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① HF equation

$E_{HF} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$

to avoid double counting of pairwise repulsion $i \to j$ and $j \to i$

$= \sum_i^{occ.} \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i,j}^{occ.} \langle ij||ij\rangle$ $\quad \left(\hat{h}(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 + \sum_I \frac{-Z_I}{r_{iI}} \right)$

$= \sum_i^{occ.} (i|\hat{h}|i) + \frac{1}{2}\sum_{i,j}^{occ.} (ii||jj)$

$= \sum_i^{occ.} (i|\hat{h}|i) + \frac{1}{2}\sum_{i,j}^{occ.} (ii|jj) - \frac{1}{2}\sum_{i,j}^{occ.} (ij|ji)$

kinetic + nuclear attraction; Coulomb J; exchange K (= purely QM effects except)

Coulomb J → includes self interaction of electrons!

exchange K → also includes self interaction of electrons!

$\underbrace{\frac{1}{2}\sum_i (ii|ii) \quad - \frac{1}{2}\sum_i (ii|ii)}_{\text{cancellation}}$

Minimize E_{HF} by varying $\{\varphi_i\}$ while maintaining $\underbrace{\langle i|j\rangle = \delta_{ij}}_{N^2 \text{ constraints}}$

$\mathcal{L} = E_{HF} - \sum_{i,j} \varepsilon_{ji}\left(\langle i|j\rangle - \delta_{ij}\right)$

N^2 undetermined multipliers

functional

$$0 = \frac{\partial \mathcal{L}}{\partial \varphi_i^*(\mathbf{r}_1)} = \hat{h}\varphi_i(\mathbf{r}_1) + \underbrace{\sum_k \int \frac{\varphi_k^*(\mathbf{r}_2)\varphi_k(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\, \varphi_i(\mathbf{r}_1)}_{\hat{J}\varphi_i(\mathbf{r}_1)} - \underbrace{\sum_k \int \frac{\varphi_k^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2\, \varphi_k(\mathbf{r}_1)}_{\hat{K}\varphi_i(\mathbf{r}_1)} - \sum_k \varepsilon_{ki}\varphi_k(\mathbf{r}_1)$$

multiply $\varphi_j^*(\mathbf{r}_1)$ and integrate

$$0 = \underbrace{\langle j|\hat{h}|i\rangle + \langle jk||ik\rangle}_{\langle j|\hat{f}|i\rangle} - \varepsilon_{ji}$$

ignoring other terms, $\int \delta\varphi_i^* \hat{h} \varphi_i \, d\mathbf{r} = 0$ for any $\delta\varphi_i$ → $\hat{h}\varphi_i = 0$

functional differentiation

Fock operator $\hat{f} = \hat{h} + \hat{J} - \hat{K}$

multiply $\varphi_a^*(x_1)$ and integrate

$$0 = \underbrace{\langle a|\hat{h}|i\rangle + \langle ak||ik\rangle}_{\langle a|\hat{f}|i\rangle}$$

The Fock matrix in the basis of HF orbitals:

$$\begin{array}{c|cc} & i & a \\ \hline j & \langle j|\hat{f}|i\rangle & 0 \\ b & 0 & \langle b|\hat{f}|a\rangle \end{array}$$

Brillouin condition

important

$\langle a|\hat{f}|i\rangle = 0$ defines HF orbitals

$\langle j|\hat{f}|i\rangle = \varepsilon_{ji}$ means HF occ. orbitals are not unique. As long as they satisfy $\langle a|\hat{f}|i\rangle = 0$, they certainly satisfy this.

② Orbital invariance of HF energy and equation

$$\varphi_i' = \sum_j \varphi_j U_{ji}$$

$\mathbb{U}$ is a matrix that transforms an orthonormal basis to another orthonormal basis $\rightarrow$ $\mathbb{U}$ is a unitary matrix

$$\mathbb{U}^\dagger \mathbb{U} = \mathbb{1}$$

$$|\mathbb{U}^\dagger||\mathbb{U}| = |\mathbb{1}| = 1$$

$$|\mathbb{U}|^*|\mathbb{U}| = 1 \qquad |\mathbb{U}| = e^{i\theta}$$

$$|\Phi_0'\rangle = |\varphi_1' \cdots \varphi_N'\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1'(x_1) & \cdots & \varphi_1'(x_N) \\ \vdots & & \vdots \\ \varphi_N'(x_1) & \cdots & \varphi_N'(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \left| \begin{pmatrix} U_{11} & \cdots & U_{N1} \\ \vdots & & \vdots \\ U_{1N} & \cdots & U_{NN} \end{pmatrix} \begin{pmatrix} \varphi_1(x_1) & \cdots & \varphi_1(x_N) \\ \vdots & & \vdots \\ \varphi_N(x_1) & \cdots & \varphi_N(x_N) \end{pmatrix} \right|$$

$$= |\mathbb{U}^\dagger| \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \cdots & \varphi_1(x_N) \\ \vdots & & \vdots \\ \varphi_N(x_1) & \cdots & \varphi_N(x_N) \end{vmatrix}$$

$$= e^{i\theta} |\Phi_0\rangle$$

essentially the same wfn! ...... inconsequential phase factor

$$E'_{HF} = \langle \Phi'_0 | \hat{H} | \Phi'_0 \rangle = \langle \Phi_0 | e^{-i\theta} \hat{H} e^{i\theta} | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = E_{HF}$$

HF energy and wfn are invariant to rotation among occupied orbitals

Important

— It gives us freedom to rotate (i.e, unitary transform) orbitals to define <u>canonical</u> ones (see below)

— HF energy and wfn are well defined for degenerate occ. orbitals (which can rotate freely among themselves) (A method which does not have this <u>invariance</u> property can/will give different results (energies) for N_2, NH_3, etc., on different computers)

Let us also prove that $\hat{f}$ is invariant to occupied orbital rotation

$$\hat{J}' \quad \sum_k \int \frac{\varphi'^*_k(\mathbf{r}_2)\varphi'_k(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 = \sum_{i,j} \sum_k \int \frac{(\varphi^*_i U^*_{ik})(\varphi_j U_{jk})}{r_{12}} d\mathbf{r}_2$$

$$= \sum_{i,j} \int \frac{\varphi^*_i \varphi_j}{r_{12}} d\mathbf{r}_2 \underbrace{\sum_k (\mathbb{U})_{jk} (\mathbb{U}^\dagger)_{ki}}_{(\mathbb{U}\mathbb{U}^\dagger)_{ji} = \delta_{ji}} = \sum_j \int \frac{\varphi^*_j(\mathbf{r}_2)\varphi_j(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 = \hat{J}$$

exchange $\mathbf{r}_1$ and $\mathbf{r}_2$ in what follows

$$\hat{K}' = \sum_k \int \frac{\varphi'^*_k(\mathbf{r}_2) P_{12} \varphi'_k(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \; \cdots \text{ same logic } \cdots = \hat{K}$$

③ Canonical HF orbitals

$$\left.\begin{array}{l} \langle j|\hat{f}|i\rangle = \varepsilon_{ji} \\ \quad \parallel \\ \langle i|\hat{f}|j\rangle^* = \varepsilon_{ij}^* \end{array}\right\}$$ Hermitian matrix $\longrightarrow$ diagonalized to yield real eigenvalues

$$\psi_i' = \sum_k \psi_k U_{ki}$$

$$\langle j'|\hat{f}|i'\rangle = \sum_{k,l} U_{kj'}^* \varepsilon_{kl} U_{li'}$$

$\downarrow$ invariance of $\hat{f}$ $\qquad$ #occ. × #occ. matrix

$$\langle j'|\hat{f}'|i'\rangle = (\mathbb{U}^\dagger \varepsilon \mathbb{U})_{j'i'} = \varepsilon_{j'} \delta_{j'i'}$$ (we can always find $\mathbb{U}$ to do this)

Canonical HF orbitals $\qquad$ HF orbital energies

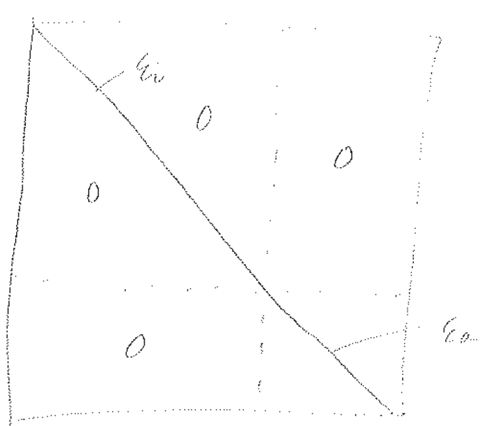
We can repeat this for $\langle b|\hat{f}|a\rangle = \varepsilon_{ba}$

#virt. × #virt. matrix

$$\langle b'|\hat{f}'|a'\rangle = (\mathbb{U}^\dagger \varepsilon \mathbb{U})_{b'a'} = \varepsilon_{b'} \delta_{b'a'}$$

$\hat{f}$ and Φ_0 don't depend on virtuals
so is obviously invariant to virt. rotation

The Fock matrix in canonical HF orbitals



④ Koopmans' theorem (NOT Koopman's · Koopmans won Nobel Prize in economics!)

$$\varepsilon_i = \langle i|\hat{f}|i\rangle = \langle i|\hat{h}|i\rangle + \sum_j \langle ij||ij\rangle$$

$$\varepsilon_a = \langle a|\hat{f}|a\rangle = \langle a|\hat{h}|a\rangle + \sum_j \langle aj||aj\rangle$$

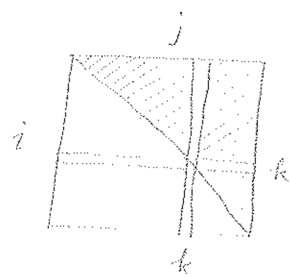
$$IP = {}^{N-1}E_{HF} - {}^{N}E_{HF}$$

a determinant constructed with HF canonical occupied orbitals minus φ_k

$$= \langle {}^{N-1}\Phi_k|\hat{H}|{}^{N-1}\Phi_k\rangle - \langle {}^{N}\Phi_0|\hat{H}|{}^{N}\Phi_0\rangle$$

$$= \sum_{i\neq k}\langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i\neq k}\sum_{j\neq k}\langle ij||ij\rangle - \sum_i\langle i|\hat{h}|i\rangle - \frac{1}{2}\sum_i\sum_j\langle ij||ij\rangle$$

$$= -\langle k|\hat{h}|k\rangle - \sum_j\langle kj||kj\rangle = -\langle k|\hat{f}|k\rangle = -\varepsilon_k$$



$$EA = {}^{N}E_{HF} - {}^{N+1}E_{HF}$$

$$= \langle {}^{N}\Phi_0|\hat{H}|{}^{N}\Phi_0\rangle - \langle {}^{N+1}\Phi_c|\hat{H}|{}^{N+1}\Phi_c\rangle$$

a determinant constructed with HF can. occ. orbitals plus φ_c

$$= -\langle c|\hat{h}|c\rangle - \sum_j\langle cj||cj\rangle = -\langle c|\hat{f}|c\rangle = -\varepsilon_c$$

($-\varepsilon_i$ and $-\varepsilon_a$ approximate IP and EA !

Limitations

- no electron correlation
- no orbital relaxation
- IP too positive (corr. and relax. cancel to some extent)
- EA too negative and useless

⑤ Roothaan-Hall eq. .... G. G. Hall – Cambridge, Kyoto
.... C. C. J. Roothaan – Chicago, Hewlett-Packard

i) Closed-shell, restricted HF

$$\psi_p(\mathbf{x}) = \begin{cases} \phi_p(\mathbf{r})\alpha \\ \text{or} \\ \phi_p(\mathbf{r})\beta \end{cases}$$

$\underbrace{\phi_p(\mathbf{r})}_{\text{shared spatial part}}$

$$E_{HF} = \sum_i \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle = \sum_i (i|\hat{h}|i) + \frac{1}{2}\sum_{i,j}(i\,i||j\,j)$$

$$= \sum_i^{\text{spatial occ.}} (\phi_i\alpha|\hat{h}|\phi_i\alpha) + \sum_i^{\text{spatial occ.}} (\phi_i\beta|\hat{h}|\phi_i\beta)$$

$$+ \frac{1}{2}\sum_{i,j}(\phi_i\alpha\phi_i\alpha|\phi_j\alpha\phi_j\alpha) + \frac{1}{2}\sum_{i,j}(\phi_i\alpha\phi_i\alpha|\phi_j\beta\phi_j\beta)$$

$$+ \frac{1}{2}\sum_{i,j}(\phi_i\beta\phi_i\beta|\phi_j\alpha\phi_j\alpha) + \frac{1}{2}\sum_{i,j}(\phi_i\beta\phi_i\beta|\phi_j\beta\phi_j\beta)$$

$$- \frac{1}{2}\sum_{i,j}(\overset{1^*}{\phi_i}\alpha\overset{1}{\phi_j}\alpha|\overset{2^*}{\phi_j}\alpha\overset{2}{\phi_i}\alpha) - \frac{1}{2}\sum_{i,j}(\phi_i\beta\phi_j\beta|\phi_j\beta\phi_i\beta)$$

$$= 2\sum_i^{\text{spatial}}(\phi_i|\hat{h}|\phi_i) + 2\sum_{i,j}^{\text{spatial}}(\phi_i\phi_i|\phi_j\phi_j) - \sum_{i,j}(\phi_i\phi_j|\phi_j\phi_i)$$

$$\langle \underset{\alpha}{p}|\hat{f}|\underset{\alpha}{q}\rangle = \langle p|\hat{h}|q\rangle + \sum_k \langle pk||qk\rangle = (p|\hat{h}|q) + \sum_k (pq||kk)$$

(β β same)

$$= (\phi_p|\hat{h}|\phi_q) + 2\sum_k^{\text{spatial}}(\overset{\alpha}{\phi_p}\overset{\alpha}{\phi_q}|\overset{\alpha\,\beta}{\phi_k}\overset{\alpha\,\beta}{\phi_k}) - \sum_k^{\text{spatial}}(\overset{\alpha}{\phi_p}\overset{\alpha}{\phi_k}|\overset{\alpha}{\phi_k}\overset{\alpha}{\phi_q})$$

$$\hat{f} = \hat{h} + \sum_k^{\text{spatial occ.}}(2\hat{J}_k - \hat{K}_k) \qquad \hat{J}_k = \int \frac{\phi_k^*(\mathbf{r}_2)\phi_k(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2$$

$$\hat{K}_k = \int \frac{\phi_k^*(\mathbf{r}_2)P_{12}\phi_k(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2$$

$$\phi_p = \sum_{\mu=1}^{m} C_p^{\mu}\chi_\mu$$

, typically, but not necessarily AO's

a basis fxn — do not have to be orthonormal

T. Dunning, D. Woon

$$\hat{f}(\mathbf{x})\psi_p(\mathbf{x}) = \varepsilon_p\psi_p(\mathbf{x})$$

/// eq for spatial orbital

$$\hat{f}(\mathbf{r})\sum_\nu C_p^\nu\chi_\nu(\mathbf{r}) = \varepsilon_p\sum_\nu C_p^\nu\chi_\nu(\mathbf{r})$$

multiply $\chi_\mu^*(\mathbf{r})$ and integrate over $\mathbf{r}$

$$\sum_\nu C_p^\nu \underbrace{\int \chi_\mu^*(\mathbf{r})\hat{f}(\mathbf{r})\chi_\nu(\mathbf{r})d\mathbf{r}}_{F_{\mu\nu}} = \varepsilon_p\sum_\nu C_p^\nu\underbrace{\int\chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r})d\mathbf{r}}_{S_{\mu\nu}}$$

$$\sum_\nu F_{\mu\nu} C_p^\nu = \sum_\nu S_{\mu\nu} C_p^\nu \varepsilon_p$$

$$\mathbb{F}\,\mathbb{C} = \mathbb{S}\,\mathbb{C}\,\varepsilon$$

unitary? No because

$\{\varphi_p\} \longrightarrow \{\chi_\mu\}$

is not orthonormal-orthonormal transform

$$F_{\mu\nu} = (\mu|\hat{f}|\nu) = (\mu|\hat{h}|\nu) + 2\sum_k^{\text{spatial occ.}} (\mu\nu|kk) - \sum_k (\mu k|k\nu)$$

$$\int \chi_\mu^* \hat{h} \chi_\nu \, d\mathbf{r} \equiv H_{\mu\nu}^{core}$$

$$\int \chi_\mu^*(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\frac{1}{r_{12}}\phi_k^*(\mathbf{r}_2)\phi_k(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

$$\int \chi_\mu^*(\mathbf{r}_1)\phi_k(\mathbf{r}_1)\frac{1}{r_{12}}\phi_k^*(\mathbf{r}_2)\chi_\nu(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

$$= H_{\mu\nu}^{core} + \sum_{\kappa\lambda}\underbrace{\left(\sum_k 2 C_k^{\kappa *} C_k^\lambda\right)}_{P_{\lambda\kappa}} (\mu\nu|\kappa\lambda) - \sum_{\kappa\lambda}\underbrace{\left(\sum_k C_k^{\kappa *} C_k^\lambda\right)}_{\frac{1}{2}P_{\lambda\kappa}}(\mu\lambda|\kappa\nu)$$

density matrix

$$= H_{\mu\nu}^{core} + \sum_{\kappa\lambda}\left\{(\mu\nu|\kappa\lambda) - \frac{1}{2}(\mu\lambda|\kappa\nu)\right\}P_{\lambda\kappa}$$

$$\int \chi_\mu^*(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\frac{1}{r_{12}}\chi_\kappa^*(\mathbf{r}_2)\chi_\lambda(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2$$

density

$$\rho(\mathbf{r}) = 2\sum_i^{\text{spatial occ.}} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

$$= 2\sum_i\left(\sum_\mu C_i^{\mu *}\chi_\mu^*(\mathbf{r})\right)\left(\sum_\nu C_i^\nu \chi_\nu(\mathbf{r})\right)$$

$$= \sum_{\mu,\nu} P_{\nu\mu}\chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r})$$

density matrix

$$E_{HF} = \sum_{\mu\nu}(\mu|\hat{h}|\nu)P_{\nu\mu}$$

$$(\mu|-\tfrac{1}{2}\nabla^2|\nu) + (\mu|\sum_I \tfrac{-Z_I}{r_I}|\nu)$$

$$+ \frac{1}{2}\sum_{\mu\nu\kappa\lambda}(\mu\nu|\kappa\lambda)P_{\nu\mu}P_{\lambda\kappa}$$

$$- \frac{1}{4}\sum_{\mu\nu\kappa\lambda}(\mu\lambda|\kappa\nu)P_{\nu\mu}P_{\lambda\kappa}$$

ii) SCF (self-consistent field)

Initial guess ($F_{\mu\nu} = H^{core}_{\mu\nu}$, $P_{\mu\nu} = 0$, for instance)

$\downarrow$

$\mathbb{F}\mathbb{C} = \mathbb{S}\mathbb{C}\varepsilon$ …… ※

$\downarrow$

$\mathbb{P} = \mathbb{C}^{\dagger}\mathbb{C}$

$\downarrow$

$E = \Sigma(\mu|\hat{h}|\nu)P + \frac{1}{2}\Sigma(\mu\nu|\kappa\lambda)PP - \frac{1}{4}(\mu\lambda|\kappa\nu)PP$

converged? — YES $\rightarrow$ END

NO $\downarrow$

$F_{\mu\nu} = (\mu|\hat{h}|\nu) + \Sigma(\mu\nu|\kappa\lambda)P - \Sigma(\mu\lambda|\kappa\nu)P$

※ How to solve this step?

$\mathbb{S}$ is a Hermitian and non-negative matrix*

$\mathbb{U}^{\dagger}\mathbb{S}\mathbb{U} = s$ (diagonal)

ⓐ Symmetric orthogonalization

$$\mathbb{X} = \mathbb{U}s^{-1/2}\mathbb{U}^{\dagger} = \mathbb{U}\begin{pmatrix} 1/\sqrt{s_{11}} & & 0 \\ & \ddots & \\ 0 & & 1/\sqrt{s_{mm}} \end{pmatrix}\mathbb{U}^{\dagger}$$

ⓑ Canonical orthogonalization

$$\mathbb{X} = \mathbb{U}s^{-1/2} = \mathbb{U}\begin{pmatrix} 1/\sqrt{s_{11}} & & 0 \\ & \ddots & \\ 0 & & 1/\sqrt{s_{mm}} \end{pmatrix}$$

either way

$$\mathbb{X}^{\dagger}\mathbb{S}\mathbb{X} = (\mathbb{U})s^{-1/2}\mathbb{U}^{\dagger}\mathbb{S}\mathbb{U}s^{-1/2}(\mathbb{U}^{\dagger})$$
$$= (\mathbb{U})s^{-1/2}s\,s^{-1/2}(\mathbb{U}^{\dagger})$$
$$= (\mathbb{U}\mathbb{U}^{\dagger}) = \mathbb{1}$$

matrices in parentheses are not there in case ⓑ

$\mathbb{C} = \mathbb{X}\mathbb{C}'$

$\mathbb{F}\mathbb{X}\mathbb{C}' = \mathbb{S}\mathbb{X}\mathbb{C}'\varepsilon$

$$\underbrace{\mathbb{X}^{\dagger}\mathbb{F}\mathbb{X}}_{\mathbb{F}'}\mathbb{C}' = \underbrace{\mathbb{X}^{\dagger}\mathbb{S}\mathbb{X}}_{\mathbb{1}}\mathbb{C}'\varepsilon$$

$\mathbb{F}'\mathbb{C}' = \mathbb{1}\mathbb{C}'\varepsilon$ $\rightarrow$ subject to usual diagonalization