Hartree-Fock approximation

Solution of the N-electron Schrödinger equation in the field of M nuclei. Non-relativistic approach. Spin-space coordinates

$\vec{x}_i \equiv \{\vec{r}_i(\omega_i)\}$ $\quad \alpha(\omega) \equiv \uparrow$, $\beta(\omega) \equiv \downarrow$

Electronic Hamiltonian (for the fixed nuclei - Born-Oppenheimer approx.):

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{j=1}^{M}\frac{z_j}{|\vec{r}_i - \vec{R}_j|} + \sum_{i=1}^{N}\sum_{j>i}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

(atomic units)

one-electron term $h = \sum_{i=1}^{N} h(i)$ — 2-electron term

- Our goal is not to look for the eigenvalues of the Hamiltonian H, but we search states $\Psi(\vec{x}_1 \dots \vec{x}_N)$ that minimize the functional $E_0 = \langle \Psi | H | \Psi \rangle$ with normalization condition $\langle \Psi | \Psi \rangle = 1$

- Approximation Hartree 1927

$$\Psi(\vec{x}_1 \dots \vec{x}_N) = \varphi_1(\vec{x}_1) \dots \varphi_N(\vec{x}_N)$$

Pauli's exclusion principle invalid → pointed out by

- Slater and V.A. Fock

- Hartree reformulated the theory in 1935. Real applications after 1950.

Slater determinants:

$$\Psi(\vec{x}_1 \dots \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_N(N) \\ \varphi_1(2) & \varphi_2(2) & \dots & \vdots \\ \vdots & & & \vdots \\ \varphi_1(N) & \dots & \dots & \varphi_N(N) \end{vmatrix} \equiv \frac{1}{\sqrt{N!}} |\varphi_1(1) \dots \varphi_N(N)|$$

$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$

φ_i .... spin-orbitals

$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \Rightarrow \Psi(\vec{x}_1 \dots \vec{x}_N)$ is normalized. But the requirement is much stronger and we know why we can do that:

Because if the column of the slater determinant is not orthogonal on the other columns, one can orthogonalize it by adding a linear combination of the other columns. However, adding a linear combination of columns to the one column in question won't change the determinant and hence $\Psi(\vec{x}_1 \dots \vec{x}_N)$ remains unaffected. Therefore, one can assume columns being orthogonal.

Back to the functional:

$$E_0 = \frac{1}{N!} \langle \varphi_1(1) \dots \varphi_N(N) \Big| \sum_{i=1}^{N} h(i) + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} \Big| \varphi_1(1) \dots \varphi_N(N) \rangle$$

(A) (B1) + (B2)

$$(A) = \frac{1}{N!} \sum_{i=1}^{N} (N-1)! \sum_{j=1}^{N} \langle \varphi_j(i) | h(i) | \varphi_j(i) \rangle = \sum_{i=1}^{N} \langle \varphi_i(1) | h(1) | \varphi_i(1) \rangle$$

$$(B_1) = \frac{1}{N!} \frac{1}{2} \sum_{i \neq j} (N-2)! \sum_{k \neq l} \langle \varphi_k(i) \varphi_l(j) | \frac{1}{r_{ij}} | \varphi_k(i) \varphi_l(j) \rangle$$

(i,j) are dummy indexes; there are $N(N-1)$ pairs

$$= \frac{1}{2} \sum_{k \neq l} \langle \varphi_k(1) \varphi_l(2) | \frac{1}{r_{12}} | \varphi_k(1) \varphi_l(2) \rangle \equiv [\varphi_k(1) \varphi_k(2) | \varphi_l(2) \varphi_l(2)]$$

$$\equiv [\varphi_k \varphi_k | \varphi_l \varphi_l] \dots \text{coulomb term}$$

$$(B_2) = -\frac{1}{N!} \frac{1}{2} \sum_{i \neq j} (N-2)! \sum_{k \neq l} \langle \varphi_k(i) \varphi_l(j) | \frac{1}{r_{ij}} | \varphi_l(i) \varphi_k(j) \rangle$$

$$= -\frac{1}{2} \sum_{k \neq l} \langle \varphi_k(1) \varphi_l(2) | \frac{1}{r_{12}} | \varphi_l(1) \varphi_k(2) \rangle \equiv [\varphi_k \varphi_l | \varphi_l \varphi_k]$$

exchange term

(non-conjugated part switches)

Hartree-Fock approximation (continued)

In Hartree-Fock approximation we get

$$E_0 = \sum_{i=1}^{N} \langle \varphi_i | h | \varphi_i \rangle + \frac{1}{2} \sum_{i,j} \left\{ [\varphi_i \varphi_i | \varphi_j \varphi_j] - [\varphi_i \varphi_j | \varphi_j \varphi_i] \right\}$$

kinetic energy + interaction with the nuclei — orbital repulsion — exchange interaction

Variational principle to find φ_i

$\delta E_0 = 0$ ... restricted variation with $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$

Method of Lagrange multipliers: $\mathcal{L} = E_0 - \underbrace{\sum_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right) \varepsilon_{ji}}_{A}$

We may require $\mathcal{L}$ real $\Rightarrow \varepsilon_{ji} = \varepsilon_{ij}^*$ ($\underline{\varepsilon}$ is Hermitian)

$$-\delta A = \sum_{ij} \varepsilon_{ji} \left[\langle \delta\varphi_i | \varphi_j \rangle + \langle \varphi_i | \delta\varphi_j \rangle \right] = \sum_{ij} \varepsilon_{ji} \langle \delta\varphi_i | \varphi_j \rangle + \underbrace{\sum_{ij} \varepsilon_{ji}^*}_{\sum_{ij} \varepsilon_{ij}} \langle \delta\varphi_j | \varphi_i \rangle^*$$

complex conjugate to the first term (CC)

$$-\delta E_0 = \sum_{i=1}^{N} \langle \delta\varphi_i | h | \varphi_i \rangle + \langle \varphi_i | h | \delta\varphi_i \rangle$$
$$+ \frac{1}{2} \sum_{ij}^{N} [\delta\varphi_i \varphi_i | \varphi_j \varphi_j] + \overset{CC}{[\varphi_i \delta\varphi_i | \varphi_j \varphi_j]} + \overset{\text{reindex } i \leftrightarrow j}{[\varphi_i \varphi_i | \delta\varphi_j \varphi_j]} + \overset{i \leftrightarrow j + CC}{[\varphi_i \varphi_i | \varphi_j \delta\varphi_j]}$$
$$- \frac{1}{2} \sum_{ij}^{N} [\delta\varphi_i \varphi_j | \varphi_j \varphi_i] + \overset{CC}{[\varphi_i \delta\varphi_j | \varphi_j \varphi_i]} + \overset{i \leftrightarrow j}{[\varphi_i \varphi_j | \delta\varphi_j \varphi_i]} + \overset{i \leftrightarrow j + CC}{[\varphi_i \varphi_j | \varphi_j \delta\varphi_i]}$$
$$= \sum_{i=1}^{N} [\delta\varphi_i | h | \varphi_i] + \sum_{ij} \left\{ [\delta\varphi_i \varphi_i | \varphi_j \varphi_j] - [\delta\varphi_i \varphi_j | \varphi_j \varphi_i] \right\} + CC$$

$$\delta \mathcal{L} = \sum_{i=1}^{N} [\delta\varphi_i | h | \varphi_i] + \sum_{ij} \left\{ [\delta\varphi_i \varphi_i | \varphi_j \varphi_j] - [\delta\varphi_i \varphi_j | \varphi_j \varphi_i] \right\} - \sum_{ij} \varepsilon_{ji} [\delta\varphi_i | \varphi_j]$$

+ Complex conjugate of it

We arrive to the first version of Fock equations:

$$\left[\hat{h} + \hat{J} - \hat{K}\right]|\varphi_i\rangle = \sum_j \varepsilon_{ji}\,|\varphi_j\rangle$$

← almost an eigenvalue problem, but not quite yet!

$$\langle \vec{r}\,|\hat{J}|\varphi_i\rangle = \sum_j^N \int \frac{|\varphi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,'\;\varphi_i(\vec{r})$$

.... Coulomb interaction of a charge density $\sum_j |\varphi_j|^2$ with orbital φ_i

$$\langle \vec{r}\,|\hat{K}|\varphi_i\rangle = \sum_j^N \int \frac{\varphi_i(\vec{r}\,')\,\varphi_j^*(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,'\;\varphi_j(\vec{r})$$

.... Non-local application on φ_i: Exchange interaction is quantum phenomena

$$\langle \vec{r}\,|\hat{h}|\varphi_i\rangle = -\frac{1}{2}\sum_{i=1}^N \nabla^2\varphi_i(\vec{r}) - \varphi_i(\vec{r})\sum_{j=1}^N \frac{z_j}{|\vec{r}-\vec{R}_j|}$$

This is almost a 1-electron eigenvalue problem. Operators $\hat{J}$ and $\hat{K}$ depend on solutions φ_i. ~~Iterativ~~ Solved by iterations as self-consistend field (SCF) problem. Fock operator $\hat{f} = \hat{h} + \hat{J} - \hat{K}$:

$$\hat{f}\,|\varphi_i\rangle = \sum_j \varepsilon_{ji}\,|\varphi_j\rangle$$

We have a flexibility in $\psi(1\ldots N) = \frac{1}{\sqrt{N!}}\,|\varphi_k(1)\ldots\varphi_N(N)|$, because an unitary transformation of $|\varphi_i\rangle$ will just give a phase factor to $\psi(1\ldots N)$:

A new set of φ_i':

$$|\varphi_i'\rangle = \sum_j U_{ji}\,|\varphi_i\rangle$$

$$\psi' = \psi\cdot\det U = \psi\, e^{i\beta}$$

Prove that $\hat{f}' = \hat{h} + \hat{J}(\varphi') - \hat{K}(\varphi') = \hat{f}$. Fock operator $\hat{f}$ is unchanged when filled by unitary-transformed spin-orbitals. Then we have

$$\langle\varphi_k|\hat{f}'|\varphi_i\rangle = \sum_j \varepsilon_{ji}\underbrace{\langle\varphi_k|\varphi_i\rangle}_{\delta_{ki}} = \varepsilon_{ki}\,,$$ so

in space of spin-orbitals we have

$$\underline{f'} = \underline{\varepsilon}$$ ... matrix equation

$$\varepsilon'_{ki} = \langle\varphi'_k|\hat{f}|\varphi'_i\rangle = \sum_{em} U_{mi}\,U^*_{ek}\,\langle\varphi_e|f|\varphi_m\rangle \Rightarrow \boxed{\underline{\varepsilon'} = \underline{U}^+\,\underline{\varepsilon}\,\underline{U}}$$

Therefore such U exists, that ε' is diagonal (ε Hermitian) and:

$$\hat{f}\,|\varphi_i\rangle = \varepsilon_i|\varphi_i\rangle$$

These $|\varphi_i\rangle$ are called canonical (spin)orbitals

← Fock equation!