Hartree-Fock Approximation

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- Hartree-Fock (HF) approximation: Determines the "<u>best single Slater determinant</u>" that minimizes the energy.

- Second-quantized Hamiltonian

$$\hat{H} = \sum_{st} \hat{c}_s^{\dagger} \langle s|h|t\rangle \hat{c}_t + \frac{1}{2}\sum_{stuv} \hat{c}_s^{\dagger}\hat{c}_t^{\dagger} \langle \overset{**}{st} | \tfrac{1}{r} | uv \rangle \hat{c}_v \hat{c}_u \quad (1)$$

$$= \sum_{st} \hat{c}_s^{\dagger} \langle s|h|t\rangle \hat{c}_t + \frac{1}{2}\sum_{stuv} \hat{c}_s^{\dagger}\hat{c}_t^{\dagger} [\underset{\mathbf{r}}{\overset{*}{s}u} | \tfrac{1}{r} | \underset{\mathbf{r}'}{\overset{*}{t}v}] \hat{c}_v \hat{c}_u \quad (2)$$

where

$$\langle s|h|t\rangle = \int d\mathbf{r}\, \phi_s^*(\mathbf{r})\, h(\mathbf{r})\, \phi_t(\mathbf{r}) \quad (3)$$

$$= \int d\mathbf{r}\, \phi_s^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) \right] \phi_t(\mathbf{r}) \quad (4)$$

$$\langle st|\tfrac{1}{r}|uv\rangle = \iint d\mathbf{r}\, d\mathbf{r}'\, \phi_s^*(\mathbf{r})\, \phi_t^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_u(\mathbf{r})\, \phi_v(\mathbf{r}') \quad (5)$$

$$[su|\tfrac{1}{r}|tv] = \iint d\mathbf{r}\, d\mathbf{r}'\, \phi_s^*(\mathbf{r})\, \phi_u(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_t^*(\mathbf{r}')\, \phi_v(\mathbf{r}') \quad (6)$$

– Single Slater determinant & energy expectation value

Consider a single Slater determinant,

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_1(\mathbf{r}_N) \\ \vdots & & \\ \phi_N(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix} \tag{7}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_{P(1)}(\mathbf{r}_1) \cdots \phi_{P(N)}(\mathbf{r}_N) \tag{8}$$

(One-electron term)

$$\langle \Phi | \sum_{st} \hat{c}_s^\dagger h_{st} c_t | \Phi \rangle$$

inner product

$$= \sum_{st} h_{st} \left(\hat{c}_s | \Phi \rangle, c_t | \Phi \rangle \right)$$

The inner product is nonzero only when $s = t \in$ occupied,

$$= \sum_{st} \delta_{st} f_s h_{st}$$

$$= \sum_s f_s h_{ss}$$

$$\equiv \sum_i^{occ} h_{ii}$$

Here, the occupation number of the s-th orbital is

$$f_s = \begin{cases} 1 & (s \in \text{occupied}) \\ 0 & (s \notin \text{occupied}) \end{cases} \tag{9}$$

(Two-electron term)

$$\langle\Phi|\frac{1}{2}\sum_{stuv} c_s^{\dagger} c_t^{\dagger} [su|\tfrac{1}{r}|tv] c_v c_u|\Phi\rangle$$

$$= \frac{1}{2}\sum_{stuv} [su|\tfrac{1}{r}|tv] \left(c_t c_s|\Phi\rangle, c_v c_u|\Phi\rangle \right)$$

The inner product is nonzero only if

$(s=u) \neq (t=v) \in$ occupied

$(s=v) \neq (t=u) \in$ occupied

$$= \frac{1}{2}\sum_{stuv} (1-\delta_{st}) f_s f_t [su|\tfrac{1}{r}|tv]$$

$$\times \Big\{ \delta_{su}\delta_{tv} \underbrace{\langle\Phi|c_s^{\dagger} c_t^{\dagger} c_t c_s|\Phi\rangle}_{\substack{\langle\Phi|s^{\dagger}(1-\cancel{tt^{\dagger}})s|\Phi\rangle \\ = \langle\Phi|(1-\cancel{ss^{\dagger}})|\Phi\rangle \\ = 1}} + \delta_{sv}\delta_{tu} \underbrace{\langle\Phi|c_s^{\dagger} c_t^{\dagger} c_s c_t|\Phi\rangle}_{\substack{-\langle\Phi|s^{\dagger}s\,t^{\dagger}t|\Phi\rangle \\ = -\langle\Phi|(1-\cancel{ss^{\dagger}})(1-\cancel{tt^{\dagger}})|\Phi\rangle \\ = -1}} \Big\}$$

$$= \frac{1}{2}\sum_{st} (1-\delta_{st}) f_s f_t \left([ss|\tfrac{1}{r}|tt] - [st|\tfrac{1}{r}|ts] \right)$$

Note, for $s=t$, the two two-electron integrals cancel out, so the sum can include the $s=t$ terms.

$$= \frac{1}{2}\sum_{st} f_s f_t \left([ss|\tfrac{1}{r}|tt] - [st|\tfrac{1}{r}|ts] \right)$$

$$= \frac{1}{2}\sum_{ij}^{occ} \left([ii|\tfrac{1}{r}|jj] - [ij|\tfrac{1}{r}|ji] \right)$$

$$\therefore E = \langle \Phi | \hat{H} | \Phi \rangle$$

$$= \sum_{i}^{occ} h_{ii} + \frac{1}{2} \sum_{ij}^{occ} \Big(\underbrace{[ii|\tfrac{1}{r}|jj]}_{\text{Coulomb integral}} - \underbrace{[ij|\tfrac{1}{r}|ji]}_{\text{exchange integral.}} \Big) \qquad (10)$$

The exchange integrals arise from the quantum-statistical requirement that a many-electron wave function is antisymmetric w.r.t. the swapping of the labels of two electrons.

– Variational principle: Hartree-Fock equation

We determine the set of N orbitals that minimizes the energy, subject to the orthonormal constraints

$$\langle i|j\rangle = \int d\mathbf{r}\, \phi_i^*(\mathbf{r})\, \phi_j(\mathbf{r}) = \delta_{ij} \tag{11}$$

We achieve this by introducing Lagrange multipliers ε_{ij} to minimize

$$\mathcal{L}[\{\phi_i\}] = E - \sum_{ij}^{N} \varepsilon_{ij} \left(\langle i|j\rangle - \delta_{ij} \right) \tag{12}$$

$$\begin{aligned}
&= \sum_{i=1}^{N} \int d\mathbf{r}\, \phi_i^*(\mathbf{r})\, h(\mathbf{r})\, \phi_i(\mathbf{r}) \\
&+ \frac{1}{2} \sum_{i,j=1}^{N} \iint d\mathbf{r} d\mathbf{r}'\, \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}') \\
&- \frac{1}{2} \sum_{i,j=1}^{N} \iint d\mathbf{r} d\mathbf{r}'\, \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}') \\
&- \sum_{i,j}^{N} \varepsilon_{ij} \left(\int d\mathbf{r}\, \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) - \delta_{ij} \right)
\end{aligned} \tag{13}$$

(Note) ε_{ij} is Hermitian, i.e.,

$$\varepsilon_{ij}^* = \varepsilon_{ji} \tag{14}$$

$\because$ $\mathcal{L}$ is real, so that

$$\left(\sum_{ij} \varepsilon_{ij} \langle i|j\rangle\right)^* = \sum_{ij} \varepsilon_{ij}^* \langle j|i\rangle \underset{i\leftrightarrow j}{=} \sum_{ij} \varepsilon_{ji}^* \langle i|j\rangle = \sum_{ij} \varepsilon_{ij} \langle i|j\rangle$$

$$\therefore \sum_{ij} \underbrace{\left(\varepsilon_{ij} - \varepsilon_{ji}^*\right)}_{=0} \langle i|j\rangle = 0$$

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$$\frac{\delta}{\delta \phi_i^*(\mathbf{r})} \times \text{Eq.}(12)$$

$$0 = \frac{\delta \mathcal{L}}{\delta \phi_i^*(\mathbf{r})}$$

$$= h(\mathbf{r})\phi_i(\mathbf{r}) + \sum_{j=1}^{N} \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}') \cdot \phi_i(\mathbf{r})$$

$$- \sum_{j=1}^{N} \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\ \phi_j(\mathbf{r})$$

$$- \sum_{j=1}^{N} \varepsilon_{ij}\phi_j(\mathbf{r})$$

$$\therefore \left[h(\mathbf{r}) + \sum_{j=1}^{N}\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')\right]\phi_i(\mathbf{r})$$

$$- \sum_{j=1}^{N}\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r}) = \sum_{j=1}^{N}\varepsilon_{ij}\phi_j(\mathbf{r}) \qquad (15)$$

Or

$$\underbrace{\left[h(\mathbf{r}) + \sum_{j=1}^{N}\left(J_j(\mathbf{r}) - K_j(\mathbf{r})\right)\right]}_{f(\mathbf{r})}\phi_i(\mathbf{r}) = \sum_{j=1}^{N}\varepsilon_{ij}\phi_j(\mathbf{r}) \qquad (16)$$

where

$$\begin{cases} J_j(\mathbf{r})\phi_i(\mathbf{r}) \equiv \displaystyle\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi_i(\mathbf{r}) & (17) \\ K_j(\mathbf{r})\phi_i(\mathbf{r}) \equiv \displaystyle\int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r}) & (18) \end{cases}$$

The Fock-operator is defined as

$$f(\mathbf{r}) = h(\mathbf{r}) + \sum_{j=1}^{N}\left[J_j(\mathbf{r}) - K_j(\mathbf{r})\right] \qquad (19)$$

– Unitary transformation: Canonical HF equations

Since the ε_{ij} matrix is Hermitian, it can be diagonalized with real eigenvalues,

$$\sum_{j=1}^{N} \varepsilon_{ij} u_j^{(\alpha)} = \varepsilon_\alpha u_i^{(\alpha)} \tag{20}$$

where $\{u_j^{(\alpha)}\}$ are orthonormal

$$\sum_{i=1}^{N} u_i^{(\alpha)*} u_i^{(\beta)} = \sum_{i=1}^{N} U_{\alpha i}^{*} U_{i\beta} = (U^\dagger U)_{\alpha\beta} = \delta_{\alpha\beta} \tag{21}$$

Here, we have introduced a unitary matrix,

$$U_{i\alpha} \equiv u_i^{(\alpha)} \tag{22}$$

Eq. (20) can be rewritten as

$$\sum_{j=1}^{N} \varepsilon_{ij} u_j^{(\alpha)} = \sum_{\beta=1}^{N} u_i^{(\beta)} \underbrace{[\delta_{\beta\alpha} \epsilon_\alpha]}_{E_{\beta\alpha}} \tag{23}$$

or

$$\epsilon U = U E \tag{24}$$

$U^\dagger *$ Eq. (24)

$$U^\dagger \epsilon U = E \tag{25}$$

Now consider a unitary transformation of orbitals

$$\phi_i'(\mathbb{r}) = \sum_{j=1}^{N} \phi_j(\mathbb{r}) \underbrace{U_{ji}}_{u_j^{(i)}} \tag{26}$$

$\sum_{i=1}^{N}$ Eq.(26) $\times \cdot U^{+}_{ik}$

$$\sum_{i=1}^{N} \phi_i'(\mathbb{r}) U^{+}_{ik} = \sum_{i=1}^{N} \sum_{j=1}^{N} \phi_j(\mathbb{r}) \underbrace{U_{ji} U^{+}_{ik}}_{\delta_{jk}} = \phi_k(\mathbb{r}) \tag{27}$$

Now $\sum_{i=1}^{N}$ Eq.(16) $\times\ U_{ik}$

$$\underbrace{\sum_{i=1}^{N} f(\mathbb{r}) \phi_i(\mathbb{r}) U_{ik}}_{\phi_k'(\mathbb{r})} = \underbrace{\sum_{i=1}^{N} \sum_{j=1}^{N} \underbrace{U_{ik}}_{U^{+}_{ki}} \varepsilon_{ij} \phi_j(\mathbb{r})}_{U^{+}\epsilon \underbrace{\ }_{UU^{+}} \phi}$$

$$= (U^{+}\epsilon U) U^{+}\phi$$

$$= E U^{+}\phi$$

$$= \sum_i \sum_j (\epsilon_k \delta_{ki}) \underbrace{U^{+}_{ij}}_{U_{ji}} \phi_j$$

$$= \sum_i \epsilon_k \delta_{ki} \underbrace{\sum_j \phi_j U_{ji}}_{\phi_i'}$$

$$= \epsilon_k \phi_k'$$

$$\therefore\ f(\mathbb{r}) \phi_k'(\mathbb{r}) = \epsilon_k \phi_k'(\mathbb{r}) \tag{28}$$

Namely, HF equation can be made in the canonical eigenvalue problem with a unitary transformation.

(Note) The Fock operator is invariant under a unitary transformation.

$\because$

$$\sum_{j=1}^{N} J_j(\mathbf{r})$$

$$= \sum_j \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}')$$

$$= \sum_j \sum_i \sum_k \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i'^*(\mathbf{r}') \underbrace{(U^\dagger_{ij})^*}_{U_{ji}} \phi_k'(\mathbf{r}') U^\dagger_{kj} \qquad (\because \text{Eq.}(27))$$

$$= \sum_i \sum_k \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i'^*(\mathbf{r}') \phi_k'(\mathbf{r}') \underbrace{\sum_j U^\dagger_{kj} U_{ji}}_{\delta_{ki}}$$

$$= \sum_i \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i'^*(\mathbf{r}') \phi_i'(\mathbf{r}')$$

$$\sum_{j=1}^{N} K_j(\mathbf{r}) \, {}^\forall\psi(\mathbf{r})$$

$$= \sum_j \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}') \psi(\mathbf{r}') \phi_j(\mathbf{r})$$

$$= \sum_j \sum_i \sum_k \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i'^*(\mathbf{r}') \underbrace{(U^\dagger_{ij})^*}_{U_{ji}} \psi(\mathbf{r}') \phi_k'(\mathbf{r}) U^\dagger_{kj} \qquad (\because \text{Eq.}(27))$$

$$= \sum_{ij} \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i'^*(\mathbf{r}') \psi(\mathbf{r}) \phi_k'(\mathbf{r}) \underbrace{\sum_j U^\dagger_{kj} U_{ji}}_{\delta_{ki}}$$

$$= \sum_i \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i'^*(\mathbf{r}') \psi(\mathbf{r}') \phi_i'(\mathbf{r}) \quad //$$

– (Summary) The Hartree-Fock energy, the generalized HF equation, Eq. (16), is invariant under any unitary transformation in the vector space spanned by the occupied HF orbitals.