* Particle - Hole Picture

* For N-body systems, it is useful to switch to basis states labeled as deviations (i.e., excitations of) from some reference N-body Slater Det. $|\Phi\rangle$ rather than states w/ $N-a^\dagger$ acting on $|0\rangle$ where all N-particles explicitly active
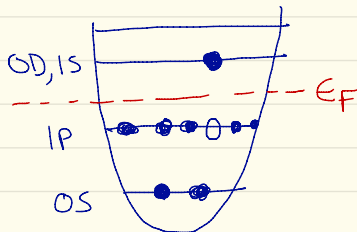

unoccupied sp. states (particle states)

ϵ_F

OP

OS

occupied sp. states (hole states)
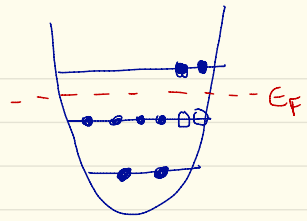
$$|\Phi\rangle = \prod_{i=1}^{N} a_i^\dagger |0\rangle$$

Important! Many different labeling conventions exist! Here, I will stick to

$$a, b, c, \ldots = \text{particle states}$$
$$i, j, k, \ldots = \text{hole states}$$
$$r, s, t, \ldots = \text{unrestricted}$$

1 particle - 1 hole (ph) excitations! $|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi\rangle$

0D, 1S

ϵ_F

1P

0S

<u>2p-2h excitations</u> : $|\Phi_{ij}^{ab}\rangle = a_a^\dagger a_i\, a_b^\dagger a_j |\Phi\rangle$

$$= a_a^\dagger a_b^\dagger a_j a_i |\Phi\rangle$$

$\Rightarrow \mathbb{1}_{F_N} = |\Phi\rangle\langle\Phi| + \sum_{a,i} |\Phi_i^a\rangle\langle\Phi_i^a|$

$$+ \sum_{\substack{a<b \\ i<j}} |\Phi_{ij}^{ab}\rangle\langle\Phi_{ij}^{ab}|$$

$$+ \cdots + \sum_{\substack{a<b<\cdots< \\ i<j<\cdots}} |\Phi_{ij\cdots}^{ab\cdots}\rangle\langle\Phi_{ij\cdots}^{ab\cdots}|$$

<u>Re-define creation/annihilation operators</u> $(a, a^\dagger) \longrightarrow (b, b^\dagger)$

$$a_a^\dagger = b_a^\dagger \qquad\qquad a_i = b_i^\dagger$$
$$a_a = b_a \qquad\qquad a_i^\dagger = b_i$$

<u>Why is this useful?</u> ① $\{a_r, a_s^\dagger\} = \delta_{rs} \longrightarrow \{b_r, b_s^\dagger\} = \delta_{rs}$

i.e., canonical transf.

i.e., Mathematically just like
$|\alpha_1 \alpha_2 \cdots \alpha_N\rangle = a_{\alpha_1}^\dagger \cdots a_{\alpha_N}^\dagger |0\rangle$

$a_\alpha |0\rangle = 0$

etc.

② $b_r |\Phi\rangle = 0$

$\langle\Phi| b_r^\dagger = 0$

③ $|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi\rangle = b_a^\dagger b_i^\dagger |\Phi\rangle$

etc...

Normal Order w/respect to $|\Phi\rangle$

$$\{B_1 B_2 \cdots B_n\} \equiv (-1)^p \, b_{p_1}^\dagger \cdots b_{p_n}$$

<u>Notation</u>: to distinguish N-ordering wrt $|\Phi\rangle$ from N-ordering wrt $|0\rangle$, // ＊ ＊
I will use $\{\cdots\}$ instead of $N[\cdots]$.

<u>ex</u>: $\{b_i b_j^\dagger\} = -b_j^\dagger b_i$

$$\{b_i b_a^\dagger b_j^\dagger b_b\} = b_a^\dagger b_j^\dagger b_i b_b = -b_a^\dagger b_j^\dagger b_b b_i \quad \text{etc}$$

<u>Note</u>: often, we don't even bother going thru the notational step
of $(a, a^\dagger) \longrightarrow (b, b^\dagger)$

eg, the previous 2 examples $\quad \{b_i b_j^\dagger\} = \{a_i^\dagger a_j\} = -a_j a_i^\dagger$

$$\{b_i b_a^\dagger b_j^\dagger b_b\} = \{a_i^\dagger a_a a_j^\dagger a_b\} = a_a^\dagger a_j a_i^\dagger a_b$$

i.e, the curly brackets are sufficient context that we push all $a_i^\dagger + a_a$ to the right
and all $a_i + a_a^\dagger$ to the left when N-ordering wrt $|\Phi\rangle$

Contractions wrt $|\Phi\rangle$:

$$\overline{B_q B_r} \equiv B_q B_r - \{B_q B_r\}$$

$$\overline{b_q b_r} = \overline{b_q^\dagger b_r^\dagger} = \overline{b_q^\dagger b_r} = 0$$

$$\overline{b_q b_r^\dagger} = \delta_{qr}$$

$$\overline{B_q B_r} \equiv B_q B_r - \{B_q B_r\}$$

$$\overline{b_q b_r} = \overline{b_q^\dagger b_r^\dagger} = \overline{b_q^\dagger b_r} = 0$$

$$\overline{b_q b_r^\dagger} = \delta_{qr}$$

* <u>In terms of the $a^\dagger, a$ - operators,</u>

$$\overline{b_q^\dagger b_r} = \delta_{qr} \implies \overline{a_a a_b^\dagger} = a_a a_b^\dagger - \{a_a a_b^\dagger\} = a_a a_b^\dagger + a_b^\dagger a_a = \delta_{ab}$$

$$\overline{a_i^\dagger a_j} = a_i^\dagger a_j - \{a_i^\dagger a_j\} = a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}$$

we can write this more compactly w/ no restriction on the indices

$$\boxed{\begin{array}{ll} \overline{a_q^\dagger a_r} = \delta_{qr} n_q & \\[2mm] \overline{a_q a_r^\dagger} = \delta_{qr} \bar{n}_q & \text{where } n_q = \begin{cases} 1 \text{ if } q \text{ occupied in } |\Phi\rangle \\ 0 \text{ else} \end{cases} \\[4mm] \overline{a_q a_r} = \overline{a_q^\dagger a_r^\dagger} = 0 & \bar{n}_q = 1 - n_q \end{array}}$$

<u>Wick's theorem wrt $|\Phi\rangle$</u> $A_1 \cdots A_n = \{A_1 \cdots A_n\}$

$$\langle \Phi | A_1 \cdots A_n | \Phi \rangle = \sum_{\substack{\text{fully} \\ \text{contracted}}}$$

$$+ \{\overline{A_1 A_2} \cdots A_n\} + \{\overline{A_1 A_2} \cdots A_n\} + \text{all single contractions}$$

$$+ \{\overline{A_1 A_2} \overline{A_3 A_4} \cdots A_n\} + \text{all double contractions}$$

$$+ \cdots$$

$$+ \{\overline{A_1 A_2} \overline{A_3 A_4} \cdots A_n\} + \text{all fully contracted}$$

Ex: find $\langle \Phi | \hat{H} | \Phi \rangle$

$$\langle \Phi | \hat{T} | \Phi \rangle = \sum_{q,r} T_{qr} \langle \Phi | a_q^\dagger a_r | \Phi \rangle = \sum_{qr} T_{qr} \langle \Phi | a_q^\dagger a_r | \Phi \rangle$$

$$= \sum_{qr} T_{qr} \, n_q \, \delta_{qr}$$

$$= \sum_{q} T_{qq} \, n_q = \sum_{i=1}^{N} T_{ii}$$

$$\langle \Phi | \hat{V} | \Phi \rangle = \frac{1}{4} \sum_{qrst} \langle qr | v | st \rangle \left(\langle \Phi | a_q^\dagger a_r^\dagger a_t a_s | \Phi \rangle + \langle \Phi | a_q^\dagger a_r^\dagger a_t a_s | \Phi \rangle \right)$$

$$\underbrace{\qquad\qquad}_{n_q n_r \, \delta_{rt} \, \delta_{qs}} \qquad\qquad \underbrace{\qquad\qquad}_{-\delta_{qt} \, \delta_{rs} \, n_q n_r}$$

$$= \frac{1}{4} \sum_{qr} \left(\langle qr | v | qr \rangle - \underbrace{\langle qr | v | rq \rangle}_{} \right) n_q n_r$$

$+ \langle qr | v | qr \rangle$

$$= \frac{1}{2} \sum_{ij} \langle ij | v | ij \rangle$$

<u>Example:</u> N-ordered H (wrt $|\Phi\rangle$)

$$\hat{H} = \sum_{qr} T_{qr} \, a_q^\dagger a_r + \frac{1}{4} \sum_{qrst} V_{qrst} \, a_q^\dagger a_r^\dagger a_t a_s$$

already in N-order wrt $|0\rangle$. It is useful to put it in N-order wrt $|\Phi\rangle$.

* just apply Wick's theorem (wrt $|\Phi\rangle$)

$$T = \sum_{qr} T_{qr}\, a_q^\dagger a_r = \sum_{qr} T_{qr}\left(\{a_q^\dagger a_r\} + \overline{a_q^\dagger a_r}\,\right) = \sum_i T_{ii} + \sum_{q,r} T_{qr}\{a_q^\dagger a_r\}$$

$$\Rightarrow \quad T \;\equiv\; \langle\Phi|T|\Phi\rangle + \hat{T}_N \qquad \text{①}$$

(here, N stands
for N-ordered
NOT # of
particles!)

$$\hat{V} = \frac{1}{4}\sum_{qrst} V_{qrst}\, a_q^\dagger a_r^\dagger a_t a_s$$

$$= \frac{1}{4}\sum_{qrst} V_{qrst}\left(\{q^\dagger r^\dagger t s\} + \{\overline{q^\dagger r^\dagger} t s\} + \{\overline{q^\dagger r^\dagger} t s\}\right.$$

$$+ \{\overline{q^\dagger r^\dagger t s}\} + \{\overline{q^\dagger r^\dagger} t s\}$$

$$\left. + \{\overline{q^\dagger \overline{r^\dagger t} s}\} + \{\overline{q^\dagger \overline{r^\dagger t} s}\}\right)$$

$$\hat{V} = \langle\Phi|\hat{V}|\Phi\rangle + \frac{1}{2}\sum_{qs}\{q^\dagger s\}\left(\sum_{i=1}^{N} V_{qisi}\right) + \frac{1}{4}\sum_{qrst} V_{qrst}\{q^\dagger r^\dagger t s\} \qquad \text{②}$$

<u>Combining ① + ②</u>: $\quad \hat{H} = E_{ref} + \sum_{qr} f_{qr}\{a_q^\dagger a_r\} + \frac{1}{4}\sum_{qrst} V_{qrst}\{a_q^\dagger a_r^\dagger a_t a_s\}$

$$= E_{ref} + \hat{f}_N + \hat{V}_N = E_{ref} + \hat{H}_N$$

$$E_{ref} = \langle\Phi|H|\Phi\rangle$$

$$f_{qr} = T_{qr} + \frac{1}{2}\sum_{i=1}^{N} V_{qiri}$$

* Especially useful as approximate treatment of 3N forces

realistic nuclear hamiltonians have 3NF's

$$H = \sum_{q,r} T_{qr}\, a_q^\dagger a_r + \frac{1}{4} \sum V_{qrst}\, a_q^\dagger a_r^\dagger a_t a_s + \frac{1}{36} \sum W_{qrstuv}\, a_q^\dagger a_r^\dagger a_s^\dagger a_v a_u a_t$$

complicates calculations
(memory, more expensive operations)

* Can N-order H wrt $|\Phi\rangle$

$$H = E_{ref} + \hat{f}_N + \hat{\Gamma}_N + \hat{W}_N$$

0-body
(#)

1-body
$\sum_{qr} f_{qr} \{q^\dagger r\}$

2-body
$\frac{1}{4}\sum \Gamma_{qrst} \{q^\dagger r^\dagger t s\}$

3-body $\frac{1}{36}\sum W_{qrstuv} \{q^\dagger r^\dagger s^\dagger u u t\}$

<u>Key Point</u>: Dominant parts of $\hat{W}$ subsumed in E_{ref}, f_{qr}, & Γ_{qrst}

e.g. $\Gamma_{qrst} = V_{qrst} + \sum_i W_{qristi}$

$f_{qr} = T_{qr} + \frac{1}{2}\sum_i V_{qiri} + \frac{1}{4}\sum_{ij} W_{qijrij}$

$\Rightarrow$ Excellent approximation $\hat{H} \approx E_{ref} + \hat{f}_N + \hat{\Gamma}_N$

no more expensive than "traditional" calculations that ignore 3N completely, yet it implicitly includes dominant 3N contributions

Derivation of HF equations

* Want to find best variational estimate of g.s. E within the restricted class of trial wf's that are simple Slater determinants

$$E_{g.s.} \leq E^{HF} = \underset{|\Phi\rangle \in \text{Slater det}}{\text{Min}} \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

$$|\Phi\rangle = \prod_{i=1}^{N} a_i^\dagger |0\rangle \qquad \text{the s.p. states } a_i^\dagger |0\rangle = |i\rangle \text{ are the a-priori unknown HF basis}$$

reminder: I use the convention $a,b,c,..$ = particles
$$i,j,k... = \text{holes}$$
$$q,r,s... = \text{unrestricted}$$

* Expand HF basis in some fixed s.p. basis (e.g., HO basis)

$$|q\rangle = \sum_\alpha |\alpha\rangle \langle \alpha | q \rangle = \sum_\alpha |\alpha\rangle D_{\alpha q}$$

HF basis   HO basis

$$\Rightarrow a_q^\dagger = \sum_\alpha C_\alpha^\dagger D_{\alpha q} \qquad \sum_\alpha D_{\alpha q} D_{\alpha q'}^* = \delta_{qq'} \quad (DD^\dagger = D^\dagger D = 1)$$

$$a_q = \sum_\alpha C_\alpha D_{\alpha q}^*$$

$$C_\alpha^\dagger = \sum_q a_q^\dagger D_{\alpha q}^* \quad \text{and} \quad C_\alpha = \sum_q a_q D_{\alpha q}$$

* (recall, any Unitary transf. amongst the N-lowest (i.e, hole states) orbitals
Only changes $|\Phi\rangle$ by a phase

$$|\Phi'\rangle = \prod_{i=1}^{N}\left(\sum_{j=1}^{N}U_{ij}a_j^\dagger\right)|0\rangle = \sum_{j_1}\cdots\sum_{j_N}U_{1j_1}U_{2j_2}\cdots U_{Nj_N}\,a_{j_1}^\dagger a_{j_2}^\dagger\cdots a_{j_N}^\dagger|0\rangle$$

$$= \text{Det}\,U \cdot |\Phi\rangle$$

irrelevant
phase since $UU^\dagger = 1$

Therefore, there is no 1-to-1 correspondence between the basis $|i\rangle$
& the S.D. $|\Phi\rangle$

* <u>However</u>, there is a 1-to-1 correspondence between $|\Phi\rangle$ and
its 1-body density matrix

$$\rho_{\alpha\beta} = \langle\Phi|C_\beta^\dagger C_\alpha|\Phi\rangle$$

$$= \sum_q\sum_r D_{\beta q}^* D_{\alpha r}\underbrace{\langle\Phi|a_q^\dagger a_r|\Phi\rangle}_{\color{red}\delta_{qr}n_r}$$

$$= \sum_q D_{\beta q}^* D_{\alpha q}n_q = \sum_i D_{\beta i}^* D_{\alpha i}$$

$$\Rightarrow \rho_{\alpha\beta} = \langle\Phi|C_\beta^\dagger C_\alpha|\Phi\rangle = \sum_{i=1}^{N}\langle\alpha|i\rangle\langle i|\beta\rangle$$

$$\Rightarrow \rho_{\alpha\beta} = \langle \Phi | c_\beta^\dagger c_\alpha | \Phi \rangle = \sum_{i=1}^{N} \langle \alpha | i \rangle \langle i | \beta \rangle$$

$\Rightarrow$ equivalently, $\rho_{\alpha\beta} = \langle \alpha | \hat{\rho} | \beta \rangle$ $\hat{\rho} = \sum_{i=1}^{N} | i \rangle \langle i |$

and

$\hat{\rho}^2 = \hat{\rho}$ projector in sp space onto
the subspace spanned by
occupied orbitals $| i \rangle$

* As we already showed, there is 1-to-1 correspondence between a Slater $| \Phi \rangle$ & its $\hat{\rho}$-operator

* Also, recall that all Slater dets. have $\hat{\rho}^2 = \hat{\rho}$

$\Downarrow$

$$E_{gs} \leq E^{HF} = \underset{|\Phi\rangle \in Slater}{Min} E[\Phi] \equiv \underset{|\Phi\rangle \in Slater\,det}{Min} \langle \Phi | H | \Phi \rangle$$

doing this variation
over all Slater dets.
equivalent to
varying $\hat{\rho}$ subject to
constraint $\hat{\rho}^2 = \hat{\rho}$

Express $E[\Phi] = \langle \Phi | H | \Phi \rangle$ in terms of 1-body density matrix

$$E[\Phi] = \sum_{\alpha\beta} T_{\alpha\beta} \underbrace{\langle \Phi | C_\alpha^\dagger C_\beta | \Phi \rangle}_{\text{Ⓐ}} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} \underbrace{\langle \Phi | C_\alpha^\dagger C_\beta^\dagger C_\delta C_\gamma | \Phi \rangle}_{\text{Ⓑ}}$$

Ⓐ $= \langle \Phi | C_\alpha^\dagger C_\beta | \Phi \rangle = \langle \Phi | C_\alpha^\dagger C_\beta | \Phi \rangle = \rho_{\beta\alpha}$

Ⓑ $= \langle \Phi | C_\alpha^\dagger C_\beta^\dagger C_\delta C_\gamma | \Phi \rangle + \langle \Phi | C_\alpha^\dagger C_\beta^\dagger C_\delta C_\gamma | \Phi \rangle$

$\qquad\qquad + \rho_{\delta\beta} \rho_{\gamma\alpha} \qquad\qquad\qquad - \rho_{\gamma\beta} \rho_{\delta\alpha}$

$\Rightarrow E[\rho] = \sum_{\alpha\beta} T_{\alpha\beta} \rho_{\beta\alpha} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} \underbrace{\left(\rho_{\delta\beta} \rho_{\gamma\alpha} - \rho_{\gamma\beta} \rho_{\delta\alpha} \right)}_{}$

$\qquad\qquad\qquad\qquad\qquad$ re-label dummy
$\qquad\qquad\qquad\qquad\qquad$ indices

$$\boxed{E[\rho] = \sum_{\alpha\beta} T_{\alpha\beta} \rho_{\beta\alpha} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} \rho_{\delta\beta} \rho_{\gamma\alpha}}$$

Variation of the E[ρ̂]

$$\delta E = E[\hat{\rho} + \delta\hat{\rho}] - E[\hat{\rho}]$$

|| What kind of variations $\delta\hat{\rho}$ can we make to stay in
|| Slater determinant space for $|\Phi\rangle$?

restricting to Slater det. $|\Phi\rangle \Longleftrightarrow \left(\hat{\rho} + \delta\hat{\rho}\right)^2 = (\hat{\rho} + \delta\hat{\rho})$ [ie, has to remain projector as we search over $\hat{\rho}$]

$$\Rightarrow \left(\hat{\rho} + \delta\hat{\rho}\right)^2 = \hat{\rho}^2 + \hat{\rho}\,\delta\hat{\rho} + \delta\hat{\rho}\,\hat{\rho} + O(\delta\rho^2)$$

$$\Rightarrow \left(\hat{\rho} + \delta\hat{\rho}\right)^2 = \cancel{\hat{\rho}^2} + \hat{\rho}\,\delta\hat{\rho} + \delta\hat{\rho}\,\hat{\rho} = \cancel{\hat{\rho}} + \delta\hat{\rho}$$

$$\boxed{\delta\hat{\rho}\,\hat{\rho} = (1 - \hat{\rho})\,\delta\hat{\rho}} \quad \otimes$$

Now, let $(1 - \hat{\rho}) \equiv \hat{\sigma}$ $\left(\hat{\rho} + \hat{\sigma} = 1,\ \hat{\rho}^2 = \hat{\rho},\ \hat{\sigma}^2 = \hat{\sigma},\ \hat{\rho}\hat{\sigma} = 0 \right)$

M. $\otimes$ by $\hat{\rho}$ from left: $\hat{\rho}\,\delta\hat{\rho}\,\hat{\rho} = \hat{\rho}\,\cancel{\hat{\sigma}}^{\,0}\,\delta\hat{\rho}$

M. $\otimes$ by $\hat{\sigma}$ from right: $\delta\hat{\rho}\,\underset{0}{\cancel{\hat{\rho}\hat{\sigma}}}\,\hat{\sigma} = \hat{\sigma}\,\delta\hat{\rho}\,\hat{\sigma}$

Thus we find that $\hat{\rho}\,\delta\hat{\rho}\,\hat{\rho} = \hat{\sigma}\,\delta\hat{\rho}\,\hat{\sigma} = 0$

$$\Rightarrow \boxed{\delta\rho_{ab} = \delta\rho_{ij} = 0} \quad \text{(hh \& pp variations vanish)}$$

$\Rightarrow$ Only variations of the ph sector $\delta P_{ai}, \delta P_{ia} \neq 0$

So then, $\quad \delta E = E[P + \delta P] - E[P] = \sum\limits_{\alpha\beta} \dfrac{\delta E}{\delta P_{\alpha\beta}} \, \delta P_{\alpha\beta} = 0$

$$\dfrac{\delta E}{\delta P_{\alpha\beta}} = \dfrac{\delta}{\delta P_{\alpha\beta}} \left[\sum\limits_{\zeta\sigma} T_{\zeta\sigma} P_{\sigma\zeta} + \dfrac{1}{2} \sum\limits_{\mu\nu\sigma\zeta} V_{\mu\nu\sigma\zeta} \, P_{\nu\zeta} \, P_{\mu\sigma} \right]$$

$$= T_{\alpha\beta} + \sum\limits_{\mu\sigma} V_{\mu\alpha\sigma\beta} \, P_{\mu\sigma} = h_{\alpha\beta}^{HF}$$

$\delta E = 0 = \sum\limits_{\alpha\beta} h_{\alpha\beta}^{HF} \, \delta P_{\alpha\beta}$ (basis indep, so write it in HF basis where we know only $\delta P_{ai}, \delta P_{ia}$ non-zero)

$$= \sum\limits_{qr} h_{qr}^{HF} \, \delta P_{qr}$$

$$= \sum\limits_{a,i} h_{ai}^{HF} \, \delta P_{ai} = 0$$

Since δP_{ai} arbitrary, this implies

$$h_{ai}^{HF} = 0 = h_{ia}^{HF} \quad \text{(Particle/hole states not mixed)}$$

$$\boxed{h_{ai}^{HF} = T_{ai} + \sum\limits_{j=1}^{N} V_{aji j} = 0}$$

* recalling that $\hat{\rho} = \sum\limits_{i=1}^{N} |i\rangle\langle i|$

$$\hat{\sigma} = \sum\limits_{a=N+1}^{\infty} |a\rangle\langle a| = 1 - \hat{\rho}$$

$$\Rightarrow \hat{\rho}\, h^{HF}(1 - \hat{\rho}) = 0$$

$$\Rightarrow \hat{\rho}\, h^{HF} - h^{HF}\hat{\rho} = 0 \qquad \hat{\rho} + h^{HF} \text{ simultaneously}$$
$$\text{diagonalizable}$$

$$h^{HF} = \left[\begin{array}{c|c} \hat{\rho}\, h^{HF}\hat{\rho} & 0 \\ \hline 0 & \hat{\sigma}\, h^{HF}\hat{\sigma} \end{array}\right] \qquad \begin{array}{l} \text{particle + hole blocks} \\ \text{can be diagonalized} \\ \text{separately} \end{array}$$

$$\Rightarrow \text{Go ahead and diagonalize } \hat{\rho} + h^{HF} \text{ simultaneously}$$

$$\boxed{\begin{array}{l} \hat{\rho}\,|q\rangle = n_q |q\rangle \qquad n_q = \begin{cases} 1 & q < N \\ 0 & q > N \end{cases} \\[2ex] h^{HF}|q\rangle = \varepsilon_q |q\rangle \end{array}}$$

$$h^{HF} |q\rangle = \mathcal{E}_q |q\rangle \quad \circledast$$

* Now expand unknown $|q\rangle = \sum_\alpha |\alpha\rangle D_{\alpha q}$

↑ Some known fixed basis (eg. HO)

* Then eq. $\circledast$ becomes

$$\sum_\beta \langle\alpha|h^{HF}|\beta\rangle D_{\beta q} = \mathcal{E}_q D_{\alpha q}$$

where $\langle\alpha|h^{HF}|\beta\rangle = \langle\alpha|T|\beta\rangle + \frac{1}{2}\sum_{\mu\nu}\langle\alpha\mu|V|\beta\nu\rangle \rho_{\mu\nu}$

Requires iterative sol'n since h^{HF} depends on the eigenfunctions $D_{\beta q}$

Via

$$\rho_{\mu\nu} \equiv \sum_{i=1}^N \langle\mu|i\rangle\langle i|\nu\rangle = \sum_{i=1}^N D_{\mu i} D_{\nu i}^*$$

<u>Schematic Sol'n Strategy</u> ① Guess initial $\rho_{\mu\nu}^{(0)}$ (eg. take the fixed $|\alpha\rangle$ basis as the initial guess for HF states

$$\Rightarrow \rho_{\mu\nu}^{(0)} = \delta_{\mu\nu} n_\mu \;)$$

② Build $\langle\alpha|h^{HF}|\beta\rangle$

③ diagonalize $\Rightarrow D_{\alpha q}^{(1)}$

$\;$ & build $\rho_{\mu\nu}^{(1)} = \sum_i D_{\mu i}^{(1)} D_{\nu i}^{(1)*}$

$\;$ & $h_{\alpha\beta}^{(1)}$

iterate till things don't change

Total E_{HF} : $= \langle \Phi | H | \Phi \rangle$

$$\boxed{E^{HF} = \sum_{\lambda} T_{\lambda\lambda} + \frac{1}{2} \sum_{\lambda j} \langle \lambda j | V | \lambda j \rangle}$$

$|\lambda\rangle$ are the converged,
self consistent orbits

from $h^{HF} |\lambda\rangle = \mathcal{E}_{\lambda} |\lambda\rangle$

* but $\langle \lambda | h^{HF} | \lambda \rangle = \mathcal{E}_{\lambda} = T_{\lambda\lambda} + \sum_{j} \langle \lambda j | V | \lambda j \rangle$

$\Downarrow$

$$\boxed{\begin{array}{l} E^{HF} = \sum_{\lambda=1}^{N} \mathcal{E}_{\lambda} - \frac{1}{2} \sum_{\lambda j} \langle \lambda j | V | \lambda j \rangle \\ \\ \qquad = \frac{1}{2} \left(\sum_{\lambda} \left(T_{\lambda\lambda} + \mathcal{E}_{\lambda} \right) \right) \end{array}}$$

<u>How it looks in $|\vec{r}, \sigma\rangle$ basis</u>

$$h_{\alpha\beta} = t_{\alpha\beta} + \frac{1}{2} \sum_{\mu\nu} \langle \alpha\mu |V|\beta\nu\rangle \rho_{\mu\nu}$$

here, $|\alpha\rangle \rightarrow |\vec{r}, \sigma\rangle$

$$\rho_{\mu\nu} \rightarrow \rho(\vec{r}\sigma, \vec{r}'\sigma') = \sum_{i=1}^{A} \langle \vec{r}\sigma | i \rangle \langle i | \vec{r}'\sigma' \rangle \quad \overset{\text{HF basis}}{}$$

* <u>For a local, spin-indep. V</u> : $\langle \vec{r}_1 \sigma_1 \vec{r}_2 \sigma_2 |V| \vec{r}_3 \sigma_3 \vec{r}_4 \sigma_4 \rangle$

$$\Bigg\{ \text{Some algebra}$$

$$\overset{\shortparallel}{V}(\vec{r}_1 - \vec{r}_2) \, \delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4} \, \delta(\vec{r}_1 - \vec{r}_3)\delta(\vec{r}_2 - \vec{r}_4)$$