I.) ph - representation

a) ref. state + excitations

b) Wick's theorem (+ gen. WT)

c) N-ordered H + approx. 3N

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II.) Density Matrix Operators

20-30

III.) HF eqns

- motivation
- derivation in $|\alpha\rangle$, E^{HF} expressions
- r-space version
-
- Thouless Stability Criteria

Derivation of HF equations

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

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

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

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

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

$$\underset{\text{HF basis}}{|q\rangle} = \sum_\alpha \underset{\text{HO basis}}{|\alpha\rangle} \langle \alpha | q \rangle = \sum_\alpha |\alpha\rangle D_{\alpha q}$$

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

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

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

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

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

$$= \underbrace{\mathrm{Det}\,U}_{\substack{\text{irrelevant}\\ \text{phase since } UU^{\dagger}=1}} \cdot |\Phi\rangle$$

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

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

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

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

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

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

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

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

and

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

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

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

$\Downarrow$

$$E_{gs} \le E^{HF} = \underbrace{\min_{|\Phi\rangle \in \text{Slater}} E[\Phi] = \min_{|\Phi\rangle \in \text{Slater det}} \langle\Phi|H|\Phi\rangle}$$

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

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

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

$$B = \underbrace{\langle \Phi | c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma | \Phi \rangle}_{+\rho_{\delta\beta}\rho_{\gamma\alpha}} + \underbrace{\langle \Phi | c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma | \Phi \rangle}_{-\rho_{\gamma\beta}\rho_{\delta\alpha}}$$

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

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

Variation of the $E[\rho]$

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

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

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

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

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

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

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

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

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

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 $\delta\rho_{ai}, \delta\rho_{ia} \neq 0$

So then, $\delta E = E[\rho+\delta\rho] - E[\rho] = \sum_{\alpha\beta} \frac{\delta E}{\delta\rho_{\alpha\beta}} \delta\rho_{\alpha\beta} = 0$

$$\frac{\delta E}{\delta\rho_{\alpha\beta}} = \frac{\delta}{\delta\rho_{\alpha\beta}}\left[\sum_{\xi\sigma} T_{\xi\sigma}\rho_{\sigma\xi} + \frac{1}{2}\sum_{\mu\nu\sigma\xi} V_{\mu\nu\sigma\xi}\,\rho_{\nu\xi}\,\rho_{\mu\sigma}\right]$$

$$= T_{\alpha\beta} + \sum_{\mu\sigma} V_{\mu\alpha\sigma\beta}\,\rho_{\mu\sigma} \equiv h^{HF}_{\alpha\beta}$$

$$\delta E = 0 = \sum_{\alpha\beta} h^{HF}_{\alpha\beta}\,\delta\rho_{\alpha\beta}$$ (basis indep, so write it in HF basis where we know only $\delta\rho_{ai}, \delta\rho_{ia}$ non-zero)

$$= \sum_{qr} h^{HF}_{qr}\,\delta\rho_{qr}$$

$$= \sum_{a,i} h^{HF}_{ai}\,\delta\rho_{ai} = 0$$

Since $\delta\rho_{ai}$ arbitrary, this implies

$$h^{HF}_{ai} = 0 = h^{HF}_{ia}$$ (particle/hole states not mixed)

$$\boxed{h^{HF}_{ai} = T_{ai} + \sum_{j=1}^{N} V_{ajij} = 0}$$

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

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

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

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

$\hat{\rho}$ & h^{HF} simultaneously diagonalizeable

$$h^{HF} = \left[\begin{array}{c|c} \hat{\rho}\, h^{HF} \hat{\rho} & 0 \\ \hline 0 & \hat{\sigma}\, h^{HF} \hat{\sigma} \end{array}\right]$$

particle & hole blocks can be diagonalized separately

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

$$\boxed{\begin{array}{ll} \hat{\rho}\,|q\rangle = n_q |q\rangle & n_q = \begin{cases} 1 & q < N \\ 0 & q > N \end{cases} \\ h^{HF} |q\rangle = \varepsilon_q |q\rangle & \end{array}}$$

$$h^{HF}|q\rangle = \varepsilon_q |q\rangle \quad (*)$$

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

Some known fixed basis (eg. HO)

* Then eq. (*) becomes

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

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

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

Schematic Sol'n Strategy:

① Guess initial $\rho^{(0)}_{\mu\nu}$ (e.g., take the fixed $|\alpha\rangle$ basis as the initial guess for HF states $\Rightarrow \rho^{(0)}_{\mu\nu} = \delta_{\mu\nu} n_\mu$)

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

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

+ build $\rho^{(1)}_{\mu\nu} = \sum_i D^{(1)}_{\mu i} D^{(1)*}_{\nu i}$

+ $h^{(1)}_{\alpha\beta}$

iterate till things don't change