$$H = \sum_{pq} h_{pq} c_p^\dagger c_q + \frac{1}{2} \sum_{pqrs} V_{pqrs} \, c_p^\dagger c_q^\dagger c_s c_r$$

spin orbitals $\{ \phi_1(\vec{x}), \dots, \phi_d(\vec{x}) \}$.

$$h_{pq} = \int d\vec{x} \; \phi_p^*(\vec{x}) \left(-\frac{1}{2} \Delta_r + V_{ext}(\vec{r}) \right) \phi_q(\vec{x})$$

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

Simplified model.

Hubbard $\quad H = \sum_\sigma \sum_{\langle pq \rangle} h_{pq} \, c_{p\sigma}^\dagger c_{q\sigma} + \sum_p U_p \, n_{p\uparrow} n_{p\downarrow}$

$$n_{p\sigma} = c_{p\sigma}^\dagger c_{p\sigma}$$

Hartree-Fock theory.

$$\underbrace{\phi_1, \cdots, \phi_N}_{\substack{\text{occupied} \\ i,j,k,l}}, \underbrace{\phi_{N+1}, \cdots, \phi_d}_{\substack{\text{unoccupied.} \\ a,b,c,d}} : \text{already HF orbitals.}$$

$$|\Psi_0\rangle = c_1^\dagger \cdots c_N^\dagger |0\rangle$$

$$\mathcal{E}_{HF} = \langle \Psi_0 | H | \Psi_0 \rangle \Rightarrow \text{compute.}$$

① $$\langle \Psi_0 | c_p^\dagger c_q | \Psi_0 \rangle$$

$$= \langle 0 | c_N \cdots c_1 \, c_p^\dagger c_q \, c_1^\dagger \cdots c_N^\dagger | 0 \rangle$$

to be nonzero, $1 \le p, q \le N$.

$$\theta_p = \begin{cases} 1, & 1 \le p \le N \\ 0, & p > N \end{cases}$$

$$[c_p^\dagger c_q, c_i^\dagger] = c_p^\dagger \delta_{qi}$$

$$\Rightarrow c_p^\dagger c_q c_1^\dagger \cdots c_N^\dagger |0\rangle = \sum_{i=1}^{N} c_1^\dagger \cdots c_p^\dagger \cdots c_N^\dagger |0\rangle \delta_{qi}$$

i

$p = i$ to be nonzero.

$$\langle \Psi_0 | c_p^\dagger c_q | \Psi_0 \rangle = \theta_p \theta_q \delta_{pq} \langle \Psi_0 | c_p^\dagger c_q | \Psi_0 \rangle$$

$$\langle \Psi_0 | \sum_{pq} h_{pq} c_p^\dagger c_q | \Psi_0 \rangle = \sum_{i=1}^{N} h_{ii}$$

② $\frac{1}{2}\sum_{pqrs} \langle \Psi_0 | c_p^\dagger c_q^\dagger c_s c_r | \Psi_0 \rangle V_{pqrs}$

$$= \frac{1}{2}\sum_{pqrs} \langle 0 | c_N \cdots c_1 \, c_p^\dagger c_q^\dagger c_s c_r \, c_1^\dagger \cdots c_N^\dagger | 0 \rangle V_{pqrs}$$

$\{p, q\} = \{r, s\} \subset \{1, \cdots, N\}$, $p \neq q$, $s \neq r$.

① $p = r$, $q = s$ ② $p = s$, $q = r$.

recall

$$\frac{1}{2}\sum_{pqrs} V_{pqrs} \, c_p^\dagger c_q^\dagger c_s c_r \, c_1^\dagger \cdots c_N^\dagger |0\rangle$$

$$= \sum_{pq} \sum_{1 \leq i < j \leq N} V_{pqij} \, c_1^\dagger \cdots \underset{\underset{i}{\uparrow}}{c_p^\dagger} \cdots \underset{\underset{j}{\uparrow}}{c_q^\dagger} \cdots c_N^\dagger |0\rangle$$

2-particle energy

$$= \sum_{i<j} \left(V_{ijij} - V_{ijji} \right)$$

$$= \frac{1}{2} \sum_{i,j} \left(\langle ij|ij \rangle - \langle ij|ji \rangle \right)$$

$$:= \frac{1}{2} \sum_{i,j} \langle ij||ij \rangle$$

$$\mathcal{E}_{HF} = \sum_{i} h_{ii} + \frac{1}{2} \sum_{ij} \langle ij||ij \rangle .$$

interpret back to integrals.

$$\mathcal{E}_{HF} = \sum_{i=1}^{N} \int \phi_i(\vec{x}) \left(-\frac{1}{2}\Delta_{\vec{r}} + V_{ext}(\vec{r})\right) \phi_i(\vec{x})$$

$$+ \frac{1}{2} \sum_{i,j} \int \frac{\phi_i^*(\vec{x})\, \phi_j^*(\vec{x}')\, \phi_i(\vec{x})\, \phi_j(\vec{x}')}{|\vec{r}-\vec{r}'|} d\vec{r}\, d\vec{r}'$$

$$- \frac{1}{2} \sum_{i,j} \int \frac{\phi_i^*(\vec{x})\, \phi_j^*(\vec{x}')\, \phi_j(\vec{x})\, \phi_i(\vec{x}')}{|\vec{r}-\vec{r}'|} d\vec{r}\, d\vec{r}'$$

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

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

E-L to optimize orbital. $\Rightarrow$ H-F eq.

$$\left(-\frac{1}{2}\Delta + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\varphi_i(\vec{x}) - \int \frac{P(\vec{x},\vec{x}\,')}{|\vec{r}-\vec{r}\,'|}\varphi_i(\vec{x}\,')\,d\vec{x}\,' = \varepsilon_i\,\varphi_i(\vec{r})$$

Fock matrix. op. in the HF basis.

Galerkin projection.

$$F = \sum_{pq} f_{pq}\, c_p^{\dagger} c_q$$

$$
\begin{aligned}
f_{pq} &= \int \phi_p^* \left(-\frac{1}{2}\Delta + V_{ext} \right) \phi_q \, d\vec{x} \\
&\quad + \sum_{j=1}^{N} \int \frac{\phi_p^*(\vec{x})\, \phi_j(\vec{x}')\, \phi_j^*(\vec{x}')\, \phi_q(\vec{x})}{|\vec{r}-\vec{r}'|} \, d\vec{x}\, d\vec{x}' \\
&\quad - \sum_{j=1}^{N} \int \frac{\phi_p^*(\vec{x})\, \phi_j(\vec{x})\, \phi_j^*(\vec{x}')\, \phi_q(\vec{x}')}{|\vec{r}-\vec{r}'|} \, d\vec{x}\, d\vec{x}' \\
&= h_{pq} + \sum_{j=1}^{N} V_{pjqj} - V_{pjjq} \\
&\equiv h_{pq} + \sum_{j=1}^{N} \langle pj || qj \rangle
\end{aligned}
$$

self - consistency : $f_{pq} = \epsilon_p \delta_{pq}$

$\downarrow$

diagonal matrix .