Hartree-Fock Energy

Nuclear repulsion energy

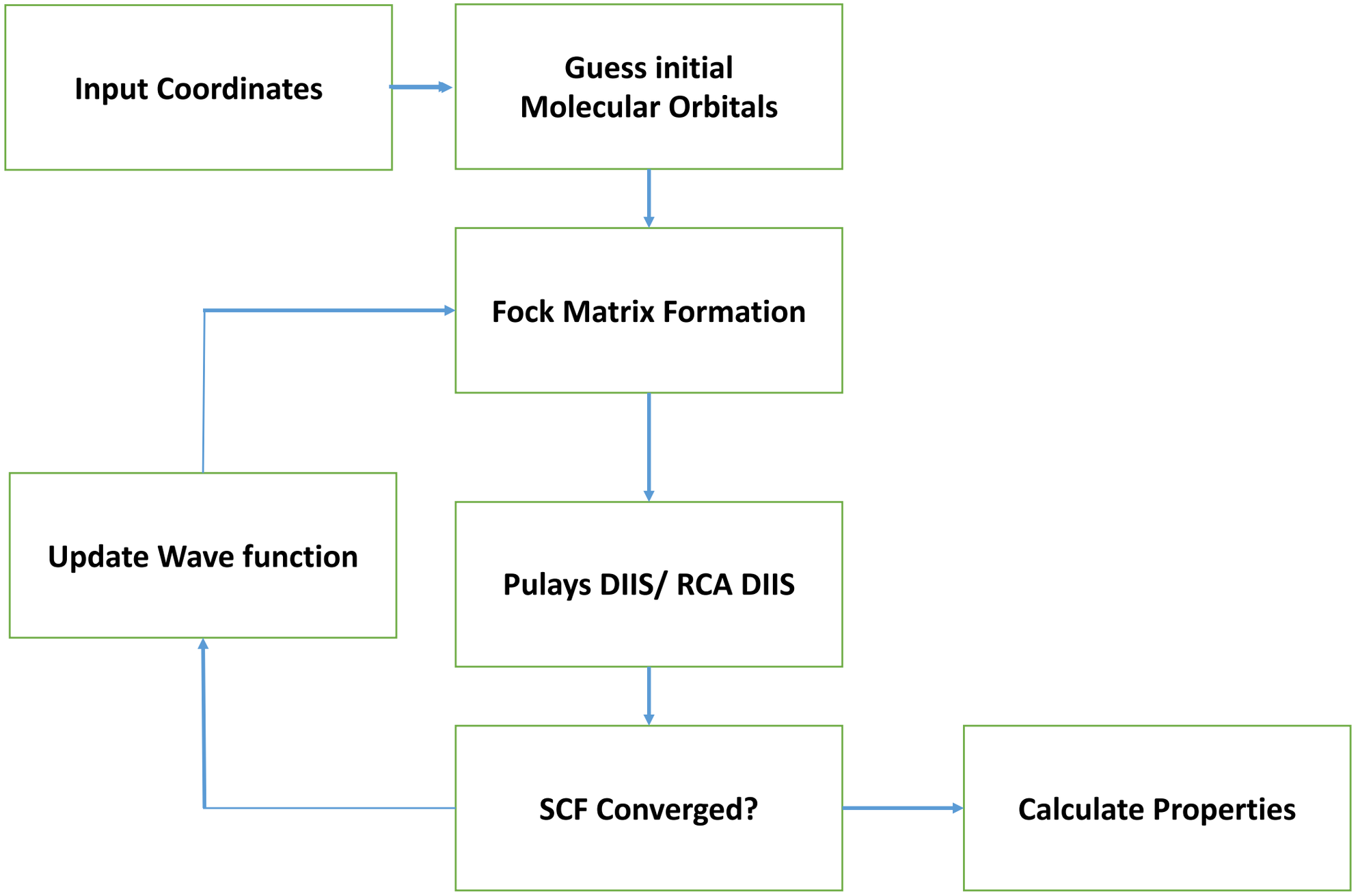
One electron term

Two electron term

Energy Units

- Atomic Unit is the Hartree
- H atom energy is -1/2 Hartree
- 1 Hartree = 627.509 kcal/mol
- 1 Hartree = 27.2114 eV

Overview of SCF procedure



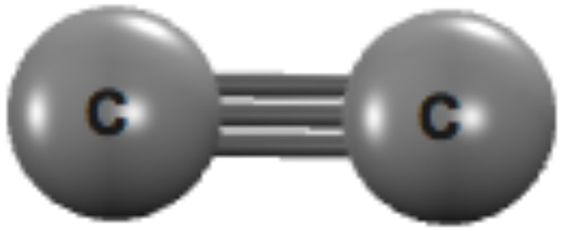
Fock Matrix

Fock matrix:

	1	2	3	4	5	6
1 -	-11.050296	0.000000	-0.000000	0.000000	0.000000	0.000000
2 -	0.000000	-11.048801	-0.000000	-0.000000	-0.000000	-0.000000
3 -	-0.000000	-0.000000	-0.969371	-0.000000	-0.000000	0.000000
4 -	0.000000	-0.000000	-0.000000	-0.426396	-0.000000	-0.000000
5 -	0.000000	-0.000000	-0.000000	-0.000000	-0.369987	0.000000
6 -	0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.369987
7 -	0.000000	0.000000	0.000000	-0.000000	-0.000000	0.000000
8 -	0.000000	-0.000000	-0.000000	-0.000000	0.000000	-0.000000
9 -	-0.000000	0.000000	0.000000	-0.000000	-0.000000	0.000000
10 -	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000

	7	8	9	10
1 -	0.000000	0.000000	-0.000000	0.000000
2 -	0.000000	-0.000000	0.000000	-0.000000
3 -	0.000000	-0.000000	0.000000	-0.000000
4 -	-0.000000	-0.000000	-0.000000	0.000000
5 -	-0.000000	0.000000	-0.000000	-0.000000
6 -	0.000000	-0.000000	0.000000	0.000000
7 -	0.031851	0.000000	-0.000000	-0.000000
8 -	0.000000	0.346504	0.000000	-0.000000
9 -	-0.000000	0.000000	0.346504	0.000000
10 -	-0.000000	-0.000000	0.000000	1.144281

Carbon Dimer!



C $1s^2 2s^2 2p^2$

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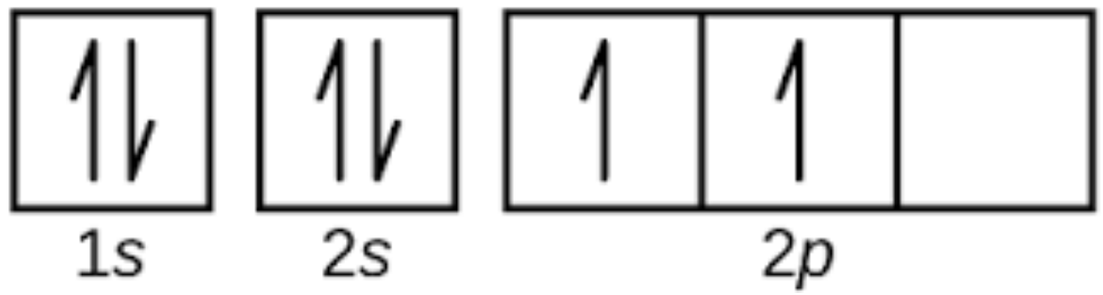

Total number of electrons: 12

Total number of molecular orbitals: 10

Molecular spin orbital

Motion of single electron

$$\chi(X)$$

$$X = (x, y, z, \omega)$$

$$\vec{r} = \{x, y, z\} \qquad \omega = \text{Spin Coordinate}$$

Spatial coordinates Spin coordinate

$$\chi(X) = \psi(\vec{r})\alpha(\omega)$$

$$\chi(X) = \psi(\vec{r})\beta(\omega)$$

Recap from last group meeting....

Hartree-Fock Energy for a Slater Determinant

- For N electrons in N molecular orbitals, the Slater determinant is

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{\sqrt{(N)!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

The energy of this Slater determinant is

$$E_{HF} = \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} [(ii|jj) - (ij|ij)]$$

where

$$\begin{aligned} h_i &= \int d\vec{r}\, \psi_i^*(\vec{r}) \left[-\frac{1}{2} \bigtriangledown^2 - \sum_A \frac{Z_A}{\left|\vec{r} - \vec{R}_A\right|} \right] \psi_i(\vec{r}) \\ (ii|jj) &= \iint d\vec{r}_1 d\vec{r}_2 \psi_i^*(\vec{r}_1) \psi_i^*(\vec{r}_1) \frac{1}{r_{12}} \psi_j(\vec{r}_2) \psi_j(\vec{r}_2) \\ (ij|ij) &= \iint d\vec{r}_1 d\vec{r}_2 \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_1) \frac{1}{r_{12}} \psi_i(\vec{r}_2) \psi_j(\vec{r}_2) \end{aligned}$$

- **One electron Integrals**

$$[i|\hat{h}|j] = \int dX_1 \psi_i{}^*(X_1)\hat{h}(\vec{r}_1)\psi_j(X_1)$$

$$[i|\hat{h}|j] = \int d\omega \sigma_i{}^*(\omega)\sigma_j(\omega) \int d\vec{r}\psi_i{}^*(\vec{r})\hat{h}(\vec{r})\psi_j(\vec{r})$$

$$[i|\hat{h}|j] = \int d\omega \sigma_i{}^*(\omega)\sigma_j(\omega) \left(i|\hat{h}|j\right)$$

- **Two electron Integrals**

$$[ij|kl] = \int dX_1 dX_2 {\Psi_i}^*(X_1){\psi_j}^*(X_1)\frac{1}{\vec{r}_{12}}\psi_k(X_2)\psi_l(X_2)$$

$$[ij|kl] = \int d\omega_1 {\sigma_i}^*(\omega_1)\sigma_j(\omega_1) \int d\omega_2 {\sigma_k}^*(\omega_2)\sigma_l(\omega_2)(ij|kl)$$

Spin Orbitals

$$E_{HF} = E_{Nuc} + \sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{i=1}^{N} \sum_{i=1}^{N} [(ii|jj) - (ij|ij)]$$

$$F_{pq} = h_{pq} + \sum_{i=1}^{N} [(pq|ii) - (pi|qi)]$$

Spatial Orbitals

$$E_{RHF} = E_{Nuc} + 2 \sum_{i=1}^{N/2} h_{ii} + \sum_{i=1}^{N/2} \sum_{i=1}^{N/2} [2(ii|jj) - (ij|ij)]$$

$$F_{pq} = h_{pq} + \sum_{i=1}^{N/2} [2(pq|ii) - (pi|qi)]$$