$$\nabla_1^2 \prod_{i=1}^{3} \exp(-\alpha \vec{r}_i^{\,2}) = \nabla_1^2 \Psi_T(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$

$$= \nabla_1^2 \exp(-\alpha \vec{r}_1^{\,2}) \exp(-\alpha \vec{r}_2^{\,2}) \exp(-\alpha \vec{r}_3^{\,2})$$

$$= \underbrace{\exp(-\alpha \vec{r}_2^{\,2}) \exp(-\alpha \vec{r}_3^{\,2})}_{A} \left(\nabla_1^2 \exp(-\alpha \vec{r}_1^{\,2})\right)$$

$$= A \left(\vec{\nabla}_1 \cdot \left(\vec{\nabla}_1 \exp(-\alpha \vec{r}_1^{\,2})\right)\right)$$

$$= A \left(\vec{\nabla}_1 \cdot \left(-2\alpha \vec{r}_1 \exp(-\alpha \vec{r}_1^{\,2})\right)\right)$$

$$= A \Big(-2\alpha d \exp(-\alpha \vec{r}_1^{\,2})$$

$$- 2\alpha \vec{r}_1 \cdot (-2\alpha \vec{r}_1) \exp(-\alpha \vec{r}_1^{\,2})\Big)$$

$$= A \Big(-2\alpha d \exp(-\alpha \vec{r}_1^{\,2}) + 4\alpha^2 \vec{r}_1^{\,2}$$

$$\times \exp(-\alpha \vec{r}_1^{\,2})\Big)$$

$$= \left(-2\alpha d + 4\alpha^2 \vec{r}_1^{\,2}\right) \Psi_T(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$

$$\rho(\vec{r}_1) = \int d\vec{r}_2 \ldots d\vec{r}_N \left|\Psi_T(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\right|^2$$

$$= \exp(-2\alpha \vec{r}_1^{\,2}) \int d\vec{r}_2 \ldots d\vec{r}_N \prod_{i=2}^{N} \exp(-2\alpha \vec{r}_i^{\,2})$$

$$= \exp(-2\alpha \vec{r}_1^{\,2}) \left(\sqrt{\frac{\pi}{2\alpha}}\right)^{d(N-1)}$$

$$\rho(r_1) = \left(\sqrt{\frac{\pi}{2\alpha}}\right)^{d(N-1)} \int_0^{2\pi}\int_0^{\pi} d\theta d\varphi \sin(\theta) \exp(-2\alpha r_1^2)$$

$$= \left(\sqrt{\frac{\pi}{2\alpha}}\right)^{d(N-1)} \exp(-2\alpha r_1^2) \cdot 4\pi$$

$$\boxed{\begin{aligned} A^2 &= \int d\vec{r}_1 \ldots d\vec{r}_N \left|\Psi_T(\vec{r}_1, \ldots, \vec{r}_N)\right|^2 \\ &= \left(\sqrt{\frac{\pi}{2\alpha}}\right)^{dN}, \quad A = \sqrt{\left(\sqrt{\frac{\pi}{2\alpha}}\right)^{dN}} \end{aligned}}$$

$$\rho(\vec{r}_1) = \frac{N\int d\vec{r}_2 \cdots d\vec{r}_N \, |\Psi_T(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)|^2}{\underbrace{\langle \Psi_T | \Psi_T \rangle}_{A^2}}$$

$$\rho(r) = \frac{N\left(\sqrt{\frac{\pi}{2\alpha}}\right)^{d(N-1)} 4\pi \exp(-2\alpha r_1^2)}{\left(\sqrt{\frac{\pi}{2\alpha}}\right)^{dN}}$$

$$\boxed{= N\left(\sqrt{\frac{\pi}{2\alpha}}\right)^{-d} 4\pi \exp(-2\alpha r^2)}$$

$$A^2 N = N\langle \Psi_T | \Psi_T \rangle = \int_0^\infty dr\, r^2 \rho(r)$$

$$\Psi_T = A\,\Psi_T^N\,,$$

$$\langle \Psi_T^N | \Psi_T^N \rangle = 1$$

$$\langle \Psi_T | \Psi_T \rangle = |A|^2 \langle \Psi_T^N | \Psi_T^N \rangle$$

$$= |A|^2 .$$

Atomic orbital (AO) system $\{\chi_\alpha\}_{\alpha=1}^{l}$

$\leadsto$ Harmonic oscillator eigenstates.

Molecular orbital (MO) system $\{\phi_i\}_{i=1}^{K}$.

$\leadsto$ Hartree-Fock orbitals.

---

1) The general spin-orbital:

$$\phi(x, m_s) = c_1 \varphi_1(x)\alpha(m_s) + c_2 \varphi_2(x)\beta(m_s),$$

$$\alpha(\uparrow) = 1, \quad \alpha(\downarrow) = 0,$$

$$\beta(\uparrow) = 0, \quad \beta(\downarrow) = 1,$$

$$|c_1|^2 + |c_2|^2 = 1.$$

2) The unrestricted spin-orbital

$$\phi(x, m_s) = \varphi_\sigma(x)\,\sigma(m_s),$$

$$\sigma \in \{\alpha, \beta\}.$$

3) The restricted spin-orbital

$$\phi(x, m_s) = \varphi(x)\,\sigma(m_s).$$

$$\begin{aligned}
\phi(x, m_s) &= \langle x, m_s | \phi \rangle \\
&\overset{③}{=} \big(\langle x| \otimes \langle m_s|\big)\big(|\varphi\rangle \otimes |\sigma\rangle\big) \\
&= \langle x|\varphi\rangle \langle m_s|\sigma\rangle \\
&= \varphi(x)\,\sigma(m_s).
\end{aligned}$$

Tensor product

Spatial harmonic oscillator basis:

$$\{\chi_\alpha(x)\}_{\alpha=1}^{\ell},$$

General harmonic oscillator basis:

$$\{\psi_\mu(x, m_s)\}_{\mu=1}^{2\ell}.$$

How do we go from

$$(h_{\alpha\beta}, u^{\alpha\beta}_{\gamma\delta}) \longrightarrow (h_{\mu\nu}, u^{\mu\nu}_{\sigma\tau})?$$

$$h_{\mu\nu} = \langle \psi_\mu | \hat{h} \otimes \hat{\mathbb{1}}_{2\times 2} | \psi_\nu \rangle$$

$$= \left(\langle \chi_\alpha | \otimes \langle \sigma |\right) \hat{h} \otimes \hat{\mathbb{1}}_{2\times 2}$$

$$\times \left(|\chi_\beta\rangle \otimes |\tau\rangle\right)$$

$$= \langle \chi_\alpha | \hat{h} | \chi_\beta \rangle \underbrace{\langle \sigma | \tau \rangle}_{\delta_{\sigma\tau}}$$

$$= h_{\alpha\beta}\, \delta_{\sigma\tau}. \qquad h \otimes \mathbb{1}_{2\times 2}$$

- ~~Demonstrate how to include spin in the matrix elements~~

- ~~Discuss the Coulomb term of the Fock matrix and the anti-symmetry of the Coulomb matrix elements.~~

- ~~Discuss iterative GHF-solver and convergence criteria.~~

$\{\varphi_\mu\}_{\mu=1}^{l}$ (general HO functions)
($l = 2$ (number of spatial functions))

$$f_{\mu\nu} = \langle \varphi_\mu | \hat{f} | \varphi_\nu \rangle$$

$$= \langle \varphi_\mu | \hat{h} | \varphi_\nu \rangle + \boxed{C^*_{\sigma i} C_{\tau i} u^{\mu\sigma}_{\nu\tau,AS}}$$

$$\hat{f} = \hat{h} + \boxed{\hat{u}^{direct}} - \hat{u}^{exchange}$$

$$u^{direct}_{\mu\nu} = \sum_{i=1}^{n} \langle \varphi_\mu \phi_i | \hat{u} | \varphi_\nu \phi_i \rangle$$

$$|\phi_i\rangle = \sum_{\mu=1}^{l} C_{\mu i} |\varphi_\mu\rangle$$

$$= \sum_{i=1}^{n} \sum_{\sigma=1}^{l} \sum_{\tau=1}^{l} C^*_{\sigma i} C_{\tau i} \langle \varphi_\mu \varphi_\sigma | \hat{u} | \varphi_\nu \varphi_\tau \rangle$$

$$D_{\tau\sigma} = \sum_{i=1}^{n} c^{*}_{\sigma i}\, c_{\tau i}$$

$$= \sum_{\sigma,\tau=1}^{l} D_{\tau\sigma} \langle \psi_\mu \psi_\sigma | \hat{u} | \psi_\nu \psi_\tau \rangle$$

$$u^{exchange}_{\mu\nu} = \sum_{i=1}^{n} \langle \psi_\mu \phi_i | \hat{u} | \phi_i \psi_\nu \rangle$$

$$= \sum_{i=1}^{n} \sum_{\sigma=1}^{l} \sum_{\tau=1}^{l} c^{*}_{\sigma i}\, c_{\tau i} \langle \psi_\mu \psi_\sigma | \hat{u} | \psi_\tau \psi_\nu \rangle$$

$$= \sum_{\sigma,\tau=1}^{l} D_{\tau\sigma} \langle \psi_\mu \psi_\sigma | \hat{u} | \psi_\tau \psi_\nu \rangle$$

$$u^{\mu\sigma}_{\nu\tau,AS} = \langle \psi_\mu \psi_\sigma | \hat{u} | \psi_\nu \psi_\tau \rangle - \langle \psi_\mu \psi_\sigma | \hat{u} | \psi_\tau \psi_\nu \rangle$$

$$f_{\mu\nu} = h_{\mu\nu} + u_{\mu\nu}^{\text{direct}} - u_{\mu\nu}^{\text{exchange}}$$

$$= h_{\mu\nu} + \sum_{\sigma,\tau=1}^{\ell} D_{\tau\sigma} \, u_{\nu\tau,AS}^{\mu\sigma}$$

$$F C = C \underset{\sim}{\varepsilon} ,$$

$$[F]_{\mu\nu} = f_{\mu\nu} ,$$

scipy.linalg.eigh

$$F^{(i)} C^{(i+1)} = C^{(i+1)} \underset{\sim}{\varepsilon}^{(i+1)} ,$$

$$F^{(i)} = F\left(C^{(i)}\right)$$

1) Construct the Fock matrix $F^{(i)}$, where $[F]_{\mu\nu} = f_{\mu\nu}$. $F^{(0)} = h$.

2) Solve Roothaan-Hall equations to find $C^{(i+1)}$ and $\vec{\varepsilon}^{(i+1)}$.

3) Build the density matrix $D^{(i+1)}$ from $C^{(i+1)}$.

4) Check for convergence.

$$\Delta E = |E^{(i+1)} - E^{(i)}| \leq \delta_E$$

$$\|\Delta D\| = \| D^{(i+1)} - D^{(i)} \| \leq \delta_D$$

Next week:

- "Expectation" values:
  - ↳ Energy
  - ↳ Particle density
  - ↳ Dipole moment

- ~~Time-dependent CCHF.~~
  ~~(maybe)~~

$$\Phi_p(x, m_s) = \underbrace{\varphi_p^\alpha(x)}\alpha(m_s) + \underbrace{\varphi_p^\beta(x)}\beta(m_s)$$

$$\boxed{\begin{aligned} &\chi_\mu(x, m_s) = \chi_\mu^\alpha(x)\alpha(m_s) + \chi_\mu^\beta(x)\beta(m_s), \\ &\underline{\text{GOS:}} \quad \chi_\mu^\alpha(x) = \chi_\mu^\beta(x) \end{aligned}}$$

We want to plot

$$|\phi_p(x)|^2 = \sum_{m_s} |\Phi_p(x, m_s)|^2$$

$$= |\Phi_p(x, \uparrow)|^2 + |\Phi_p(x, \downarrow)|^2$$

$$= |\varphi_p^\alpha(x)|^2 + |\varphi_p^\beta(x)|^2$$

$$\phi_{p}^{\alpha}(x) = C_{\mu p}^{\alpha} \chi_{\mu}(x)$$

$$\phi_{p}(x, m_s) = C_{\mu p} \chi_{\mu}(x, m_s)$$

$$\phi_{0}(x, m_s) = C_{\mu 0} \chi_{\mu}(x, m_s)$$

$$\phi_{1}(x, m_s) = C_{\mu 1} \chi_{\mu}(x, m_s)$$

$$|\phi_{p}(x, m_s)|^{2} = |C_{\mu p} \chi_{\mu}(x, m_s)|^{2}$$

$$\phi_p(x, m_s) = \phi_p^\alpha(x)\alpha(m_s) + \phi_p^\beta(x)\beta(m_s)$$

$$\begin{aligned}
1 &= \langle \phi_p | \phi_p \rangle \\
&= \sum_{m_s} \int dx\, \phi_p^*(x, m_s)\, \phi_p(x, m_s) \\
&= \sum_{m_s} \int dx\, |\phi_p(x, m_s)|^2 \\
&= \int dx \left(|\phi_p^\alpha(x)|^2 + |\phi_p^\beta(x)|^2 \right)
\end{aligned}$$

$\{|\alpha\rangle, |\beta\rangle\}, \quad \alpha(m_s) = \langle m_s | \alpha \rangle$

Energy expectation value

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle ,$$

$$|\Psi\rangle \simeq |HF\rangle = |\phi_1 \dots \phi_n\rangle ,$$

where $\{\phi_p\}_{p=1}^{l}$ are the HF-orbitals.

We know that

$$\langle \phi_p | \phi_q \rangle = \delta_{pq} .$$

$$E = \langle HF | \hat{h} | HF \rangle + \frac{1}{4} \langle HF | \hat{u} | HF \rangle$$

$$\boxed{= \sum_{i}^{n} \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_{i,j}^{n} \langle \phi_i \phi_j | \hat{u} | \phi_i \phi_j \rangle_{AS} ,}$$

$$|\phi_p\rangle = \sum_{\mu=1}^{l} C_{\mu p} |\varphi_\mu\rangle$$

$$\rho_{qp} = \langle HF | \hat{c}^{+}_{p} \hat{c}_{q} | HF \rangle$$

$$= \delta_{p \in \{HF\}} \delta_{pq} \, , \quad p \in \{1, \dots, n\},$$

$$p = q \, .$$

$$\rho_{\mu\nu} = \sum_{i}^{n} C^{*}_{\nu i} C_{\mu j} \, ,$$

$$\langle x \rangle = \langle HF | \hat{x} | HF \rangle$$

$$= x_{pq} \langle HF | \hat{c}^{+}_{p} \hat{c}_{q} | HF \rangle$$

$$= x_{pq} \rho_{qp} \overset{!}{=} \langle \phi_p | \hat{x} | \phi_q \rangle \rho_{qp}$$

$$= x_{\mu\nu} \rho_{\nu\mu} \overset{!}{=} \langle \psi_\mu | \hat{x} | \psi_\nu \rangle \rho_{\nu\mu}$$

$$\rho(x) = \sum_{p=1}^{l} \phi_p^{\star}(x)\, \rho_{qp}\, \phi_q(x)$$

$$MO = \sum_{i=1}^{n} |\phi_p(x)|^2$$

$$AO = \sum_{\mu=1}^{l} \psi_\mu^{\star}(x)\, \rho_{\nu\mu}\, \psi_\nu(x)$$

$$\rho_{pq}^{rs} = \langle \Phi | \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r | \Phi \rangle ,$$

where $\hat{c}_p$ ($\hat{c}_p^\dagger$) are the annihilation (creation) operators in the molecular orbital basis.

They are given by

$$\hat{c}_p = C_{\alpha p}^* \hat{a}_\alpha ,$$

$$\hat{c}_p^\dagger = C_{\alpha p} \hat{a}_\alpha^\dagger ,$$

where $\hat{a}_\alpha$ ($\hat{a}_\alpha^\dagger$) are the annihilation (creation) operators in the atomic orbital basis.

We also have

$$\hat{a}_\alpha = C_{\alpha p} \hat{c}_p ,$$

$$\hat{a}_\alpha = C_{\alpha p}^* \hat{c}_p^\dagger .$$

This lets us construct

$$\rho_{\alpha\beta}^{\gamma\delta} = \langle \Phi | \hat{a}_\alpha^+ \hat{a}_\beta^+ \hat{a}_\delta \hat{a}_\gamma | \Phi \rangle$$

$$= \langle \Phi | C_{\alpha p}^* \hat{c}_p^+ C_{\beta q}^* \hat{c}_q^+$$

$$\times \; C_{\delta s} \hat{c}_s \; C_{\gamma r} \hat{c}_r \; | \Phi \rangle$$

$$= C_{\alpha p}^* C_{\beta q}^* C_{\delta s} C_{\gamma r} \langle \Phi | \hat{c}_p^+ \hat{c}_q^+ \hat{c}_s \hat{c}_r | \Phi \rangle$$

$$= C_{\alpha p}^* C_{\beta q}^* C_{\delta s} C_{\gamma r} \; \rho_{pq}^{rs} .$$

$$\rho^{rs}_{pq} = \langle \Phi | \hat{c}^{+}_{p} \hat{c}^{+}_{q} \hat{c}_{s} \hat{c}_{r} | \Phi \rangle$$

$$= - \delta_{p \in \{\Phi\}} \delta_{ps} \delta_{q \in \{\Phi\}} \delta_{qr}$$

$$+ \delta_{p \in \{\Phi\}} \delta_{pr} \delta_{q \in \{\Phi\}} \delta_{qs}$$

$$= - \rho^{s}_{p} \rho^{r}_{q} + \rho^{r}_{p} \rho^{s}_{q}$$

$$\rho^{\beta}_{\alpha} = C^{*}_{\alpha p} C_{\beta q} \rho^{q}_{p}$$

$$C^{*}_{\alpha p} C_{\alpha q} = \delta_{pq} ,$$

$$C^{*}_{\alpha p} C_{\beta p} = \delta_{\alpha\beta} .$$

$$\rho^{\beta}_{\alpha} C_{\alpha r} C^{*}_{\beta s} = C_{\alpha r} C^{*}_{\alpha p} C^{*}_{\beta s} C_{\beta q} \rho^{q}_{p}$$

$$= \delta_{rp} \delta_{sq} \rho^{q}_{p}$$

$$= \rho^{s}_{r}$$

$$\rho^{s}_{r} = \rho^{\beta}_{\alpha} \, C_{\alpha r} C^{*}_{\beta s}$$

$$= C^{*}_{\alpha i} C_{\beta i} \, C_{\alpha r} C^{*}_{\beta s}$$

$$= \delta^{i}_{r} \, \delta^{s}_{i}$$

$$\langle \chi_\alpha | \chi_\beta \rangle = S^{\alpha}_{\beta} \neq \delta^{\alpha}_{\beta}$$

$$| \phi_p \rangle = C_{\alpha p} \, | \chi_\alpha \rangle$$

$$= C_{\alpha p} \, C^{*}_{\alpha q} \, | \phi_q \rangle$$

$$|\Psi(t)\rangle = |\Phi(t)\rangle = |\phi_1(t)\phi_2(t)\cdots\phi_n(t)\rangle,$$

$$|\phi_p(t)\rangle = \sum_{\mu=1}^{\ell} C_{\mu p}(t)\,|\chi_\mu\rangle$$

$$i\hbar\frac{d}{dt}|\phi_p(t)\rangle = \hat{f}(t)\,|\phi_p(t)\rangle$$

$$\Rightarrow i\hbar\frac{d}{dt}\sum_{\nu=1}^{\ell} C_{\nu p}(t)|\chi_\nu\rangle = \hat{f}(t)\sum_{\nu=1}^{\ell} C_{\nu p}(t)|\chi_\nu\rangle$$

$$\Rightarrow i\hbar\sum_{\nu=1}^{\ell}\dot{C}_{\nu p}(t)\underbrace{\langle\chi_\mu|\chi_\nu\rangle}_{\delta_{\mu\nu}}$$

$$= \sum_{\nu=1}^{\ell}\langle\chi_\mu|\hat{f}(t)|\chi_\nu\rangle\, C_{\nu p}(t)$$

$$\Rightarrow i\hbar\,\dot{C}_{\mu p}(t) = \sum_{\nu=1}^{\ell} f_{\mu\nu}(t)\, C_{\nu p}(t)$$

$$\Rightarrow \boxed{\dot{C}(t) = -i\, F(t)\, C(t)}$$

$$\hat{H}(t) = \hat{h}_{HO} + \hat{u} + \hat{h}_I(t) ,$$

$$\hat{h}_I(t) = - f(t)\,\hat{d}$$

$$= - f(t)\, q\,\hat{x} = f(t)\,\hat{x} ,$$

$$\boxed{f(t) = \varepsilon_0 \sin(\omega t)} ,$$

$$\hat{H}\,|\psi_k\rangle = E_k\,|\psi_k\rangle , \quad \hat{H}(t) = \hat{H}(0)$$

$$|\psi(t)\rangle = e^{i\hat{H}t}\,|\psi(0)\rangle$$

$$= e^{i\hat{H}t} \sum_k c_k\,|\psi_k\rangle$$

$$= \sum_k c_k\, e^{iE_k t}\,|\psi_k\rangle$$

$$\hat{f}(t) = \underbrace{\hat{h}(t)}_{\hat{h}_{HO} + \hat{h}_I(t),} + \hat{u}^{direct} - \hat{u}^{exchange}$$

$$x_{\mu\nu} = \langle \psi_\mu | \hat{x} | \psi_\nu \rangle$$

$$d_{\mu\nu} = \langle \psi_\mu | \hat{d} | \psi_\nu \rangle$$

$$\langle \psi_\mu | \hat{f}(t) | \psi_\nu \rangle$$

$$= \langle \psi_\mu | \hat{h}_{HO} | \psi_\nu \rangle + \langle \psi_\mu | \hat{h}_I(t) | \psi_\nu \rangle$$

$$+ \sum_{i=1}^{n} \langle \psi_\mu \phi_i(t) | \hat{u} | \psi_\nu \phi_i(t) \rangle_{AS}$$

$$= (h_{HO})_{\mu\nu} + f(t)\, x_{\mu\nu}$$

$$+ \sum_{\kappa,\lambda=1}^{l} \sum_{i=1}^{n} C^*_{\kappa i} C_{\lambda i} \langle \psi_\mu \psi_\kappa | \hat{u} | \psi_\nu \psi_\lambda \rangle_{AS}$$

$$= (h_{1e0})_{\mu\nu} + f(t)\, X_{\mu\nu}$$

$$+ \sum_{\kappa,\lambda=1}^{l} D_{\lambda\kappa}(t)\, u^{\mu\kappa}_{\nu\lambda}$$

$$= f_{\mu\nu}(t) = [F]_{\mu\nu}(t)$$

---

1) Choose an initial state $C(0)$. For example, use the converged ground state C from GHF.

2) Construct $F(t)$ (the time-dependent Fock matrix) from $C(t)$ and $\hat{H}(t)$.

3) Solve the RHS of the time-dependent Hartree-Fock equation, that is

$$\dot{C}(t) = -iF(t)C(t).$$

4) Repeat steps 2 & 3 in an ODE-solver.

Assume we have a $C(0)$, and we can solve

$$\dot{C}(t) = -iF(t)C(t).$$

We can then propagate using Euler's method

$$C(t+\Delta t) = C(t) + \Delta t\,\dot{C}(t)$$
$$= C(t) - i\Delta t\,F(t)\,C(t).$$