \psi_j^{\,*}(\mathbf{x}_1)\psi_i^{\,*}(\mathbf{x}_2) h(\mathbf{r}_1) \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2) \Big] \\
&= 2^{-1} \int \psi_i^{\,*}(\mathbf{x}_1) h(\mathbf{r}_1) \psi_i(\mathbf{x}_1) d\mathbf{x}_1 + 2^{-1} \int \psi_j^{\,*}(\mathbf{x}_1) h(\mathbf{r}_1) \psi_j(\mathbf{x}_1) d\mathbf{x}_1 \\
&= 2^{-1} \Big(\left\langle \psi_i \middle| h \middle| \psi_i \right\rangle + \left\langle \psi_j \middle| h \middle| \psi_j \right\rangle \Big) \\
\left\langle 0 \middle| h_2 \middle| 0 \right\rangle &= 2^{-1} \Big(\left\langle \psi_i \middle| h \middle| \psi_i \right\rangle + \left\langle \psi_j \middle| h \middle| \psi_j \right\rangle \Big)
\end{aligned}$$

Two Electron Operator Matrix Element

$$\begin{aligned}
\left\langle 0 \middle| |\mathbf{r}_{12}|^{-1} \middle| 0 \right\rangle = 2^{-1} \iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)^* \\
\times |\mathbf{r}_{12}|^{-1}\left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right) \\
= 2^{-1} \iint d\mathbf{x}_1 d\mathbf{x}_2 \Big[\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) \\
+ \psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2) \\
- \psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2) \\
- \psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\Big]
\end{aligned}$$

Since $|\mathbf{r}_{12}|$ is equal to $|\mathbf{r}_{21}|$ perform interchange of electron 1 and electron 2 and first and second are the same and third and fourth are the same

Two Electron Operator 2

$$\left\langle 0 \middle| \left|\mathbf{r}_{12}\right|^{-1} \middle| 0 \right\rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \left[\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\left|\mathbf{r}_{12}\right|^{-1}\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\right.$$

$$\left. -\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\left|\mathbf{r}_{12}\right|^{-1}\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right]$$

$$= \langle ij \mid ij \rangle - \langle ij \mid ji \rangle$$

$$\langle ij \mid kl \rangle = \langle ji \mid lk \rangle = \langle kl \mid ij \rangle^* = \langle lk \mid ji \rangle^*$$

Symbols physics people use: $\langle ij \| kl \rangle = \langle ij \mid kl \rangle - \langle ij \mid lk \rangle$

Symbols chemistry people use:

$$[ij \mid kl] = \langle ik \mid jl \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \left[\psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1)\left|\mathbf{r}_{12}\right|^{-1}\psi_k^*(\mathbf{x}_2)\psi_l(\mathbf{x}_2)\right.$$

So the expectation value of the hamiltonian with the Slater determinant for two electron system is

$$\langle 0 | H | 0 \rangle = \langle \psi_i | h | \psi_i \rangle + \langle \psi_j | h | \psi_j \rangle + \langle ij \mid ij \rangle - \langle ij \mid ji \rangle$$

Expectation Value of Slater Det

$$|\psi_1\psi_2\ldots\psi_n\rangle = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \cdots\cdots\cdots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \cdots\cdots\cdots & \psi_n(\mathbf{x}_2) \\ \cdots\cdots & \cdots\cdots & \cdots\cdots\cdots & \cdots\cdots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \cdots\cdots\cdots & \psi_n(\mathbf{x}_n) \end{vmatrix}$$

For one electron operators we consider the sum of each electron, for two electron operators the sum of pairs of electrons

two electron system Hamiltonian was $\left[h_1 + h_2 + \frac{1}{|\mathbf{R}|} + \frac{1}{|\mathbf{r}_{12}|}\right]$

one electron operators for n electron system $\sum_{i=1}^{n} h_i$

two electron operator for n electron system $\sum_{i=1}^{n}\sum_{j\neq i}^{n} |\mathbf{r}_{ij}|^{-1}$

Expectation of One Electron Operator of Slater Det

$$\left\langle \psi_1\psi_2\ldots\psi_n \left| \sum_{i=1}^{n} h_i \right| \psi_1\psi_2\ldots\psi_n \right\rangle = \langle \psi_1\psi_2\ldots\psi_n | h_1 + h_2 + \ldots h_n | \psi_1\psi_2\ldots\psi_n \rangle$$

Since electron in slater determinant is indistinguishable we consider for just electron 1 and multiply by the number of electrons

$$\left\langle \psi_1\psi_2\ldots\psi_n \left| \sum_{i=1}^{n} h_i \right| \psi_1\psi_2\ldots\psi_n \right\rangle = n\langle \psi_1\psi_2\ldots\psi_n | h_1 | \psi_1\psi_2\ldots\psi_n \rangle$$

$$= \sum_{i=1}^{n} \langle \psi_i | h_1 | \psi_i \rangle$$

Expectation Value of a Two electron Operator for Slater Det

$$\left\langle \psi_1\psi_2\ldots\psi_n \left| \sum_{i=1}^{n}\sum_{j\neq i}^{n} \left|\mathbf{r}_{ij}\right|^{-1} \right| \psi_1\psi_2\ldots\psi_n \right\rangle$$

$$= \left\langle \psi_1\psi_2\ldots\psi_n \left| \left|\mathbf{r}_{12}\right|^{-1} + \left|\mathbf{r}_{13}\right|^{-1} + \ldots \left|\mathbf{r}_{n-1n}\right|^{-1} \right| \psi_1\psi_2\ldots\psi_n \right\rangle$$

Since electron in slater determinant is indistinguishable we solve for electron 1 and 2 and multiply by the number of pairs

$$\left\langle \psi_1\psi_2\ldots\psi_n \left| \sum_{i=1}^{n}\sum_{j\neq i}^{n} \left|\mathbf{r}_{ij}\right|^{-1} \right| \psi_1\psi_2\ldots\psi_n \right\rangle$$

$$= \frac{n(n-1)}{2} \left\langle \psi_1\psi_2\ldots\psi_n \left| \left|\mathbf{r}_{12}\right|^{-1} \right| \psi_1\psi_2\ldots\psi_n \right\rangle$$

$$= \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \left(\langle ij \mid ij \rangle - \langle ij \mid ji \rangle \right)$$

Hartree Fock Approximation 1

$$\hat{H}^{0}(\mathbf{r};\mathbf{R}) = \sum_{i=1}^{n} h_i + \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

$$\left|\psi_1\psi_2\ldots\psi_n\right\rangle = \frac{1}{\sqrt{n!}}\begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \cdots\cdots\cdots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \cdots\cdots\cdots & \psi_n(\mathbf{x}_2) \\ \cdots\cdots & \cdots\cdots & \cdots\cdots\cdots & \cdots\cdots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \cdots\cdots\cdots & \psi_n(\mathbf{x}_n) \end{vmatrix}$$

$$\left\langle \psi_1\psi_2\ldots\psi_n \middle| \hat{H}^{0} \middle| \psi_1\psi_2\ldots\psi_n \right\rangle = \sum_{i=1}^{n} \left\langle \psi_i \middle| h_1 \middle| \psi_i \right\rangle + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\langle ij \mid ij\rangle - \langle ij \mid ji\rangle\right)$$

$$\left\langle \psi_i \mid \psi_j \right\rangle = \delta_{ij}$$

How do you find the best answer for the spin orbitals?

Hartree Fock Approximation 2

Functional minimization with constraint

$$\Im(\{\psi_i\}) = \left\langle \psi_1\psi_2\ldots\psi_n \middle| \hat{H}^0 \middle| \psi_1\psi_2\ldots\psi_n \right\rangle - \sum_{i=1}^{n}\sum_{j=1}^{n} \varepsilon_{ji}\left(\langle \psi_i \mid \psi_j \rangle - \delta_{ij}\right) \to \min$$

Functional derivative with respect to change of spin orbital

$\psi_i \to \psi_i + \delta\psi_i$ should be zero

$$\Im(\{\psi_i + \delta\psi_i\}) - \Im(\{\psi_i\}) = \delta\Im(\{\psi_i\}) = 0$$

$$\delta\Im(\{\psi_i\}) = \delta\left\langle \psi_1\psi_2\ldots\psi_n \middle| \hat{H}^0 \middle| \psi_1\psi_2\ldots\psi_n \right\rangle - \sum_{i=1}^{n}\sum_{j=1}^{n} \varepsilon_{ji}\left(\delta\langle \psi_i \mid \psi_j \rangle\right) = 0$$

$$\delta\langle \psi_i \mid \psi_j \rangle = \langle \delta\psi_i \mid \psi_j \rangle + \langle \psi_i \mid \delta\psi_j \rangle$$

Hartree Fock Approximation 3

$$\delta\left\langle \psi_1\psi_2\ldots\psi_n \middle| \hat{H}^0 \middle| \psi_1\psi_2\ldots\psi_n \right\rangle = \sum_{i=1}^{n}\left\langle \delta\psi_i \middle| h_1 \middle| \psi_i \right\rangle + \sum_{i=1}^{n}\left\langle \psi_i \middle| h_1 \middle| \delta\psi_i \right\rangle$$

$$+\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle \delta i j \mid i j\rangle - \langle \delta i j \mid j i\rangle\Big) + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle i \delta j \mid i j\rangle - \langle i \delta j \mid j i\rangle\Big)$$

$$+\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle i j \mid \delta i j\rangle - \langle i j \mid \delta j i\rangle\Big) + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle i j \mid i \delta j\rangle - \langle i j \mid j \delta i\rangle\Big)$$

Remember the exchange relationship of two electron integral

$$\langle ij \mid kl\rangle = \langle ji \mid lk\rangle = \langle kl \mid ij\rangle^* = \langle lk \mid ji\rangle^*$$

$$\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle i \delta j \mid i j\rangle - \langle i \delta j \mid j i\rangle\Big) = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle \delta j i \mid j i\rangle - \langle \delta j i \mid i j\rangle\Big)$$

$$= \frac{1}{2}\sum_{j=1}^{n}\sum_{i=1}^{n}\Big(\langle \delta i j \mid i j\rangle - \langle \delta i j \mid j i\rangle\Big)$$

Hartree Fock Approximation 4

$$\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle ij \mid \delta ij\rangle - \langle ij \mid \delta ji\rangle\Big) = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle \delta ij \mid ij\rangle * - \langle \delta ji \mid ij\rangle *\Big)$$

$$= \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle \delta ij \mid ij\rangle * - \langle \delta ij \mid ji\rangle *\Big)$$

$$\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle ij \mid i\delta j\rangle - \langle ij \mid j\delta i\rangle\Big) = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle i\delta j \mid ij\rangle * - \langle j\delta i \mid ij\rangle *\Big)$$

$$= \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle \delta ji \mid ji\rangle * - \langle \delta ij \mid ji\rangle *\Big)$$

$$= \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\Big(\langle \delta ij \mid ij\rangle * - \langle \delta ij \mid ji\rangle *\Big)$$

Hartree Fock Approximation 5

$$\delta\Im(\{\psi_i\}) = \delta\left\langle \psi_1\psi_2\ldots\psi_n \middle| \hat{H}^0 \middle| \psi_1\psi_2\ldots\psi_n \right\rangle - \sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ji}\left(\delta\left\langle \psi_i \mid \psi_j \right\rangle\right) = 0$$

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ji}\left(\left\langle \delta\psi_i \mid \psi_j \right\rangle + \left\langle \psi_i \mid \delta\psi_j \right\rangle\right) = \sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ji}\left(\left\langle \delta\psi_i \mid \psi_j \right\rangle\right) + cc$$

$$\delta\left\langle \psi_1\psi_2\ldots\psi_n \middle| \hat{H}^0 \middle| \psi_1\psi_2\ldots\psi_n \right\rangle = \sum_{i=1}^{n}\left\langle \delta\psi_i \middle| h_1 \middle| \psi_i \right\rangle + \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\left\langle \delta ij \mid ij \right\rangle - \left\langle \delta ij \mid ji \right\rangle\right) + cc$$

$$\sum_{i=1}^{n}\left\langle \delta\psi_i \middle| h_1 \middle| \psi_i \right\rangle + \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\left\langle \delta ij \mid ij \right\rangle - \left\langle \delta ij \mid ji \right\rangle - \varepsilon_{ji}\left\langle \delta\psi_i \mid \psi_j \right\rangle\right) + cc = 0$$

$$\sum_{i=1}^{n}\int \delta\psi_i^*(\mathbf{x}_1)h(\mathbf{r}_1)\psi_i(\mathbf{x}_1)d\mathbf{x}_1 + \sum_{i=1}^{n}\sum_{j=1}^{n}\iint d\mathbf{x}_1 d\mathbf{x}_2\left(\delta\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\left|\mathbf{r}_{12}\right|^{-1}\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\right)$$

$$-\sum_{i=1}^{n}\sum_{j=1}^{n}\iint d\mathbf{x}_1 d\mathbf{x}_2\left(\delta\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\left|\mathbf{r}_{12}\right|^{-1}\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right) - \sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ji}\iint \delta\psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1)d\mathbf{x}_1$$

Coulomb and Exchange Integral

Coulomb Integral

$$\iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\delta\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\right)$$

$$= \int \delta\psi_i^*(\mathbf{x}_1)\left(\int \psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_j(\mathbf{x}_2)d\mathbf{x}_2\right)\psi_i(\mathbf{x}_1)d\mathbf{x}_1$$

$$= \int \delta\psi_i^*(\mathbf{x}_1)J_j(\mathbf{x}_1)\psi_i(\mathbf{x}_1)d\mathbf{x}_1$$

Exchange Integral

$$\iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\delta\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)$$

$$= \int \delta\psi_i^*(\mathbf{x}_1)\left(\int \psi_j^*(\mathbf{x}_2)|\mathbf{r}_{12}|^{-1}\psi_i(\mathbf{x}_2)d\mathbf{x}_2\right)\psi_j(\mathbf{x}_1)d\mathbf{x}_1$$

$$= \int \delta\psi_i^*(\mathbf{x}_1)K_j(\mathbf{x}_1)\psi_i(\mathbf{x}_1)d\mathbf{x}_1$$

$$\left\langle \psi_1\psi_2\ldots\psi_n\middle|\hat{H}^0\middle|\psi_1\psi_2\ldots\psi_n\right\rangle = \sum_{i=1}^{n}\left\langle\psi_i\middle|h_1\middle|\psi_i\right\rangle + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\langle ij \mid ij\rangle - \langle ij \mid ji\rangle\right)$$

$$= \sum_{i=1}^{n} h_{ii} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij} - K_{ij}\right)$$

Hartree Fock Approximation 6

$$\delta\Im(\{\psi_i\}) = \sum_{i=1}^{n} \int \delta\psi_i^*(\mathbf{x}_1) \left[h(\mathbf{r}_1)\psi_i(\mathbf{x}_1) + \sum_{j=1}^{n} \left(J_j(\mathbf{x}_1) - K_j(\mathbf{x}_1) \right) \psi_i(\mathbf{x}_1) - \sum_{j=1}^{n} \varepsilon_{ji}\psi_j(\mathbf{x}_1) \right] d\mathbf{x}_1 + cc$$

$$= 0$$

Since $\delta\psi_i^*(\mathbf{x}_1)$ is arbitrary [..] must be zero

$$\left[h(\mathbf{r}_1) + \sum_{j=1}^{n} \left(J_j(\mathbf{x}_1) - K_j(\mathbf{x}_1) \right) \right] \psi_i(\mathbf{x}_1) = \sum_{j=1}^{n} \varepsilon_{ji}\psi_j(\mathbf{x}_1) \qquad i = 1,2,\ldots n$$

$$f(1)\psi_i(\mathbf{x}_1) = \sum_{j=1}^{n} \varepsilon_{ij}\psi_j(\mathbf{x}_1) \qquad i = 1,2,\ldots n$$

Fock Operator of spin orbitals

Canonical Hartree Fock

Unitary Transform of the Hartree Fock occupied orbitals

$$\psi_i'(\mathbf{x}_1) = \sum_{j=1}^{n} U_{ji}\psi_j(\mathbf{x}_1) \qquad i = 1,2,\ldots n$$

$$\mathbf{U}^{+} = \mathbf{U}^{-1}$$

$$\mathbf{A} = \begin{pmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots & \psi_n(\mathbf{x}_2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \ldots & \psi_n(\mathbf{x}_n) \end{pmatrix}$$

$$\mathbf{A}' = \mathbf{AU} = \begin{pmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots & \psi_n(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots & \psi_n(\mathbf{x}_2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \ldots & \psi_n(\mathbf{x}_n) \end{pmatrix} \begin{pmatrix} U_{11} & U_{12} & \ldots & U_{1n} \\ U_{21} & U_{22} & \ldots & U_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ U_{n1} & U_{n2} & \ldots & U_{nn} \end{pmatrix} = \begin{pmatrix} \psi'_i(\mathbf{x}_1) & \psi'_j(\mathbf{x}_1) & \ldots & \psi'_n(\mathbf{x}_1) \\ \psi'_i(\mathbf{x}_2) & \psi'_j(\mathbf{x}_2) & \ldots & \psi'_n(\mathbf{x}_2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi'_i(\mathbf{x}_n) & \psi'_j(\mathbf{x}_n) & \ldots & \psi'_n(\mathbf{x}_n) \end{pmatrix}$$

Canonical Hartree Fock

$$\left|\psi_1\psi_2\ldots\psi_n\right\rangle=\frac{1}{\sqrt{n!}}\begin{vmatrix}\psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_1)\\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_2)\\ \ldots\ldots & \ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\\ \psi_i(\mathbf{x}_n) & \psi_j(\mathbf{x}_n) & \ldots\ldots\ldots\ldots & \psi_n(\mathbf{x}_n)\end{vmatrix}$$

$$=\frac{1}{\sqrt{n!}}\det(\mathbf{A})$$

$$\left|\psi'_1\psi'_2\ldots\psi'_n\right\rangle=\frac{1}{\sqrt{n!}}\det(\mathbf{A}')=\frac{1}{\sqrt{n!}}\det(\mathbf{AU})=\frac{1}{\sqrt{n!}}\det(\mathbf{A})\det(\mathbf{U})$$

$$\mathbf{U}^+\mathbf{U}=1\rightarrow\det\left(\mathbf{U}^+\mathbf{U}\right)=\det\left(\mathbf{U}^+\right)\det(\mathbf{U})=\left(\det(\mathbf{U})\right)^*\det(\mathbf{U})$$

$$=\left|\det(\mathbf{U})\right|^2=\det(1)=1$$

$$\det(\mathbf{U})=\exp(i\phi)$$

Unitary Transform of the orbital only gives change of phase

Canonical Hartree Fock

$$f(\mathbf{x}_1)\psi_i(\mathbf{x}_1) = \sum_{j=1}^{n} \varepsilon_{ji}\psi_j(\mathbf{x}_1) \qquad i = 1,2,\ldots n$$

Fock Operators are invariant to unitary transformation of occupied spin orbitals

$$f(\mathbf{x}_1) = f'(\mathbf{x}_1)$$

$$\langle \psi_i | f | \psi_j \rangle = \sum_{k=1}^{n} \varepsilon_{kj} \langle \psi_i | \psi_k \rangle = \varepsilon_{ij}$$

therefore

$$\varepsilon'_{ij} = \langle \psi'_i | f | \psi'_j \rangle = \sum_{l=1}^{n}\sum_{m=1}^{n} U_{li}^{*} U_{mj} \langle \psi_l | f | \psi_m \rangle = \sum_{l=1}^{n}\sum_{m=1}^{n} U_{li}^{*} U_{mj} \varepsilon_{lm} = \left(\mathbf{U}^{+}\varepsilon\mathbf{U}\right)_{ij}$$

If we find a unitary matrix that diagonalizes ε then

$$f(\mathbf{x}_1)\psi'_i(\mathbf{x}_1) = \varepsilon'_i \psi'_i(\mathbf{x}_1) \qquad i = 1,2,\ldots n$$

Canonical spin orbitals are eigen function of canonical fock operator

Orbital Energy and Total Hartree Fock Energy

$$\left[h(\mathbf{r}_1)+\sum_{j=1}^{n}\left(J_j(\mathbf{x}_1)-K_j(\mathbf{x}_1)\right)\right]\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

$$f(1)\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

ε_i : orbital energy $\quad \varepsilon_i=\langle\psi_i|f|\psi_i\rangle=h_{ii}+\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$

Sum of orbital energy

$$\sum_{i=1}^{n}\varepsilon_i=\sum_{i=1}^{n}h_{ii}+\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$$

$$\left\langle\psi_1\psi_2\ldots\psi_n\left|\hat{H}^0\right|\psi_1\psi_2\ldots\psi_n\right\rangle=\sum_{i=1}^{n}\left\langle\psi_i|h_1|\psi_i\right\rangle+\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\langle ij\mid ij\rangle-\langle ij\mid ji\rangle\right)$$

$$=\sum_{i=1}^{n}h_{ii}+\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$$

Closed Shell Hartree Fock Approximation

$$\left[h(\mathbf{r}_1)+\sum_{j=1}^{n}\left(J_j(\mathbf{x}_1)-K_j(\mathbf{x}_1)\right)\right]\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

$$f(\mathbf{r}_1)=h(\mathbf{r}_1)+\sum_{j=1}^{n}\left(J_j(\mathbf{x}_1)-K_j(\mathbf{x}_1)\right)$$

The above equation is based on spin orbitals assuming that we will only consider closed shell systems with same orbital for different spin

$$\left|\psi_1\psi_2\ldots\psi_n\right\rangle=\left|\phi_1\bar{\phi}_1..\phi_i\bar{\phi}_i\ldots\phi_{n/2}\bar{\phi}_{n/2}\right\rangle$$

$$\psi_1(\mathbf{x}_1)=\phi_1(\mathbf{r}_1)\alpha(s_1)\rightarrow\phi_1$$

$$\psi_2(\mathbf{x}_1)=\phi_1(\mathbf{r}_1)\beta(s_1)\rightarrow\bar{\phi}_1$$

Closed Shell HF Approximation

$$\left[h(\mathbf{r}_1)+\sum_{b=1}^{n/2}\left(2J_b(\mathbf{r}_1)-K_b(\mathbf{r}_1)\right)\right]\phi_a(\mathbf{r}_1)=\varepsilon_a\phi_a(\mathbf{r}_1)\qquad a=1,2,\ldots n/2$$

$$f(\mathbf{r}_1)=h(\mathbf{r}_1)+\sum_{b=1}^{n/2}\left(2J_b(\mathbf{r}_1)-K_b(\mathbf{r}_1)\right)$$

The Hartree Fock approximation energy is

$$\left\langle \phi_1\bar{\phi}_1\ldots\phi_{n/2}\bar{\phi}_{n/2}\right|\hat{H}^0\left|\phi_1\bar{\phi}_1\ldots\phi_{n/2}\bar{\phi}_{n/2}\right\rangle$$

$$=2\sum_{a=1}^{n/2}\left\langle\phi_a\right|h_1\left|\phi_a\right\rangle+\sum_{a=1}^{n/2}\sum_{b=1}^{n/2}\left(2\langle ab\,|\,ab\rangle-\langle ab\,|\,ba\rangle\right)$$

$$=2\sum_{a=1}^{n/2}h_{aa}+\sum_{a=1}^{n/2}\sum_{b=1}^{n/2}\left(2J_{ab}-K_{ab}\right)$$

Can use numerical basis to solve the HF equation.