Identical particles

$$\mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^2) := \left\{ \psi(\vec{r},\sigma) \,\middle|\, \sum_{\sigma \in \{|\uparrow\rangle, |\downarrow\rangle\}} \int_{\mathbb{R}^3} |\psi(\vec{r},\sigma)|^2 d\vec{r} < \infty \right\}$$

$$\int d\vec{x} := \sum_\sigma \int_{\mathbb{R}^3} d\vec{r} \quad , \quad \vec{x} = (\vec{r},\sigma)$$

$$\mathcal{H} = \left\{ \psi(\vec{x}) \,\middle|\, \int d\vec{x}\, |\psi(\vec{x})|^2 < \infty \right\}.$$

2 particles $\mathcal{H} \otimes \mathcal{H}$. $\psi(\vec{x}_1, \vec{x}_2)$

Permutation operator

$$P_{12}\, \psi(\vec{x}_1, \vec{x}_2) = \psi(\vec{x}_2, \vec{x}_1)$$

$$P_{12}\psi = a\psi. \quad P_{12}^2 = I. \Rightarrow a^2 = 1 \Rightarrow a = \pm 1.$$

$$H = -\frac{1}{2}\left(\Delta_{\vec{r}_1} + \Delta_{\vec{r}_2}\right) + V(\vec{r}_1, \vec{r}_2).$$

$$[H, P_{12}]\psi = [V, P_{12}]\psi = V(\vec{r}_1, \vec{r}_2)\psi(\vec{x}_2, \vec{x}_1)$$

$$- V(\vec{r}_2, \vec{r}_1)\psi(\vec{x}_2, \vec{x}_1)$$

$$V(\vec{r}_1, \vec{r}_2) = V(\vec{r}_2, \vec{r}_1) \Longleftrightarrow [H, P_{12}] = 0.$$

$$H\psi = E\psi$$

① $\psi(\vec{x}_1, \vec{x}_2) = \psi(\vec{x}_2, \vec{x}_1)$ Boson

② $\psi(\vec{x}_1, \vec{x}_2) = -\psi(\vec{x}_2, \vec{x}_1)$ Fermion

Ex. $H = -\frac{1}{2}\Delta_{\vec{r}_1} - \frac{1}{2}\Delta_{\vec{r}_2} - \frac{2}{|\vec{r}_1|} - \frac{2}{|\vec{r}_2|} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}$

$\mathcal{A}_2 = \Lambda^2 L^2(\mathbb{R}^3; \mathbb{C}^2) \subset L^2(\mathbb{R}^3, \mathbb{C}^2) \otimes L^2(\mathbb{R}^3, \mathbb{C}^2)$

$[\vec{S}^{tot\,2}, H] = [S_z^{tot}, H] = 0.$

$\Psi(\vec{x}_1, \vec{x}_2) = \varphi(\vec{r}_1, \vec{r}_2)\,\chi(\sigma_1, \sigma_2)$

Singlet : χ anti-sym. φ sym.

triplet : χ sym. φ anti-sym.

Simplest approximation "rank 1"

singlet $\qquad \varphi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1)\,\phi(\vec{r}_2)$

triplet $\qquad \varphi(\vec{r}_1, \vec{r}_2) = \dfrac{1}{\sqrt{2!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) \\ \phi_2(\vec{r}_1) & \phi_2(\vec{r}_2) \end{vmatrix}$

Slater determinant.

Proj. 1D Helium. singlet / triplet energy.

$$L^2(\mathbb{R}, \mathbb{C}^2) \approx \mathrm{span}\{\tilde{\phi}_1(x), \tilde{\phi}_2(x)\} =: \mathcal{U}$$

$$-\frac{1}{2}\frac{d^2}{dx^2}\tilde{\phi}_i - 2V_c(x)\tilde{\phi}_i = \epsilon_i \tilde{\phi}_i \quad , i=1,2.$$

① Project H to $\mathcal{U}\otimes\mathcal{U}$. Eigen-decomposition and examine symmetry

② Find the best rank 1 approximation for singlet / triplet, and compare w. ①.

N-particle system.

$$|\Psi\rangle \in \bigotimes^N L^2(\mathbb{R}^3; \mathbb{C}^2)$$

$$P_{ij}\, \Psi(\vec{x}_1, \cdots, \vec{x}_N) = \Psi(\vec{x}_1, \cdots, \underset{\substack{\uparrow \\ i}}{\vec{x}_j}, \cdots, \underset{\substack{\uparrow \\ j}}{\vec{x}_i}, \cdots, \vec{x}_N)$$

$$P_{ij}^2 = 1.$$

<u>Postulation</u>: $|\Psi\rangle$ simulataneously eigenstate of all P_{ij}. w. the same eigenvalue ($+1$ or -1)

$$S_N := \mathrm{Sym}^N L^2(\mathbb{R}^3; \mathbb{C}^2)$$

$$A_N := \bigwedge^N L^2(\mathbb{R}^3; \mathbb{C}^2) \leftarrow \text{electrons.}$$

N single particle functions

$$\{\psi_i(\vec{x})\}_{i=1}^N$$

$$\Psi_B(\vec{x}_1, \cdots, \vec{x}_N) = C_B \sum_{\pi \in S_N} \psi_{\pi_1}(\vec{x}_1) \cdots \psi_{\pi_N}(\vec{x}_N)$$

$$\Psi_F(\vec{x}_1, \cdots, \vec{x}_N) = C_F \sum_{\pi \in S_N} (-1)^\pi \psi_{\pi_1}(\vec{x}_1) \cdots \psi_{\pi_N}(\vec{x}_N)$$

$$= C_F \begin{vmatrix} \psi_1(\vec{x}_1) & \cdots & \psi_1(\vec{x}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\vec{x}_1) & \cdots & \psi_N(\vec{x}_N) \end{vmatrix}$$

$$\int \psi_i^*(\vec{x}) \psi_j(\vec{x}) \, dx = \delta_{ij}$$

$$\Rightarrow \quad C_F = \frac{1}{\sqrt{N!}} \qquad \text{(exer)}.$$

exer: Write "rank 1" approx. to Helium atom using spin orbitals.

$$\psi(\vec{x}_1, \cdots, \vec{x}_N) = 0. \quad \vec{x}_i = \vec{x}_j$$

Pauli exclusion principle.

$\phi(\vec{x})$ spin orbital.

$\phi(\vec{r})\chi(\sigma)$ spatial orbital.

Quantum many body Hamiltonian.

$$\hat{H} = \underbrace{\sum_{i=1}^{N} -\frac{1}{2}\Delta_{\vec{r}_i}}_{T} + \underbrace{\sum_{i=1}^{N} V_{ext}(\vec{r}_i ; \{R_I\})}_{V_{en}}$$

$$+ \underbrace{\sum_{i<j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{V_{ee}} + \underbrace{\sum_{I<J}^{M} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}}_{E_{II}}$$

Variational principle

$$E_0 = \inf_{\substack{|\Psi\rangle \in \mathcal{A}_N, \\ \langle\Psi|\Psi\rangle = 1}} \langle \Psi | H | \Psi \rangle$$

Finite dimensional approx.

$$L^2(\mathbb{R}^3; \mathbb{C}^2) \approx \mathcal{U}_d = \mathrm{span}\{\phi_1(\vec{x}), \cdots, \phi_d(\vec{x})\}$$

$$\mathcal{A}_{N,d} = \bigwedge^N \mathcal{U}_d$$

$d > N$. Pick d basis. antisymmetrize

$$\Rightarrow \quad \Phi_{[i_1 \cdots i_N]}(\vec{x}_1, \cdots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{i_1}(\vec{x}_1) & \cdots & \phi_{i_1}(\vec{x}_N) \\ \vdots & \ddots & \vdots \\ \phi_{i_N}(\vec{x}_1) & \cdots & \phi_{i_N}(\vec{x}_N) \end{vmatrix}$$

$$\in \mathcal{A}_{N,d} \subset \mathcal{A}_N .$$

<u>Thm</u>. $\{ \Phi_{[i_1, \cdots, i_N]} \}$ is an orthonormal basis of $\mathcal{A}_{N,d}$

Pf: ① All det orthonormal.

② $\mathrm{span}\{ \varphi_{i_1}(\vec{x}_1) \cdots \varphi_{i_N}(\vec{x}_N) \} = \bigotimes^N \mathcal{U}_d$

antisymmetrize $\Rightarrow \mathcal{A}_{N,d}$

Cor. $\dim \mathcal{A}_{N,d} = \binom{d}{N}$

Full configuration interaction

$$E_{0,N} = \inf_{\substack{\Psi \in \mathcal{A}_{N,d} \\ \langle \Psi | \Psi \rangle = 1}} \langle \Psi | H | \Psi \rangle .$$

Hartree-Fock:

best, single Slater determinant

$$\Psi(\vec{x}_1, \cdots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \cdots & \psi_1(\vec{x}_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\vec{x}_1) & \cdots & \psi_N(\vec{x}_N) \end{vmatrix}$$

$$\psi_i(\vec{x}) = \sum_{\mu=1}^{d} \phi_\mu(\vec{x})\, C_{\mu i}$$

$\phi_\mu(\vec{x})$ "=" $\delta(\vec{r} - \vec{r}_\mu)\, \chi_\mu(\sigma)$ real space representation.

$\mathring{\mathcal{A}}_N$: all Slater det of N elec in $\mathcal{A}_N$.

$\mathring{\mathcal{A}}_{N,d}$: all Slater det of N elec in $\mathcal{A}_{N,d}$.

$$E_{HF} = \inf_{\substack{\Psi \in \mathcal{A}_N^0 \\ \langle \Psi | \Psi \rangle = 1}} \langle \Psi | H | \Psi \rangle .$$

$E_c = E_0 - E_{HF}$: correlation energy. ≤ 0.

$$\Psi(\vec{x}_1, \cdots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \sum_{\pi \in \mathrm{Sym}(N)} (-1)^{\pi} \psi_{\pi(1)}(\vec{x}_1) \cdots \psi_{\pi(N)}(\vec{x}_N)$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$$\langle \Psi | \sum_{i=1}^{N} \left(-\frac{1}{2} \Delta_{\vec{r}_i} + V_{ext}(\vec{r}_i) \right) | \Psi \rangle$$

$$= N \langle \Psi | -\frac{1}{2}\Delta_{\vec{r}_1} + V_{ext}(\vec{r}_1) | \Psi \rangle$$

$$= \frac{N}{N!} \sum_{\pi,\pi' \in Sym(N)} (-1)^{\pi} (-1)^{\pi'} \langle \psi_{\pi(1)} | -\frac{1}{2}\Delta_{\vec{r}} + V_{ext} | \psi_{\pi'(1)} \rangle$$

$$\langle \psi_{\pi(2)} | \psi_{\pi'(2)} \rangle \cdots \langle \psi_{\pi(N)} | \psi_{\pi'(N)} \rangle$$

$$= \sum_{i=1}^{N} \langle \psi_i | -\frac{1}{2}\Delta_{\vec{r}} + V_{ext} | \psi_i \rangle$$

$$\langle \Psi | \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} | \Psi \rangle$$

$$= \binom{N}{2} \langle \Psi | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \Psi \rangle$$

$$= \frac{1}{2(N-2)!} \sum_{\substack{\pi, \pi' \\ \in Sym(N)}} (-1)^{\pi+\pi'} \int \psi^*_{\pi(1)}(\vec{x}_1) \psi^*_{\pi(2)}(\vec{x}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_{\pi'(1)}(\vec{x}_1) \psi_{\pi'(2)}(\vec{x}_2) d\vec{x}_1 d\vec{x}_2$$

$$\langle \psi_{\pi(3)} | \psi_{\pi'(3)} \rangle \cdots \langle \psi_{\pi(N)} | \psi_{\pi'(N)} \rangle$$

$$= \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \int \psi^*_i(\vec{x}_1) \psi^*_j(\vec{x}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_i(\vec{x}_1) \psi_j(\vec{x}_2) d\vec{x}_1 d\vec{x}_2$$

$$- \sum_{\substack{ij=1 \\ i \neq j}}^{N} \int \psi^*_i(\vec{x}_1) \psi^*_j(\vec{x}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \psi_j(\vec{x}_1) \psi_i(\vec{x}_2) d\vec{x}_1 d\vec{x}_2$$

$$\rho(\vec{x}) = N \int \left|\Psi(\vec{x}, \vec{x}_2, \cdots, \vec{x}_N)\right|^2 d\vec{x}_2 \cdots d\vec{x}_N$$

$$\rho(\vec{r}) = \sum_{\sigma} \rho(\vec{r}, \sigma)$$

(exer) $\rho(\vec{x}) = \sum_{i=1}^{N} \left|\psi_i(\vec{x})\right|^2.$

$$P(\vec{x}, \vec{x}') = \int \Psi(\vec{x}, \vec{x}_2, \cdots, \vec{x}_N)\, \Psi(\vec{x}', \vec{x}_2, \cdots, \vec{x}_N)\, d\vec{x}_2 \cdots d\vec{x}_N$$

$$\rho(\vec{x}) = P(\vec{x}, \vec{x}')$$

$$\mathcal{E}^{HF}(\{\psi_i\}_{i=1}^{N}) = \sum_{i=1}^{N} \langle \psi_i | -\frac{1}{2}\Delta_{\vec{r}} | \psi_i \rangle + \int V_{ext}(\vec{r})\,\rho(\vec{r})\,d\vec{r}$$

$$+ \frac{1}{2}\int \frac{\rho(\vec{r})\,\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}\,d\vec{r}'$$

$$- \frac{1}{2}\int \frac{|P(\vec{x},\vec{x}')|^2}{|\vec{r}-\vec{r}'|}\,d\vec{x}\,d\vec{x}' + E_{II}$$

GHF.

UHF:

$$\psi_i(\vec{x}) = \varphi_i(\vec{r})\chi_i(\sigma) \quad , \quad \chi_i(\sigma) = \langle\sigma|\uparrow\rangle \text{ or } \langle\sigma|\downarrow\rangle.$$

RHF. $N = 2N_{occ}$

$$\psi_i(\vec{x}) = \varphi_i(\vec{r})\langle\sigma|\uparrow\rangle \quad , i=1,\cdots,N_{occ}$$

$$\psi_{i+N_{occ}}(\vec{x}) = \varphi_i(\vec{r})\langle\sigma|\downarrow\rangle.$$

$$E_0 \leq E^{GHF} \leq E^{UHF} \leq E^{RHF}.$$

(exer) Energy for UHF, RHF.

Sol fr HF.

RHF

$$\mathcal{E}^{RHF}\left(\{\varphi_i\}_{i=1}^{N_{occ}}\right) = \sum_{i=1}^{N_{occ}} \int |\nabla \varphi_i(\vec{r})|^2 + \int V_{ext}(\vec{r})\, \rho(\vec{r})\, d\vec{r}$$

$$+ \frac{1}{2} \iint \frac{\rho(\vec{r})\, \rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,' - \int \frac{|P(\vec{r},\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,'.$$

$$\rho(\vec{r}) = 2 \sum_{i=1}^{N_{occ}} |\varphi_i(\vec{r})|^2$$

Note

$$P(\vec{r},\vec{r}\,') = \sum_{i=1}^{N_{occ}} \varphi_i(\vec{r})\, \varphi_i^*(\vec{r}\,')$$

$$\delta\rho(\vec{r}) = 2 \sum_{i=1}^{N_{occ}} \delta\varphi_i^*(r)\, \varphi_i(r) + \varphi_i^*(r)\, \delta\varphi_i(r))$$

$$\mathcal{L} = \mathcal{E}^{RHF} - 2 \sum_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right) \lambda_{ji}$$

$$\frac{1}{2} \frac{\delta \mathcal{L}}{\delta \varphi_i^*(r)} = \left[-\frac{1}{2} \Delta + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\,' \right] \varphi_i(\vec{r})$$

$$- \int \frac{P(\vec{r}, \vec{r}\,') \varphi_i(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\,' = \sum_j \varphi_j(\vec{r}) \lambda_{ji}$$

$$H^{RHF} \varphi_i = \sum_j \varphi_j \lambda_{ji}$$

$$\lambda_{ji} = \langle \varphi_j | H^{RHF} | \varphi_i \rangle = \lambda_{ij}^*$$

$$\Lambda = U \Xi U^* , \quad \Xi = \begin{pmatrix} \varepsilon_1 & & \\ & \ddots & \\ & & \varepsilon_{N_{occ}} \end{pmatrix}$$

$$\psi_i(\vec{r}) = \sum \varphi_j(\vec{r})\, U_{ji} \qquad \Psi = \Phi U .$$

$$\rho(\vec{r}) = 2 \sum_{i=1}^{N_{occ}} |\psi_i(\vec{r})|^2 . \qquad P(\vec{r},\vec{r}') = \sum_{i=1}^{N_{occ}} \psi_i(\vec{r})\, \psi_i^*(\vec{r})$$

$$H^{RHF}[\Psi]\psi_i = \varepsilon_i \psi_i$$

① Solve RHF in a basis.

$$\mathcal{V}_d = \{ \phi_1(\vec{r}), \cdots, \phi_d(\vec{r}) \}.$$

ψ_λ

$$\psi_i(\vec{r}) = \sum_{\mu=1}^{d} \phi_\mu(\vec{r})\, C_{\mu i}$$

$$F_{\mu\nu} = \langle \phi_\mu | H^{RHF} | \phi_\nu \rangle = \underbrace{\langle \phi_\mu | -\tfrac{1}{2}\Delta + V_{ext} | \phi_\nu \rangle}_{h_{\mu\nu}}$$

$$+ 2 \sum_{\lambda\sigma} \int \frac{\phi_\mu^*(\vec{r})\, \phi_\nu(\vec{r})\, \phi_\lambda(\vec{r}')\, \phi_\sigma^*(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}\, d\vec{r}'\, P_{\lambda\sigma}$$

$$- \sum_{\lambda\sigma} \int \frac{\phi_\mu^*(\vec{r})\, \phi_\nu(\vec{r}')\, \phi_\lambda(\vec{r})\, \phi_\sigma^*(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}\, d\vec{r}'\, P_{\lambda\sigma}$$

$$P_{\lambda\sigma} = \sum_{i=1}^{N_{occ}} C_{\mu\lambda} C_{\nu\sigma}^{*} \quad \text{DM (in abasis)}$$

$$V_{pqrs} = \int \frac{\phi_p^*(\vec{r}) \phi_q^*(\vec{r}') \phi_r(\vec{r}) \phi_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \equiv (pq|rs)$$

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} \left[2(\mu\sigma|\nu\lambda) - (\mu\sigma|\lambda\nu) \right] P_{\lambda\sigma}.$$

$O(d^4)$ cost.

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$$

$$FC = SC \mathcal{E}.$$

(exer) UHF HF eq.

Large basis . L16. QG paper 18 .

density fitting .

Total energy computation (GHF)

$$E_0^{HF} = \sum_{i=1}^{N} \varepsilon_i + E_{II} \quad ?$$

(exer) Correct after neglecting Hartree-Fock terms.

$$\sum_{i=1}^{N} \varepsilon_i = \frac{1}{2}\sum_{i=1}^{N} \int |\nabla_{\vec{r}} \psi_i(\vec{x})|^2 \, d\vec{x} + \int \rho V_{ext}$$

$$+ \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \, d\vec{r} d\vec{r}' - \int \frac{|P(\vec{x},\vec{x}')|^2}{|\vec{r}-\vec{r}'|} \, d\vec{x} d\vec{x}',$$

$$E_0^{HF} = \sum_{i=1}^{N} \varepsilon_i + E_{II}$$

$$\underbrace{- \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d\vec{r}\, d\vec{r}\,' + \frac{1}{2} \int \frac{|P(\vec{x},\vec{x}\,')|^2}{|\vec{r}-\vec{r}\,'|} d\vec{x}\, d\vec{x}\,'}_{\text{Double counting}}$$

(exer) Derive UHF eq. How many occupied states per spin channel?