Interacting Fermions

Hartree-Fock Approximation

- Consider the Hamiltonian

$$\hat{\mathcal{H}} \equiv \hat{K} + \hat{U}$$

with $\hat{K} \equiv \int dx\, \hat{K}(x)$, $\hat{U} \equiv \frac{1}{2}\int dx \int dy\, \hat{U}(x,y)$

$$\hat{K}(x) \equiv \hat{\psi}^{+}(x) K(x) \hat{\psi}(x), \quad \hat{U}(xy) = \hat{\psi}^{+}(x)\hat{\psi}^{+}(y) U(x,y) \psi(y)\psi(x)$$

$$K(x) \equiv -\frac{1}{2}\frac{\partial^2}{\partial x^2} + w(x), \quad w(x) \equiv -\frac{Z}{|x|}$$

$$U(xy) \equiv \frac{1}{|x-y|}$$

where we have used the unit-system in which $\frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar^2}{m_e} = 1$.

- In the Hartree-Fock (HF) approximation, we assume that the ground state is of the form of the Slater determinant $\Phi_{\text{slater}}(\{\phi_n\}|X)$ with some single-particle state. To be more specific, the HF approximation is the variational-principle approximation with the single-particle states as the variational parameters:

$$\Phi_{HF} = \Phi_{\text{slater}}(\{\phi_n^{(HF)}\})$$

$$\{\phi_n^{(HF)}\} \equiv \underset{\{\phi_n(x)\}}{\operatorname{argmin}} \left(\langle \Phi_{\text{slater}}(\{\phi_n\}) | \hat{\mathcal{H}} | \Phi_{\text{slater}}(\{\phi_n\}) \rangle \right)$$

(dependence on x or X are omitted.)

More Details of HF Approximation

- 2nd quantization form

$$\bar{\Phi} = \bar{\Phi}_{\text{slater}}(\{\phi_\kappa\}) = \left(\prod_{\kappa=1}^{N} c_\kappa^+\right)|\Phi\rangle$$

$$\langle\bar{\Phi}|\hat{K}|\bar{\Phi}\rangle = \sum_{\kappa\kappa'} K_{\kappa\kappa'}\langle\bar{\Phi}|c_\kappa^+ c_{\kappa'}|\bar{\Phi}\rangle$$

$$= \sum_\kappa{}' K_{\kappa\kappa} \quad \left(K_{\kappa\kappa'} \equiv \int dx\, \phi_\kappa^*(x) K(x)\, \phi_{\kappa'}(x)\right)$$

($\sum_\kappa'$ ... the summation over all κ below the fermi level)

$$\langle\bar{\Phi}|\hat{U}|\bar{\Phi}\rangle = \frac{1}{2}\sum_{\substack{\kappa\lambda\\ \kappa'\lambda'}} U_{\kappa'\lambda';\kappa\lambda}\langle\bar{\Phi}|c_{\kappa'}^+ c_{\lambda'}^+ c_\lambda c_\kappa|\bar{\Phi}\rangle$$

$$= \frac{1}{2}\sum_{\kappa\lambda}{}'(U_{\kappa\lambda;\kappa\lambda} - U_{\kappa\lambda;\lambda\kappa})$$

$$\left(U_{\kappa'\lambda';\kappa\lambda} \equiv \int dx \int dy\, \phi_{\kappa'}^*(x)\, \phi_{\lambda'}^*(y)\, U(x,y)\, \phi_\lambda(y)\, \phi_\kappa(x)\right)$$

- $E(\{\phi_\kappa\}) \equiv \langle\bar{\Phi}|\hat{\mathcal{H}}|\bar{\Phi}\rangle$

$$= \sum_\kappa \epsilon_\kappa^0 + \frac{1}{2}\sum_{\kappa\lambda}(U_{\kappa\lambda}^{(D)} - U_{\kappa\lambda}^{(X)})$$

$$\epsilon_\kappa^0 \equiv K_{\kappa\kappa}$$
$$U_{\kappa\lambda}^{(D)} \equiv U_{\kappa\lambda;\kappa\lambda}$$
$$U_{\kappa\lambda}^{(X)} \equiv U_{\kappa\lambda;\lambda\kappa}$$

- $\bar{E}_{HF} \equiv \min_{\{\phi_\kappa\}} E(\{\phi_\kappa\})$

$$\{\phi_\kappa^{(HF)}\} \equiv \operatorname{argmin}_{\{\phi_\kappa\}} E(\{\phi_\kappa\})$$

$$\bar{\Phi}_{HF} \equiv \bar{\Phi}_{\text{slater}}(\{\phi_\kappa\})$$

$$\langle \Phi | \hat{U} | \Phi \rangle = ?$$

$$\hat{U} \equiv \frac{1}{2} \int dx dy \, \hat{\psi}^{+}(x) \hat{\psi}^{+}(y) U(x,y) \psi(y) \psi(x)$$

$$|\Phi\rangle \equiv \left(\prod_{k \in \text{fermi sea}} c_k^{+} \right) |0\rangle$$

$$\hat{\psi}(x) = \sum_k c_k \phi_k(x)$$

Because $\hat{U}$ is evaluated for the fermi sea state $|\Phi\rangle$, the only terms in $\hat{U}$ that yield non-zero contributions are the following two terms:

$$\hat{U} \Rightarrow \frac{1}{2} \int dx dy \sum_{\substack{k_1 k_2 \\ k_1' k_2'}}{}' \phi_{k_1'}^{*}(x) \phi_{k_2'}^{*}(y) U(x,y) \phi_{k_2}(y) \phi_{k_1}(x) \quad \text{(1)}$$

$$\times \; c_{k_1'}^{+} c_{k_2'}^{+} c_{k_2} c_{k_1} \qquad U_{k_1' k_2' k_1 k_2}$$

$$= \frac{1}{2} \sum_{\substack{k_1 k_2 \\ k_1' k_2'}}{}' U_{k_1' k_2' k_1 k_2} \, c_{k_1'}^{+} c_{k_2'}^{+} c_{k_2} c_{k_1}$$

$$= \frac{1}{2} \sum_{k_1 k_2}{}' \left(U_{k_1 k_2 k_1 k_2} \, c_{k_1}^{+} c_{k_2}^{+} c_{k_2} c_{k_1} + U_{k_2 k_1 k_1 k_2} \, c_{k_2}^{+} c_{k_1}^{+} c_{k_2} c_{k_1} \right)$$

$$= \frac{1}{2} \sum_{k_1 k_2}{}' \left(U_{k_1 k_2}^{(D)} - U_{k_1 k_2}^{(X)} \right) c_{k_1}^{+} c_{k_2}^{+} c_{k_2} c_{k_1}$$

Variational Calculation

We want to minimize $E(\{\phi_n\})$ with the constraint $\langle \phi_{n'} | \phi_n \rangle = \delta_{nn'}$.
Therefore, by introducing Lagrange multipliers, we demand

$$0 = \frac{\delta}{\delta \phi_n^*(x)} \left(E(\{\phi_n\}) - \sum_{nn'} \eta_{n'n} \int dx\, \phi_n^*(x)\, \phi_{n'}(x) \right)$$

$$\frac{\delta}{\delta \phi_n^*(x)} \sum_\lambda K_{\lambda\lambda} = \frac{\delta}{\delta \phi_n^*(x)} \sum_\lambda \int dy\, \phi_\lambda^*(y) K(y) \phi_\lambda(y)$$

$$= K(x)\phi_n(x) \equiv (K \circ \phi_n)(x)$$

$$\frac{\delta}{\delta \phi_n^*(x)} \frac{1}{2} \sum_{\lambda\lambda'} U^{(D)}_{\lambda\lambda'}$$

$$= \frac{1}{2} \frac{\delta}{\delta \phi_n^*(x)} \sum_{\lambda\lambda'} \int dy dy'\, \phi_\lambda^*(y) \phi_{\lambda'}^*(y') U(y y') \phi_{\lambda'}(y') \phi_\lambda(y)$$

$$= \sum_\lambda \int dy\, \phi_\lambda(y) U(y x) \phi_\lambda(y) \phi_n(x)$$

$$\equiv (D \circ \phi_n)(x)$$

$$\frac{\delta}{\delta \phi_n^*(x)} \frac{1}{2} \sum_{\lambda\lambda'} U^{(X)}_{\lambda\lambda'}$$

$$= \frac{1}{2} \frac{\delta}{\delta \phi_n^*(x)} \sum_{\lambda\lambda'} \int dy dy'\, \phi_\lambda^*(y) \phi_{\lambda'}^*(y') U(y y') \phi_\lambda(y') \phi_{\lambda'}(y)$$

$$= \sum_\lambda \int dy\, \phi_\lambda^*(y) U(y x) \phi_\lambda(x) \phi_n(y)$$

$$\equiv (X \circ \phi_n)(x)$$

$$\frac{\delta}{\delta \phi^*_\kappa(x)} \sum_{\lambda\lambda'} \eta_{\lambda\lambda'} \int dx\, \phi^*_{\lambda'}(x)\, \phi_\lambda(x)$$

$$= \sum_\lambda \eta_{\lambda\kappa}\, \phi_\lambda(x)$$

To sum up, we obtain

$$(K + D - X) \circ \phi_\kappa = \sum_\lambda \eta_{\lambda\kappa}\, \phi_\lambda \quad \text{---①}$$

By applying $\int dx\, \phi^*_{\kappa'}(x) \times$ to both sides,

$$K_{\kappa'\kappa} + D_{\kappa'\kappa} - X_{\kappa'\kappa} = \eta_{\kappa'\kappa} \quad \text{---②}$$

$$K_{\kappa'\kappa} \equiv \int dx\, \phi^*_{\kappa'}(x)\, K(x)\, \phi_\kappa(x) = \langle \kappa' | K | \kappa \rangle$$

$$D_{\kappa'\kappa} \equiv \sum_\lambda \int dx\, dy\, \phi^*_{\kappa'}(x)\, \phi_\lambda(y)\, U(x,y)\, \phi_\lambda(y)\, \phi_\kappa(x)$$

$$\equiv \langle \lambda\, \kappa' | U | \lambda\, \kappa \rangle$$

$$X_{\kappa'\kappa} \equiv \sum_\lambda \int dx\, dy\, \phi^*_{\kappa'}(x)\, \phi^*_\lambda(y)\, U(x,y)\, \phi_\kappa(y)\, \phi_\lambda(x)$$

$$\equiv \langle \lambda\, \kappa' | U | \kappa\, \lambda \rangle$$

$$\left(X^*_{\kappa\kappa'} = \sum_\lambda \int dx\, dy\, \phi_\kappa(x)\, \phi_\lambda(y)\, U(xy)\, \phi^*_{\kappa'}(y)\, \phi^*_\lambda(x) \right.$$

$$= \sum_\lambda \int dx\, dy\, \phi^*_{\kappa'}(y)\, \phi^*_\lambda(x)\, U(xy)\, \phi_\kappa(x)\, \phi_\lambda(y)$$

$$\left. = X_{\kappa'\kappa} \quad (\text{if } U(xy) = U(yx)) \right)$$

Without loss of generality, we can assume that Eq. ① or ② is diagonal, i.e.,

$$K_{\kappa'\kappa} + D_{\kappa'\kappa} - X_{\kappa'\kappa} = \eta_{\kappa'\kappa}\delta_{\kappa'\kappa} \quad -②'$$

$$(K + D - X) \circ \phi_\kappa = \eta_{\kappa\kappa}\phi_\kappa \quad -①'$$

This is because the matrix $F \equiv K+D-X$ (Fock matrix) is covariant under the unitary transformation; and the Slater determinant is unitary-invariant, as we see later.

Since the Slater determinant is unitary invariant, for an optimal solution that satisfies ① or ②, its unitary transformation must be also the optimal solution.

Then, because $F \equiv K+D-X$ is unitary covariant and hermitian, its always possible to find a unitary that diagonalizes them.

Therefore, there must be an optimal solution that satisfies ①′ or ②′.

Slater determinants are unitary-invariant

$$c_\kappa^+ = \sum_{\eta \in \Lambda \equiv \{\lambda_1, \lambda_2 \cdots, \lambda_N\}} u_{\kappa\eta}\, c_\eta'^+$$

$$\Psi \equiv \prod_\alpha c_{\kappa_\alpha}^+ |0\rangle$$

$$= \prod_\alpha \left(\sum_{\eta_\alpha} u_{\kappa_\alpha \eta_\alpha} c_{\eta_\alpha}'^+ \right) |0\rangle$$

$$= \sum_{\{\eta_\alpha\}} \prod_\alpha u_{\kappa_\alpha \eta_\alpha} \prod_\alpha c_{\eta_\alpha}'^+ |0\rangle$$

$\prod_\alpha c_{\eta_\alpha}'^+ |0\rangle = 0$ unless $\{\eta_1, \eta_2 \cdots \eta_N\} = \{\lambda_1, \lambda_2 \cdots \lambda_N\}$

$$= \sum_P \prod_\alpha u_{\kappa_\alpha \lambda_{P(\alpha)}} \prod_\alpha c_{\lambda_{P(\alpha)}}'^+ |0\rangle$$

$$= \sum_P (-1)^P \prod_\alpha u_{\kappa_\alpha \lambda_{P(\alpha)}} \prod_\alpha c_{\lambda_\alpha}'^+ |0\rangle$$

$$= |U| \left(\prod_\alpha c_{\lambda_\alpha}'^+ \right) |0\rangle$$

$$= \prod_\alpha c_{\lambda_\alpha}'^+ |0\rangle = \Psi'$$

$F = K + D - X$ is covariant

$$F_{\kappa\kappa'} \equiv \int dx\, \phi^*_\kappa(x) \frac{\delta E}{\delta \phi'^*_{\kappa'}(x)}$$

$$\phi_\kappa = \sum_\lambda u_{\lambda\kappa} \phi'_\lambda \qquad \phi'_\lambda = \sum_\kappa u^*_{\lambda\kappa} \phi_\kappa$$

$$\frac{\delta F}{\delta \phi^*_{\kappa'}(x)} = \sum_\lambda \frac{\partial \phi'^*_\lambda}{\partial \phi^*_{\kappa'}} \frac{\delta E}{\delta \phi'^*_\lambda(x)}$$

$$= \sum_\lambda u_{\lambda\kappa'} \frac{\delta E}{\delta \phi'^*_\lambda(x)}$$

$$F_{\kappa\kappa'} = \int dx \sum_\lambda u^*_{\lambda\kappa} \phi'_\lambda(x) \sum_{\lambda'} u_{\lambda'\kappa'} \frac{\delta E}{\delta \phi'^*_{\lambda'}(x)}$$

$$= \sum_{\lambda\lambda'} u^*_{\lambda\kappa} u_{\lambda'\kappa'} \int dx\, \phi'_\lambda(x) \frac{\delta E}{\delta \phi'^*_{\lambda'}(x)}$$

$$= \sum_{\lambda\lambda'} u^*_{\lambda\kappa} u_{\lambda'\kappa'} F'_{\lambda\lambda'}$$

$$\longrightarrow F = U^+ F' U$$

(Actually, K, D and X are each covariant.)

Numerical Solution of HF Approximation

Now, ① becomes the diagonalization problem of the matrix H defined by

$$H \equiv K + D - X$$

These matrices are $N \times N$ hermitian matrices where N is the number of electrons.
This is much easier than the original problem whose complexity is exponential in N, rather than polynomial. However, this is still too much to solve by pen and paper. So we typically use computers. We solve the eigen value problem numerically

$$H \phi_\lambda = \eta_\lambda \phi_\lambda$$

to obtain the N lowest modes ϕ_λ, then we update the matrix elements of H using the new $\{\phi_\lambda\}$. We iterate this procedure until convergence.

Koopmans' Theorem

- Within the HF approximation, the first ionization energy is the difference between the original $|\Psi_{HF}\rangle$ and the state after removing an electron at the highest energy, i.e., $|\Psi'_{HF}\rangle \equiv c_\kappa |\Psi_{HF}\rangle$.

- Specifically, $|\Psi'_{HF}\rangle = \left(\prod' c^+_{\kappa'}\right)|0\rangle$ where $\prod'$ is the product of the lowest N levels except κ.

- $E' \equiv \langle \Psi'_{HF} | \mathcal{H} | \Psi'_{HF} \rangle$

$$= \sum_{\kappa'}{}' \epsilon^0_{\kappa'} + \frac{1}{2}\sum_{\kappa'\lambda'}{}' \left(U^{(D)}_{\kappa'\lambda'} - U^{(X)}_{\kappa'\lambda'}\right)$$

$$\Rightarrow \quad \Delta E = E - E' = \epsilon^0_\kappa + \sum_\lambda{}' \left(U^{(D)}_{\kappa\lambda} - U^{(X)}_{\kappa\lambda}\right)$$

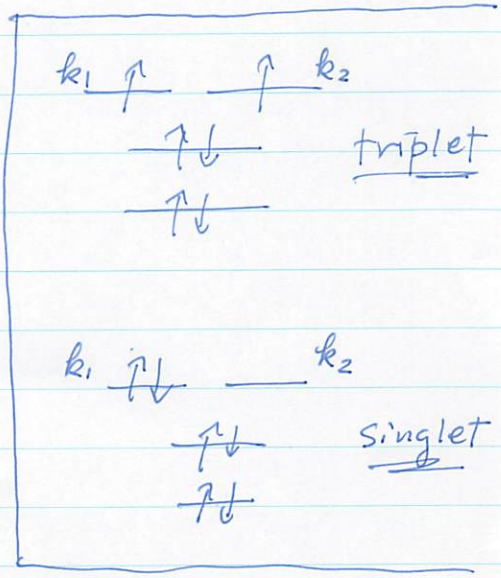
- Here we need remember that $\kappa = (k, \sigma)$ where k and σ are the orbital and the spin d.o.f. respectively. For the hamiltonian that do not mix the two, $\epsilon_\kappa = \epsilon_k$ (indep. of σ) and, for $\lambda = (k'\sigma')$,

$$U^{(D)}_{\kappa\lambda} = U^{(D)}_{(k\sigma)(k'\sigma')} = U_{(k\sigma)(k'\sigma');(k\sigma)(k'\sigma')} = U_{kk';kk'}$$
$$\equiv U^{(D)}_{kk'} \quad \text{(independent of } \sigma\text{)}$$
$$U^{(X)}_{\kappa\lambda} = U^{(X)}_{(k\sigma)(k'\sigma')} = U_{(k\sigma)(k'\sigma');(k'\sigma')(k\sigma)} = U_{kk';k'k}\,\delta_{\sigma\sigma'}$$
$$= U^{(X)}_{kk'}\,\delta_{\sigma\sigma'}$$

Therefore, $\left(\because U_{(k_1\sigma_1)(k_2\sigma_2);(k_3\sigma_3)(k_4\sigma_4)} = U_{k_1k_2;k_3k_4} \times \delta_{\sigma_1\sigma_3}\delta_{\sigma_2\sigma_4}\right)$

$$\Delta E = \epsilon^0_k + \sum_{k'}{}' \left(2U^{(D)}_{kk'} - U^{(X)}_{kk'}\right)$$

Hund's Rule and Its HF Explanation



- When we have degeneracy in the highest levels, and have multiple electrons in them, we have several configurations that would be degenerated if the interaction were absent.

- By introducing the interaction, even if it doesn't explicitly mix the orbitals and the spins, the configurational degeneracy is lifted. In such a circumstance, Hund's rule says that the configuration with spins aligned with each other is generally favored (i.e. has a lowest energy).

- An explanation based on the HF approximation (maybe wrong): Consider the situation depicted in the figure. The contribution of the two electrons at the highest level (k_1 and k_2) to the total HF energy is

$$\Delta E = \epsilon^0_{\kappa_1} + \epsilon^0_{\kappa_2} + \{ U^{(D)}_{\kappa_1\kappa_2} - U^{(X)}_{\kappa_1\kappa_2} + \sum_\lambda \left(U^{(D)}_{\kappa_1\lambda} + U^{(D)}_{\kappa_2\lambda} - U^{(X)}_{\kappa_1\lambda} - U^{(X)}_{\kappa_2\lambda} \right) \}$$

$(\kappa_1 \equiv (k_1\sigma_1)\ \ \kappa_2 \equiv (k_2\sigma_2))$

For the triplet case ($k_1 \neq k_2$ and $\sigma_1 = \sigma_2$),

$$\Delta E_t = \epsilon^0_{k_1} + \epsilon^0_{k_2} + (U^{(D)}_{k_1k_2} - U^{(X)}_{k_1k_2} + \sum_{k'} \left(2U^{(D)}_{k_1k'} + 2U^{(D)}_{k_2k'} - U^{(X)}_{k_1k'} - U^{(X)}_{k_2k'} \right) \}$$

For the singlet case ($k_1 = k_2$ and $\sigma_1 \neq \sigma_2$)

$$\Delta E_S = 2\epsilon^0_{k_1} + \left(U^{(D)}_{k_1k_1} + \sum_{k'} \left(4U^{(D)}_{k_1k'} - 2U^{(X)}_{k_1k'} \right) \right)$$

If for some reason (like some symmetry w.r.t. $k_1 \leftrightarrow k_2$) we can assume that

$$\epsilon^0_{k_1} = \epsilon^0_{k_2} \quad \sum_{k'} U^{(D)}_{k_1 k'} = \sum_{k'} U^{(D)}_{k_2 k'} \quad \sum_{k'} U^{(X)}_{k_1 k'} = \sum_{k'} U^{(X)}_{k_2 k'}$$

then we can simplify the energy difference as

$$\Delta E_S - \Delta E_t = U^{(D)}_{k_1 k_1} - U^{(D)}_{k_1 k_2} + U^{(X)}_{k_1 k_2}.$$

This is usulally positive. (see below)

- $U^{(X)}_{k_1 k_2} = \int dx \int dy\ \phi^*_{k_1}(x)\, \phi^*_{k_2}(y)\, U(x,y)\, \phi_{k_2}(x)\, \phi_{k_1}(y)$

$= \int dx \int dy\ u^*(x)\, U(x,y)\, u(y)$

$= u^+ U u \qquad (u(x) \equiv \phi_{k_1}(x)\, \phi^*_{k_2}(x))$

When viewed as a matrix, $U(x,y)$ is typically the diagnal-dominant ($U(x,y) \to \infty$ ($|x-y| \to 0$)). Therefore, we can expect that $U(x,y)$ is positive definite. If so, $u^+ U u > 0$. In fact, for $U(x,y) = 1/|x-y|$ we can prove U is positive definite. (see below)

- $U^{(D)}_{k_1 k_1} - U^{(D)}_{k_1 k_2}$ is also positive under the present symmetry assumption. With $v_\alpha \equiv \phi_{k_\alpha}(x)\, \phi^*_{k_\alpha}(x)$

$$U^{(D)}_{k_1 k_1} = v_1^+ U v_1 = U_{11} = U_{22}$$
$$U^{(D)}_{k_1 k_2} = v_1^+ U v_2 \equiv U_{12} = U_{21}$$

Since U is (nearly) positive definite, $(v_1 - v_2)^+ U (v_1 - v_2) = U_{11} + U_{22} - U_{12} - U_{21} \geq 0$

$\longrightarrow U_{11} \geq U_{12}$

$U(x,y) \equiv \dfrac{1}{|x-y|}$ is positive definite.

We can "diagonalize" $U(x,y)$ by Fourier transformation.

$$U_{k'k} \equiv \int dx\,dy\, e^{ikx - ik'y} \frac{1}{|x-y|} \underbrace{e^{-\epsilon|x-y|}}_{\text{regularization}}$$

$$= \int d(x-y)\,dy\, e^{ik(x-y) + i(k-k')y} \frac{e^{-\epsilon|x-y|}}{|x-y|}$$

$$= \delta_{kk'} \int dr\, e^{ikr} \frac{e^{-\epsilon r}}{r}$$

$$= \delta_{kk'} \int_0^\infty dr \int_{-1}^{1} d\xi\; r^2 \cdot e^{ikr\xi} \frac{e^{-\epsilon r}}{r}$$

$$= \delta_{kk'} \int_0^\infty dr\; r \frac{1}{ikr}\left(e^{ikr} - e^{ikr}\right) e^{-\epsilon r}$$

$$= \delta_{kk'} \frac{1}{ik} \int_0^\infty dr \left(e^{-(\epsilon - ik)r} - e^{-(\epsilon + ik)r}\right)$$

$$= \delta_{kk'} \frac{1}{ik} \left(\frac{1}{\epsilon - ik} - \frac{1}{\epsilon + ik}\right)$$

$$= \delta_{kk'} \frac{1}{ik} \frac{2ik}{\epsilon^2 + k^2} = \delta_{kk'} \frac{2}{k^2 + \epsilon^2} \to \frac{2\delta_{kk'}}{k^2}$$

So, U is positive-definite.