Homonuclear Diatomic Molecule

Energy Diagram

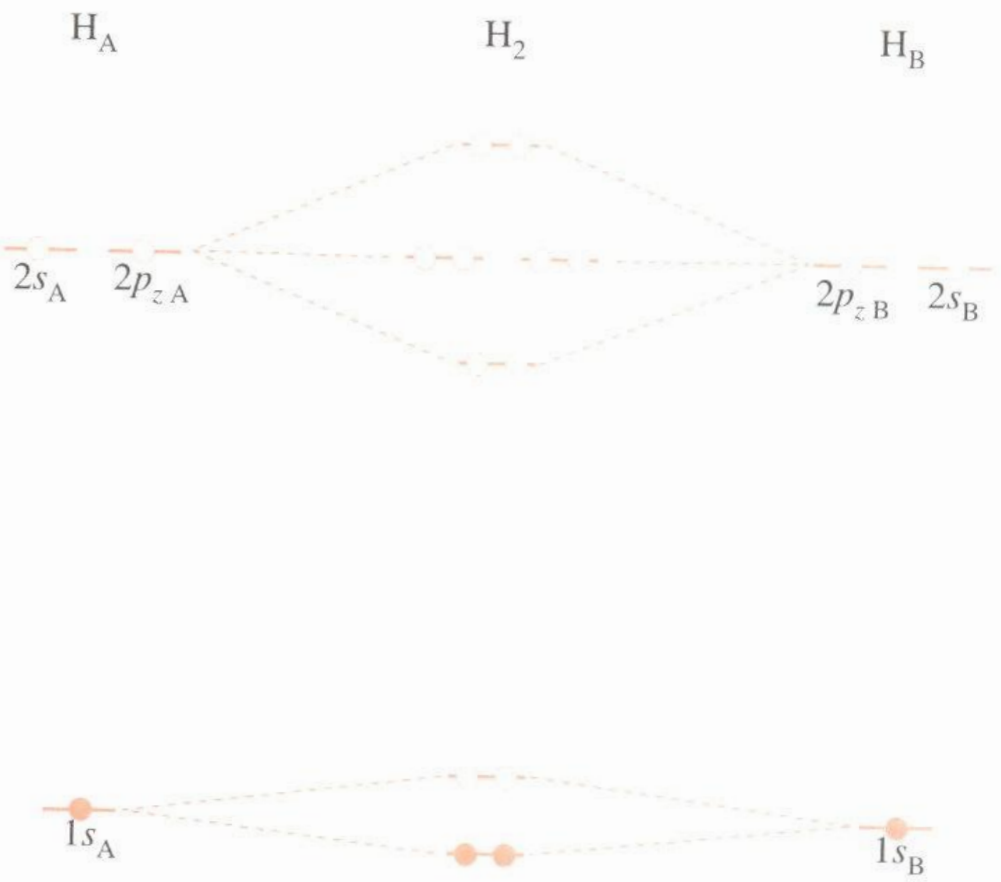
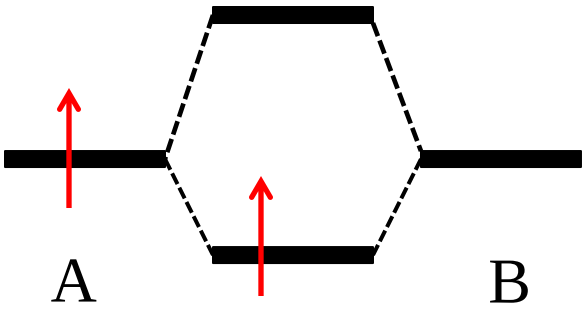
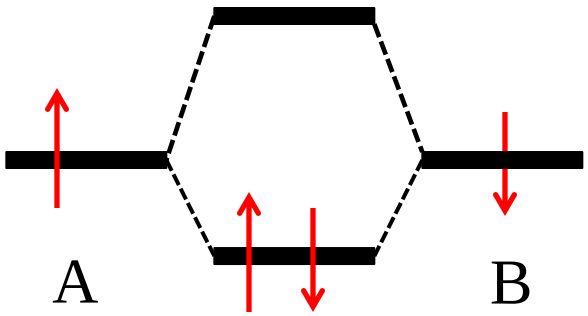


FIGURE 10.28
The six spatial molecular orbitals that are obtained when the LCAO-MO is a linear combination of six atomic orbitals, as in Equation 10.55. Only the molecular orbital of the lowest energy is occupied in the ground electronic state of H_2. The five unoccupied orbitals are called virtual orbitals.

H_2^+, H_2, He_2^+, He_2



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



H_2 R_{eq}= Angstrom
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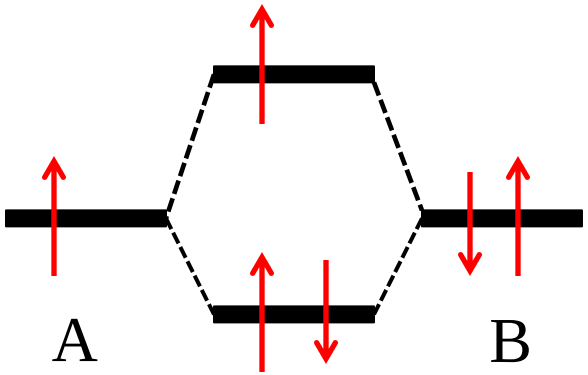
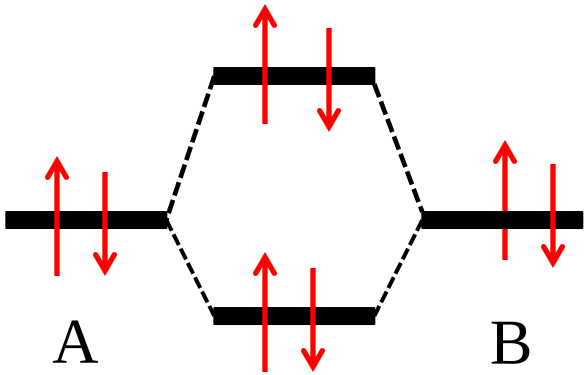
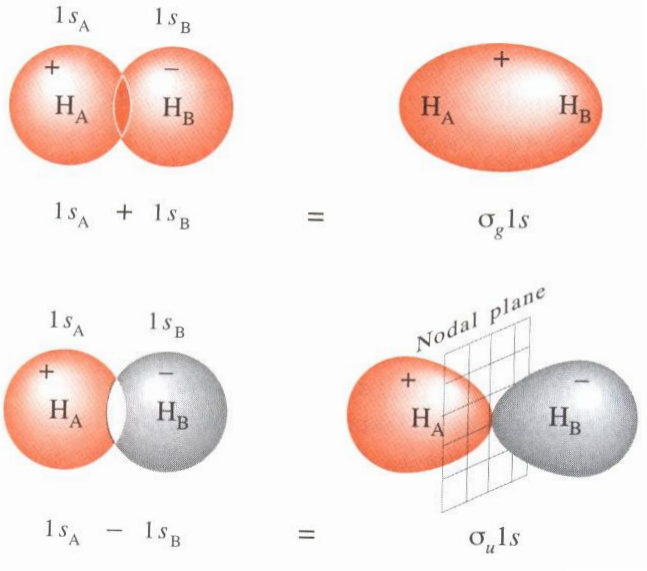


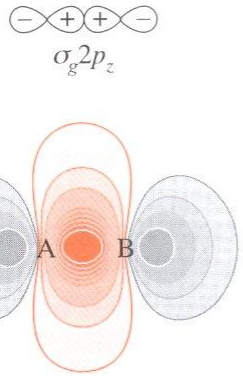
He_2^+ R_{eq}= Angstrom
Binding Energy kcal/mol

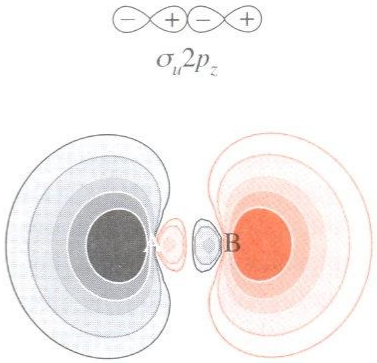


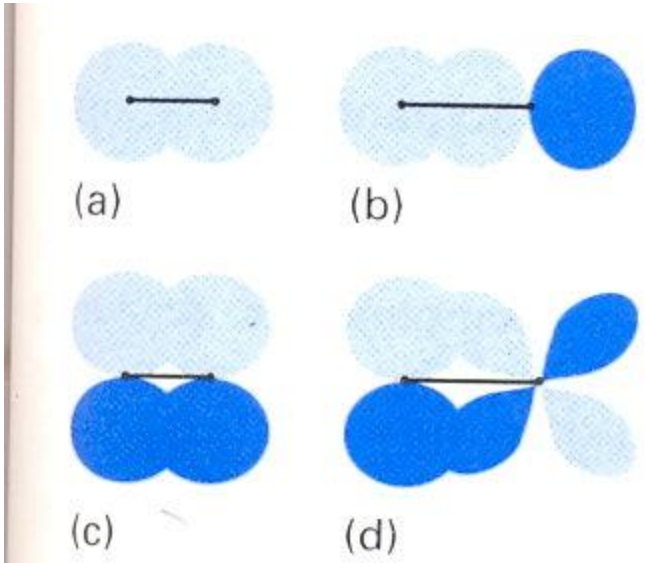
He_2 R_{eq}=
Binding Energy Kcal mol

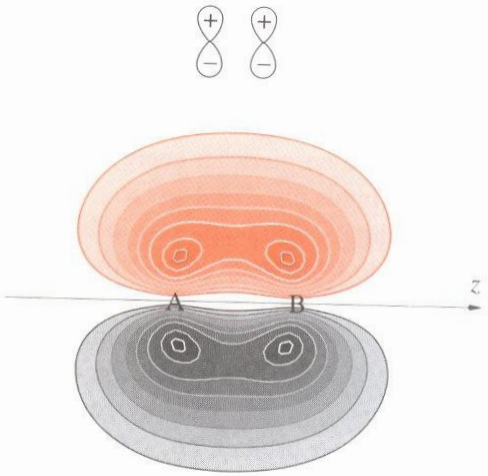
Molecular Orbitals: Sum of Atomic Orbitals Sigma and Pi

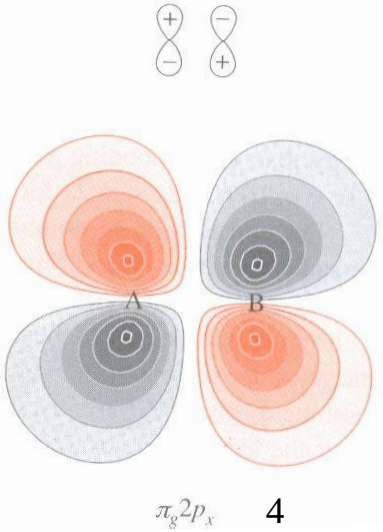






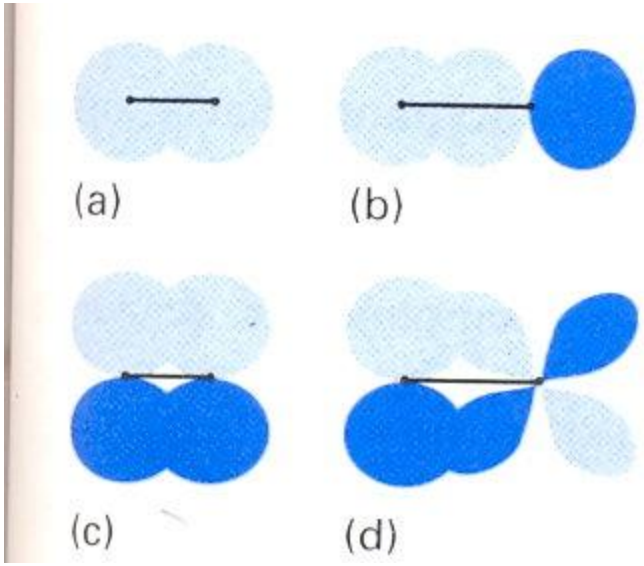






Symmetry of Orbitals Important

Allowed Combinations



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

Binding Energy: Orbital Interaction

- Binding depends on overlap of atomic orbitals:

Energies of atomic orbital closer the better

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

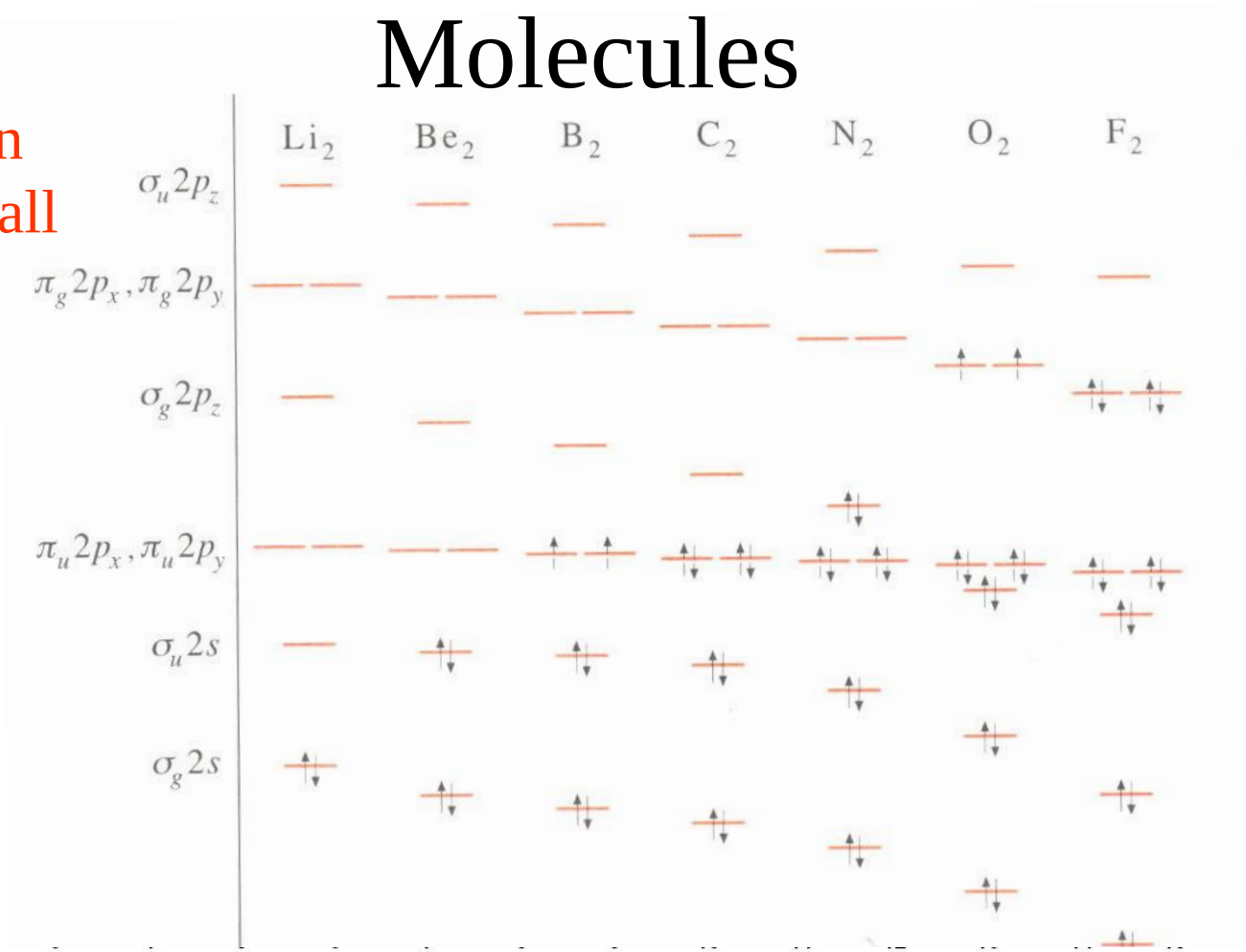
$$\begin{vmatrix} H_{AA}-E & H_{AB}-ES \\ H_{BA}-ES & H_{BB}-E \end{vmatrix} = \begin{vmatrix} \alpha_A-E & \beta-ES \\ \beta-ES & \alpha_B-E \end{vmatrix} = 0$$

Assume S=0 and $|E_A-E_B| >> E_{AB}$

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

Second Row Homonuclear diatomic Molecules

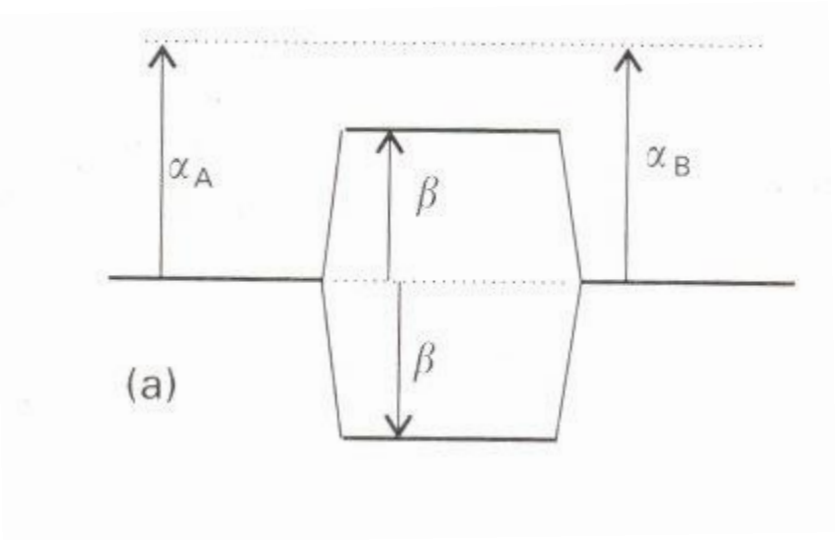
Ignore
1S interaction
Since too small

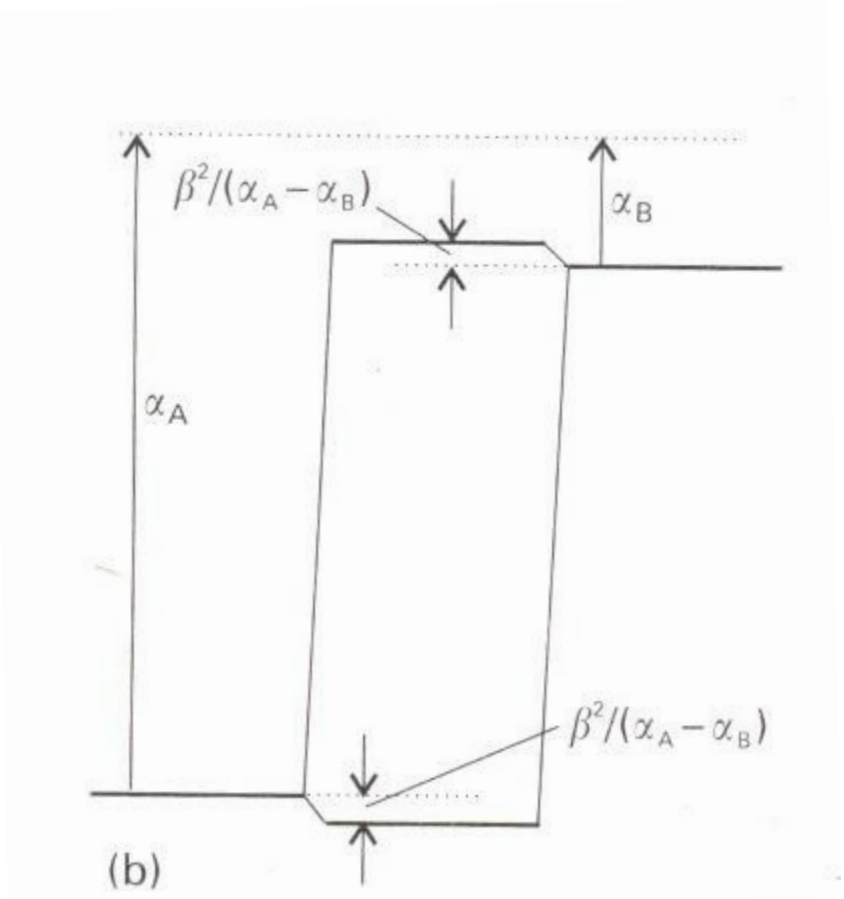


Valance Orbitals are considered

HOMO LUMO Gap ↔ Band Gap

Homo/Heteronuclear Diatomic Molecules





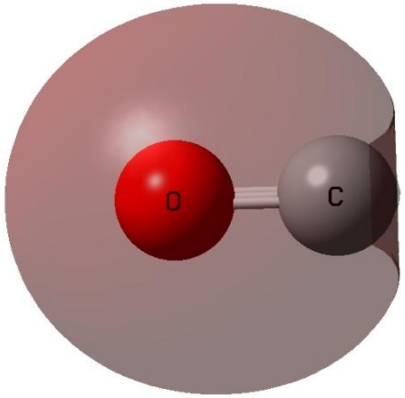
CO Molecule: Orbitals

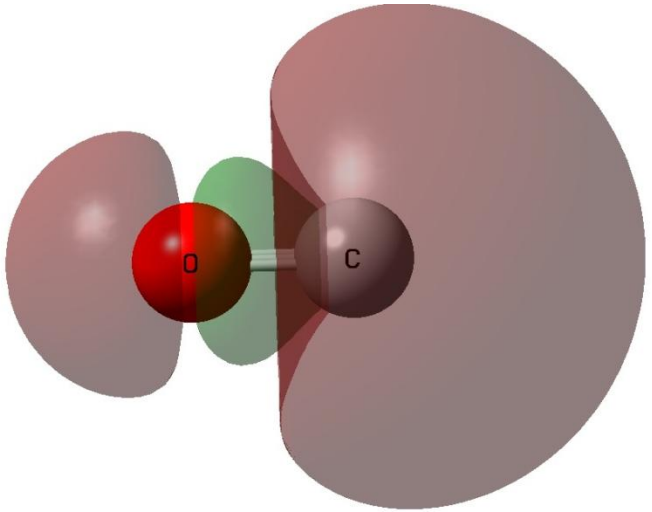
In heterodiatomic molecules electronegativity of the atoms determine the shape of the orbital

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

C_A and C_B define the density on A and B

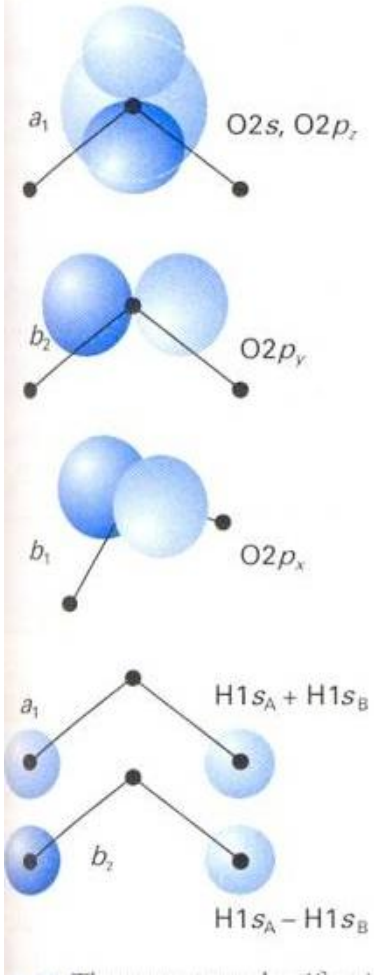
If A is more electronegative:

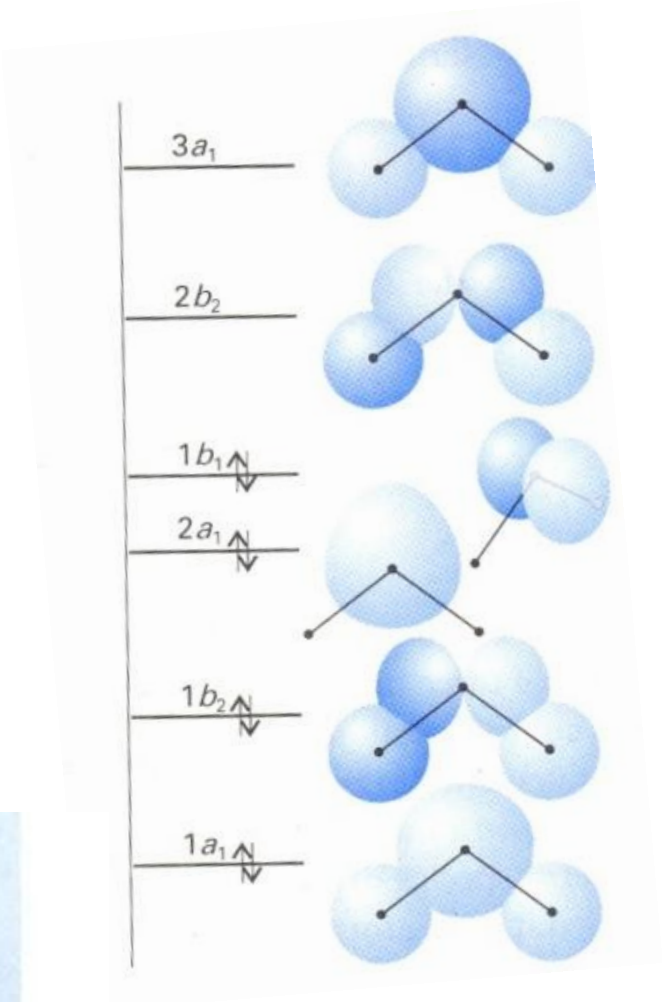




Polyatomic Molecules

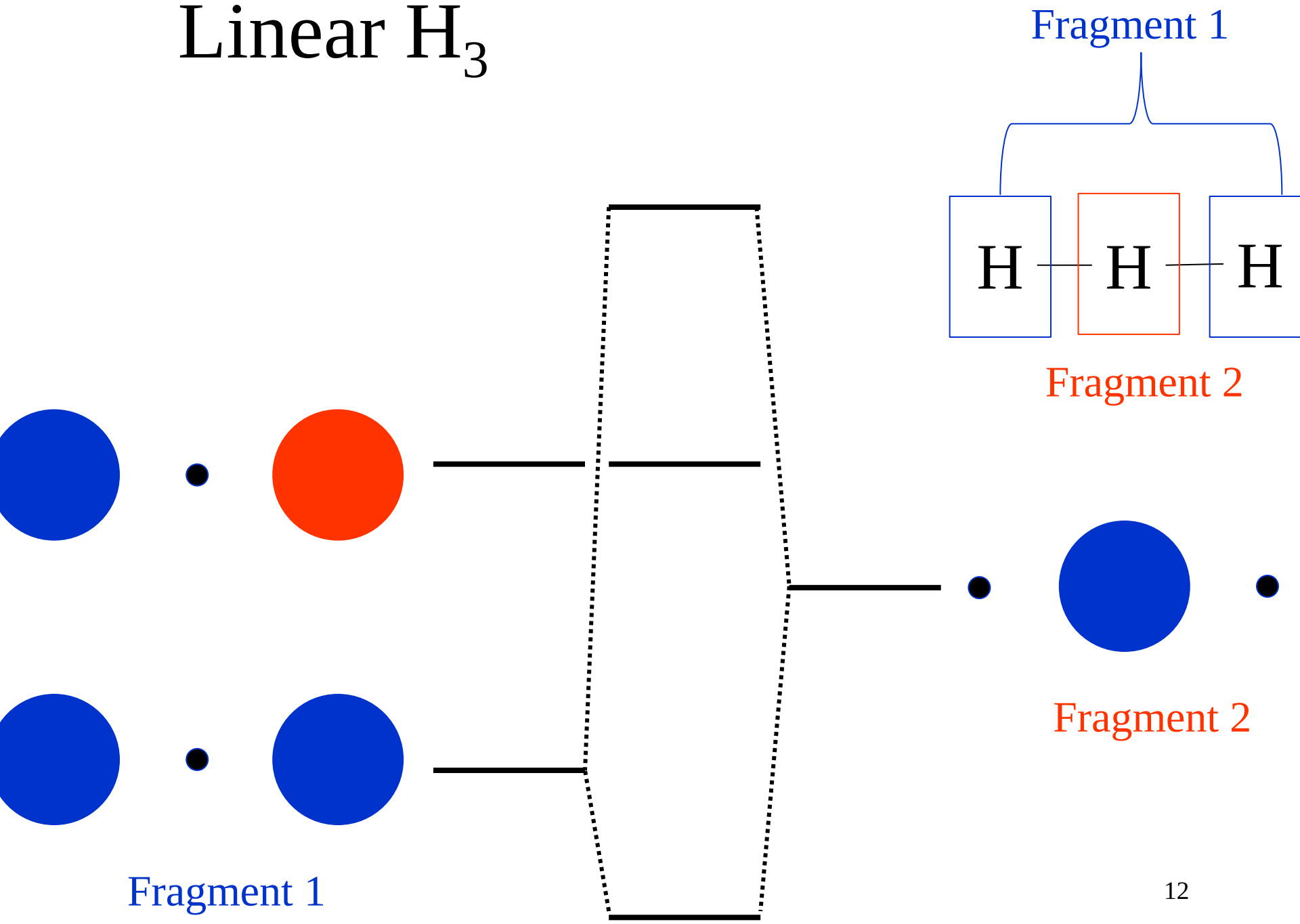
Water H_2O





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$_B$

Linear H_3



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 with trial WF

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

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

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

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

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

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

One Electron Operator Matrix Element

$$\langle 0|h_1|0\rangle = 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)^* \times h(\mathbf{r}_1)\left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)$$

$$= 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 [$$

$$]$$

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

One Electron Operator 2

$$\langle 0|h_1|0\rangle = 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 \left[\psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)h(\mathbf{r}_1)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\right.$$
$$\left. + \psi_j^*(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)h(\mathbf{r}_1)\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right]$$
$$= 2^{-1}\int \psi_i^*(\mathbf{x}_1)h(\mathbf{r}_1)\psi_i(\mathbf{x}_1)d\mathbf{x}_1 + 2^{-1}\int \psi_j^*(\mathbf{x}_1)h(\mathbf{r}_1)\psi_j(\mathbf{x}_1)d\mathbf{x}_1$$
$$= 2^{-1}\left(\langle\psi_i|h|\psi_i\rangle + \langle\psi_j|h|\psi_j\rangle\right)$$
$$\langle 0|h_2|0\rangle = 2^{-1}\left(\langle\psi_i|h|\psi_i\rangle + \langle\psi_j|h|\psi_j\rangle\right)$$

Two Electron Operator Matrix Element

$$\left\langle 0\left|\left|\mathbf{r}_{12}\right|^{-1}\right|0\right\rangle = 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 \left(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\right)^*$$

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

$$= 2^{-1}\iint d\mathbf{x}_1 d\mathbf{x}_2 [$$

$$]$$

Two Electron Operator 2

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

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

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

Expectation Value of Slater Det

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

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

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

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

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

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

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

Hartree Fock Approximation 1

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

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

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

$$\langle\psi_i\,|\,\psi_j\rangle = \delta_{ij}$$

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

Hartree Fock Approximation 2

Functional minimization with constraint

Functional derivative with respect to change of spin orbital

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

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

$$\delta\langle\psi_i \,|\, \psi_j\rangle = \langle\delta\psi_i \,|\, \psi_j\rangle + \langle\psi_i \,|\, \delta\psi_j\rangle$$

Hartree Fock Approximation 3

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

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

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

Remember the exchange relationship of two electron integral

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

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

$$=$$

Hartree Fock Approximation 4

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

$$=$$

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

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

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

Hartree Fock Approximation 5

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

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

$$\sum_{i=1}^{n}\int\delta\psi_i^{*}\left(\mathbf{x}_1\right)h\left(\mathbf{r}_1\right)\psi_i\left(\mathbf{x}_1\right)d\mathbf{x}_1+\sum_{i=1}^{n}\sum_{j=1}^{n}\iint d\mathbf{x}_1d\mathbf{x}_2\left(\delta\psi_i^{*}\left(\mathbf{x}_1\right)\psi_j^{*}\left(\mathbf{x}_2\right)\left|\mathbf{r}_{12}\right|^{-1}\psi_i\left(\mathbf{x}_1\right)\psi_j\left(\mathbf{x}_2\right)\right)$$

$$-\sum_{i=1}^{n}\sum_{j=1}^{n}\iint d\mathbf{x}_1d\mathbf{x}_2\left(\delta\psi_i^{*}\left(\mathbf{x}_1\right)\psi_j^{*}\left(\mathbf{x}_2\right)\left|\mathbf{r}_{12}\right|^{-1}\psi_j\left(\mathbf{x}_1\right)\psi_i\left(\mathbf{x}_2\right)\right)-\sum_{i=1}^{n}\sum_{j=1}^{n}\varepsilon_{ji}\iint\delta\psi_i^{*}\left(\mathbf{x}_1\right)\psi_j\left(\mathbf{x}_1\right)d\mathbf{x}_1$$

Coulomb and Exchange Integral

Coulomb Integral

Exchange Integral

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

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

Hartree Fock Approximation 6

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

$$=0$$

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

Fock Operator of spin orbitals

Canonical Hartree Fock

Unitary Transform of the Hartree Fock occupied orbitals

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

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

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

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

Canonical Hartree Fock

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

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

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

Canonical Hartree Fock

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

Fock Operators are invariant to unitary transformation of spin orbitals

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

therefore

If we find a unitary matrix that diagonalizes ε then

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

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 $\quad \varepsilon_i =$

Sum of orbital energy

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

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

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

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

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

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

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

Can use numerical basis to solve the HF equation.