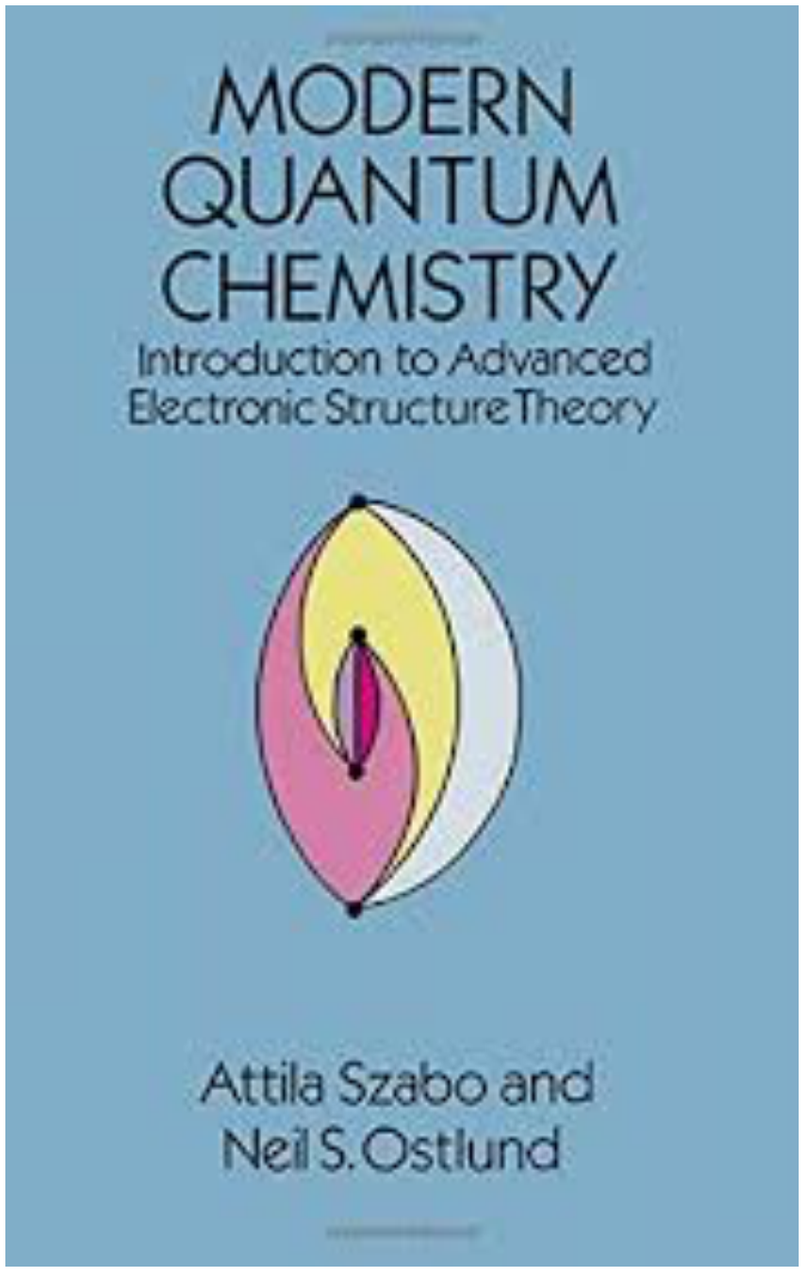
Introduction to Hartree-Fock Theory


MODERN
QUANTUM
CHEMISTRY
Introduction to Advanced
Electronic Structure Theory
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What we are trying to solve?

Time independent Schrödinger equation in Born-Oppenheimer approximation

$$\hat{H}_{el}(r;R)\psi(r;R) = E_{el}(R)\psi(r;R)$$

$$H_{elec} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

$$= \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

One electron term

Two electron term

The Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

John Slater

Shorthand: $|\chi_i \chi_j \cdots \chi_k\rangle$ or $|ij \cdots k\rangle$

We will assume the electronic wavefunction can be written as a single Slater Detrminant (this is an approximation). This enforces an antisymmetric wavefunction. The Hartree-Fock procedure will give us the orbitals.

Images from Wikipedia

The Slater Rule

For One Electron Operator $O_1 = \sum_{i=1}^{N} h(i)$

$$\langle \bullet\bullet\bullet mn \bullet\bullet\bullet | O_1 | \bullet\bullet\bullet mn \bullet\bullet\bullet \rangle = \sum_{m}^{N} \langle m | h | m \rangle$$

$$\langle \bullet\bullet\bullet mn \bullet\bullet\bullet | O_1 | \bullet\bullet\bullet mp \bullet\bullet\bullet \rangle = \langle n | h | p \rangle$$

$$\langle \bullet\bullet\bullet mn \bullet\bullet\bullet | O_1 | \bullet\bullet\bullet pq \bullet\bullet\bullet \rangle = 0$$

For two electron operator $O_2 = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$

$$\langle \bullet\bullet\bullet mn \bullet\bullet\bullet | O_2 | \bullet\bullet\bullet mn \bullet\bullet\bullet \rangle = \frac{1}{2} \sum_{m}^{N} \sum_{n}^{N} \langle mn \| mn \rangle$$

$$\langle \bullet\bullet\bullet mn \bullet\bullet\bullet | O_2 | \bullet\bullet\bullet mp \bullet\bullet\bullet \rangle = \sum_{m}^{N} \langle mn \| mp \rangle$$

$$\langle \bullet\bullet\bullet mn \bullet\bullet\bullet | O_2 | \bullet\bullet\bullet pq \bullet\bullet\bullet \rangle = \langle mn \| pq \rangle$$

for orthonormal χ

$$E = \langle \psi | H | \psi \rangle = ?$$

Physical Meaning of the Terms

- Each pair of electrons (in orbitals *i* and *j*) has a "Coulomb integral":

$$[ii|jj] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2)$$

Probability electron 1 in orbital *i* is located at x_1

Probability electron 2 in orbital *j* is located at x_2

Integrate over all possible locations for the electrons

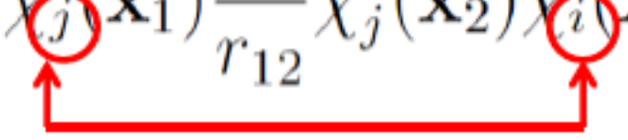
Coulomb repulsion between electron at x_1 and electron at x_2

Overall this integral represents the Coulomb repulsion between electron 1 in orbital *i* and electron 2 in orbital *j*

Exchange term

- Each pair of electrons (in orbitals *i* and *j*) has also has an "Exchange integral":

$$[ij|ji] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \; \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)$$



- This is like the Coulomb integral

$$[ii|jj] = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \; \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)\frac{1}{r_{12}}\chi_j^*(\mathbf{x}_2)\chi_j(\mathbf{x}_2)$$

Except two of the orbital indices have been "exchanged"!

No direct physical meaning .. consequence of Slater Determinant

Constrained Variation

$$L\left[\{\chi_a\}\right] = E_0\left[\{\chi_a\}\right] - \sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ab}\left(\langle\chi_a\|\chi_b\rangle - \delta ab\right)$$

$$\frac{\partial L}{\partial \chi} = 0 \qquad\qquad \chi_a \rightarrow \chi_a + \delta\chi_a$$

For the derivation see David Sherils lectures (https://www.youtube.com/watch?v=6XFOF8-QkAM&feature=relmfu, http://www.youtube.com/watch?v=1jHkt1Qzv1A&feature=relmfu)

$$f_i(1)\chi_i(1) = \varepsilon_i\chi_i(1)$$

where

$$f_i(1) = h_i(1) + \sum_{j=1}^{N}\int \chi_j^*(2)\frac{(1-P_{12})}{r_{12}}\chi_j d\tau_2$$

$$\varepsilon_i = \langle\chi_i|f_i|\chi_i\rangle = \langle\chi_i|h_i|\chi_i\rangle + \sum_{j=1}^{N}\langle\chi_i\chi_j\|\chi_i\chi_j\rangle \qquad E_{HF} \neq \sum_i \varepsilon_i$$

$$E_{HF} = \sum_{i=1}^{N}\varepsilon_i - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\chi_i\chi_j\|\chi_i\chi_j\rangle$$

Spin integration

$$\chi_1 = \phi_1\alpha \qquad \chi_2 = \phi_1\beta$$
$$\chi_3 = \phi_2\alpha \qquad \chi_4 = \phi_2\beta$$
$$\vdots \qquad\qquad \vdots$$
$$\chi_{N-1} = \phi_{\frac{N}{2}}\alpha \qquad \chi_N = \phi_{\frac{N}{2}}\beta$$

$$f_i(1)\chi_i(1) = \varepsilon_i\chi_i(1)$$

$$f_i(\vec{r}_1,\omega_1)\phi_i(1)\alpha(1) = \varepsilon_i\phi_i(1)\alpha(1)$$

Left multiplying with α and integrating

$$\int \alpha^*(1) f_i(\vec{r}_1,\omega_1)\phi_i(1)\alpha(1)d\omega_1 = \varepsilon_i \int \alpha(1)\phi_i(1)\alpha(1)d\omega_1$$

$$\int\left[\alpha^*(1) f_i(\vec{r}_1,\omega_1)\alpha(1)d\omega_1\right]\phi_i(1) = \varepsilon_i \int \alpha(1)\phi_i(1)\alpha(1)d\omega_1$$

Spin integration

$$\int\left[\alpha^*(1) f_i(\vec{r}_1,\omega_1)\alpha(1)d\omega_1\right]\phi_i(1)=\varepsilon_i\phi_i$$

$$f(\vec{r}_1)=\int d\omega_1\alpha^*(1) f_i(\vec{r}_1,\omega_1)\alpha(1)=\int d\omega_1\alpha^*(1) h_i(\vec{r}_1)\alpha(1)+$$

$$\sum_{j=1}^{N}\int d\omega_1\, d\tau_2\alpha^*(1)\chi_j^*(\vec{r}_2,\omega_2)\frac{1}{r_{12}}\chi_j(\vec{r}_2,\omega_2)\alpha(1)-$$

$$\sum_{j=1}^{N}\int d\omega_1\, d\tau_2\alpha^*(1)\chi_j^*(\vec{r}_2,\omega_2)\frac{1}{r_{12}}\chi_j(\vec{r}_1,\omega_1)\alpha(2)$$

Now

$$\chi_j(\vec{r}_2,\omega_2)\to\phi_j(\vec{r}_2)\alpha(\omega_2)$$

$$\chi_j(\vec{r}_2,\omega_2)\to\phi_j(\vec{r}_2)\beta(\omega_2)$$

$$\sum_{j=1}^{N}\ \to\sum_{j=1}^{N/2}+\sum_{j=1}^{N/2}$$

$$f(\vec{r}_1)=\int d\omega_1\alpha^*(1)f_i(\vec{r}_1,\omega_1)\alpha(1)=\int d\omega_1\alpha^*(1)h_i(\vec{r}_1)\alpha(1)+$$

$$\sum_{j=1}^{N}\int d\omega_1\, d\tau_2\alpha^*(1)\chi_j^*(\vec{r}_2,\omega_2)\frac{1}{r_{12}}\chi_j(\vec{r}_2,\omega_2)\alpha(1)-$$

$$\sum_{j=1}^{N}\int d\omega_1\, d\tau_2\alpha^*(1)\chi_j^*(\vec{r}_2,\omega_2)\frac{1}{r_{12}}\chi_j(\vec{r}_1,\omega_1)\alpha(2)$$

$$f(\vec{r}_1)=h(\vec{r}_1)+\sum_{j=1}^{N/2}\int d\omega_1\, d\omega_2\, dr_2\alpha^*(1)\phi_j^*(2)\alpha^*(2)\frac{1}{r_{12}}\phi_j(2)\alpha(2)\alpha(1)+$$

$$\sum_{j=1}^{N/2}\int d\omega_1\, d\omega_2\, dr_2\alpha^*(1)\phi_j^*(2)\beta^*(2)\frac{1}{r_{12}}\phi_j^*(2)\beta^*(2)\alpha(1)$$

$$-\sum_{j=1}^{N/2}\int d\omega_1\, d\omega_2\, dr_2\phi_j^*(2)\alpha^*(2)\alpha^*(1)\frac{1}{r_{12}}\phi_j(1)\alpha(1)\alpha(2)$$

$$-\sum_{j=1}^{N/2}\int d\omega_1\, d\omega_2\, dr_2\phi_j^*(2)\beta^*(2)\alpha^*(1)\frac{1}{r_{12}}\phi_j(1)\beta(1)\alpha(2)$$

Restricted Hartree- Fock equation

$$f_i(1)=h_i(1)+\sum_{j=1}^{N/2}\int\phi_j^*(2)\frac{(2-P_{12})}{r_{12}}\phi_j(2)dr_2$$

Roothan Equation

$$f_i(1)\phi_i(1) = \varepsilon_i\phi_i(1)$$

Introduction of Basis

$$\phi_i(\vec{r}) = \sum_{\mu=1}^{M} C_{\mu i} A_\mu(\vec{r})$$

Molecular Orbital

LCAO-MO coefficient

Atomic Orbital

$$f_i \sum_\mu C_{\mu i} A_\mu = \varepsilon_i \sum_\mu C_{\mu i} A_\mu$$

Left multiply the the above equation with a particular member of the basis

$$\int dr A_\nu f_i \sum_\mu C_{\mu i} A_\mu = \varepsilon_i \int dr A_\nu \sum_\mu C_{\mu i} A_\mu$$

Fock Matrix in AO basis

$$\sum_{\mu}\left\langle A_{\nu}\middle|f_{i}\middle|A_{\mu}\right\rangle C_{\mu i}=\varepsilon_{i}\sum_{\mu}\left\langle A_{\nu}\middle|A_{\mu}\right\rangle C_{\mu i}\qquad\sum_{\mu}F_{\nu\mu}C_{\mu i}=\varepsilon_{i}\sum_{\mu}S_{\nu\mu}C_{\mu i}$$

$$f_{i}(1)=h_{i}(1)+\sum_{j=1}^{N/2}\int\phi_{j}^{*}(2)\frac{\left(2-P_{12}\right)}{r_{12}}\phi_{j}(2)\,dr_{2}$$

$$F_{\nu\mu}=\int dr_{1}\,A_{\nu}^{*}(1)h(1)\,A_{\mu}$$

$$+\sum_{j=1}^{N/2}\int dr_{1}\,dr_{2}\,A_{\nu}^{*}(1)\phi_{j}^{*}(2)\frac{\left(2-P_{12}\right)}{r_{12}}\phi_{j}(2)\,A_{\mu}(1)$$

$$=H_{\nu\mu}^{Core}+\sum_{j=1}^{N/2}\sum_{\lambda}\sum_{\sigma}\int dr_{1}\,dr_{2}\,A_{\nu}^{*}(1)\,A_{\lambda}^{*}(2)\frac{\left(2-P_{12}\right)}{r_{12}}\,A_{\sigma}(2)\,A_{\mu}(1)$$

where $\phi_{j}=\sum_{\sigma}C_{\sigma j}A_{j}$

$$F_{\nu\mu}=H_{\nu\mu}^{Core}+\sum_{j=1}^{N/2}\sum_{\lambda}\sum_{\sigma}C_{\lambda j}^{*}C_{\sigma j}\left(2\left\langle\nu\lambda\middle|\mu\sigma\right\rangle-\left\langle\nu\lambda\middle|\sigma\mu\right\rangle\right)$$

Two electron integrals has eight fold Symmetry

$$F_{\nu\mu}=H_{\nu\mu}^{Core}+\sum_{\lambda}\sum_{\sigma}P_{\sigma\lambda}\left(\left\langle\nu\lambda\middle|\mu\sigma\right\rangle-\frac{1}{2}\left\langle\nu\lambda\middle|\sigma\mu\right\rangle\right)\qquad P_{\sigma\lambda}=\sum_{j}2C_{\lambda j}^{*}C_{\sigma j}$$

Charge density bond order matrix

Hatree-Fock equation in Canonical Basis

$$\sum_{\mu} F_{\nu\mu} C_{\mu i} = \varepsilon_i \sum_{\mu} S_{\nu\mu} C_{\mu i}$$

In matrix notation $FC = SC\varepsilon$

Define a new orthonormal basis

$$A'_{\mu} = \sum_{\lambda} X_{\lambda\mu} A_{\lambda}$$

How to get X ?

$$\left\langle A'_{\mu} \middle| A'_{\nu} \right\rangle = \sum_{\lambda}\sum_{\sigma} X^{*}_{\lambda\mu} X_{\sigma\nu} \left\langle A_{\lambda} \middle| A_{\sigma} \right\rangle$$

$$\sum_{\lambda}\sum_{\sigma} \left(X\right)^{\dagger}_{\mu\lambda} \left\langle A_{\lambda} \middle| A_{\sigma} \right\rangle X_{\sigma\nu} = \left(X^{\dagger} S X\right)_{\mu\nu} = \delta_{\mu\nu}$$

A simple choice $X = S^{-\frac{1}{2}}$ **Löwdin Orthogonalization**

Hatree-Fock equation in Canonical Basis

$$FC = SC\varepsilon$$

Now premultiplying $X^{\dagger}$

$$X^{\dagger}FC = X^{\dagger}SC\varepsilon$$

$$X^{\dagger}FX\left(X^{-1}C\right) = X^{\dagger}SX\left(X^{-1}C\right)\varepsilon$$

Taking $C' = X^{-1}C$ and $F' = X^{\dagger}FX$

$$F'C = C'\varepsilon$$

Choose Geometry