The following educational matrial has been prepared and made freely available by the financial support of National Science Foundation (CAREER, CHE-084448) and Camille and Henry Dreyfus Foundation, Inc.

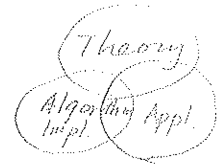
However, any opinions, findings, and conclusions or recommendations expressed in this material are those of the author and do not necessarily reflect the views of the sponsoring agencies.

So Hirata
Univ. of Illinois, Urbana, IL

⓪ Objective

TDDFT (TDHF) formalism, algorithm, (performance)

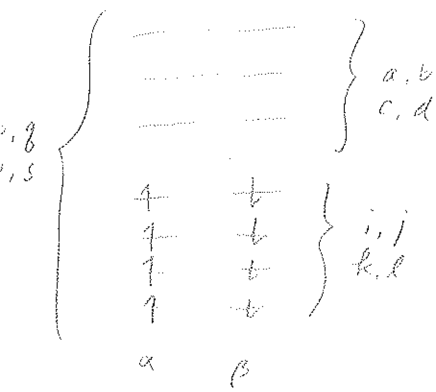
(Linear) response theory



① HF (ground state)

avoid double counting

$$E_{HF} = \langle \Phi | \hat{H} | \Phi \rangle = \sum_i^{occ.} \sum_\sigma^{\alpha,\beta} \underbrace{H_{ii\sigma}^{core}}_{\text{kinetic, nuclear attraction}} + \frac{1}{2} \sum_{i,j}^{occ.} \sum_{\sigma,\tau}^{\alpha,\beta} (i_\sigma i_\sigma || j_\tau j_\tau)$$



anti-symmetrized 2-e integrals in chemists' notation

$$(\overset{1^*}{i_\sigma} \overset{1}{i_\sigma} | \overset{2^*}{j_\tau} \overset{2}{j_\tau}) - (\overset{1^*}{i_\sigma} \overset{1}{j_\tau} | \overset{2^*}{j_\tau} \overset{2}{i_\sigma})$$

Coulomb J — exchange K $= 0$ if $\sigma \neq \tau$

$$\int \varphi_{i\sigma}^*(1) \varphi_{i\sigma}(1) \frac{1}{r_{12}} \varphi_{j\tau}^*(2) \varphi_{j\tau}(2) \, d1 d2 \quad \text{(Hund's rule)}$$

(self-interaction)

$$(i_\sigma i_\sigma | i_\sigma i_\sigma) - (i_\sigma i_\sigma | i_\sigma i_\sigma)$$

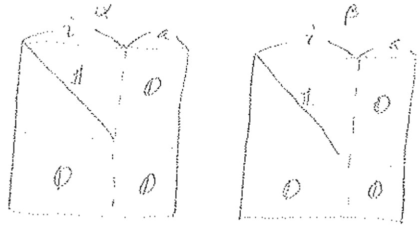
exact cancellation in HF

Density matrix $\rho(1) = \sum_{r,s} \sum_\tau P_{rs\tau} \varphi_{r\tau}(1) \varphi_{s\tau}^*(1)$ — ☆

$$E_{HF} = \sum_{p,q}^{all} \sum_\sigma^{\alpha,\beta} P_{pq\sigma}^* H_{pq\sigma}^{core} + \frac{1}{2} \sum_{p,q,r,s}^{all} \sum_{\sigma,\tau}^{\alpha,\beta} P_{pq\sigma}^* P_{rs\tau} (p_\sigma q_\sigma || s_\tau r_\tau)$$

Canonical HF orbital basis

P



$$\varphi'_{i\sigma} = \sum_{q}^{all} \varphi_{q\sigma} \underbrace{C_{qi\sigma}}_{\text{expansion coeff.}}$$

$$\rho(1) = \sum_{i}^{occ,\,\alpha,\beta}\sum_{\sigma} \varphi'^{*}_{i\sigma}(1)\varphi'_{i\sigma}(1) = \sum_{p,q}^{all}\sum_{\sigma}^{\alpha\beta} \underbrace{\left(\sum_{i}^{occ.} C^{*}_{pi\sigma} C_{qi\sigma}\right)}_{} \varphi^{*}_{p\sigma}(1)\varphi_{q\sigma}(1)$$

Comparing with ☆, $P_{qp\sigma} = P^{*}_{pq\sigma}$

Orthonomality

$$\delta_{ij} = \int \varphi'^{*}_{i\sigma}\varphi'_{j\sigma}\, d1 = \sum_{q} C^{*}_{qi\sigma} C_{qj\sigma}$$

$$\underbrace{\sum_{i,j} C_{pi\sigma}\,\delta_{ij}\, C^{*}_{rj\sigma}}_{P_{pr\sigma}} = \sum_{i,j}\sum_{q} \underbrace{C_{pi\sigma} C^{*}_{qi\sigma}}_{P_{pq\sigma}}\ \underbrace{C_{qj\sigma} C^{*}_{rj\sigma}}_{P_{qr\sigma}}$$

D. B. Cook "Handbook of Comp. Quant. Chem."

Orthonomality $\equiv$ $\sum_{q} P_{pq\sigma} P_{qr\sigma} = P_{pr\sigma}$

or

$\mathbb{P}\mathbb{P} = \mathbb{P}$ "idempotency" condition

Minimize E_{HF} with $\mathbb{P}\mathbb{P} = \mathbb{P}$ constraint.

Lagrange's undetermined multiplier for each condition

$$0 = \frac{\partial \mathcal{L}}{\partial P^{*}_{pq\sigma}} = \frac{\partial}{\partial P^{*}_{pq\sigma}}\left\{ E_{HF} - \sum_{r,p}\sum_{\tau}\lambda_{rp\tau}\left(\sum_{q} P_{rq\tau}P_{qr\tau} - P_{rr}\right)\right\}$$

$\underbrace{\frac{\partial E_{HF}}{\partial P^{*}_{pq\sigma}}}_{F_{pq\sigma}}$

$$= F_{pq\sigma} - \sum_{r} P_{pr\sigma}\lambda_{rq\sigma} - \sum_{r}\lambda_{pr\sigma}P_{rq\sigma} + \lambda_{pq\sigma}$$

We know λ, when diagonalized, contains orbital energies as diagonal elements. But at this point it's unknown Lagrange multipliers. Can we obtain eqs for F and P (without λ)?

$$0 = \sum_{q} F_{pq\sigma}P_{qs\sigma} - \sum_{r,q} P_{pr\sigma}\lambda_{rq\sigma}P_{qs\sigma} - \underbrace{\sum_{r,q}\lambda_{pr\sigma}\overbrace{P_{rq\sigma}P_{qs\sigma}}^{P_{rs\sigma}} + \sum_{q}\lambda_{pq\sigma}P_{qs\sigma}}_{}$$

$$0 = \sum_{p} P_{sp\sigma}F_{pq\sigma} - \underbrace{\sum_{r,p} \overbrace{P_{sp\sigma}P_{pr\sigma}}^{P_{sr\sigma}}\lambda_{rq\sigma}}_{\text{cancel}} - \underbrace{\sum_{r,p} P_{sp\sigma}\lambda_{pr\sigma}P_{rq\sigma} + \sum_{p} P_{sp\sigma}\lambda_{pq\sigma}}_{\text{cancel}}$$

☆☆

Comparing ☆☆

$$\sum_q F_{pq\sigma} P_{qs\sigma} = \sum_{r,q} P_{pr\sigma} \lambda_{rq\sigma} P_{qs\sigma} = \underbrace{\sum_q P_{pq\sigma} F_{qs\sigma}}_{\text{rename } p\to q,\ s\to p,\ q\to s \text{ in the second eq.}}$$

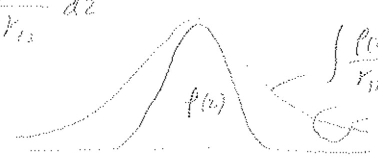
or

$$\mathbb{F}\mathbb{P} = \mathbb{P}\mathbb{F}$$

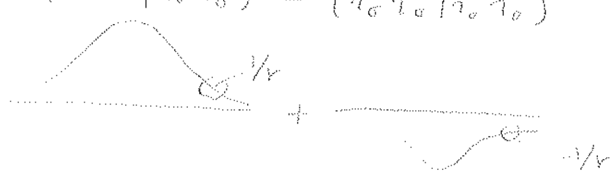
Fock matrix

$$F_{pq\sigma} = \frac{\partial E_{HF}}{\partial P^*_{pq\sigma}} = H^{core}_{pq\sigma} + \sum_{r,s}\sum_{\tau} P_{rs\tau}\,(p_\sigma q_\sigma || s_\tau r_\tau)$$

$$\int \varphi^*_{p\sigma}(1)\varphi_{q\sigma}(1)\left[\underbrace{\int \frac{1}{r_{12}} \sum_{r,s}\sum_{\tau} P_{rs\tau}\,\varphi^*_{s\tau}(2)\varphi_{r\tau}(2)\,d2}_{\int \frac{\rho(2)}{r_{12}}\,d2}\right] d1 - \cdots \quad \text{(exchange)}$$



$$(i_\sigma i_\sigma | i_\sigma i_\sigma) - (i_\sigma i_\sigma | i_\sigma i_\sigma)$$



② DFT (ground state)

$$E_{DFT} = \sum_i^{occ,\alpha,\beta}\sum_\sigma H^{core}_{ii\sigma} + \frac{1}{2}\sum_{i,j}^{occ,\alpha,\beta}\sum_{\sigma,\tau}(i_\sigma i_\sigma | j_\tau j_\tau) + E_{xc}[\rho] \;\rightarrow\; \text{e.g. } \int \underbrace{c\rho^{4/3}}_{f[\rho]}\, d1$$

$$= \sum_{p,q}^{all\,\alpha,\beta}\sum_\sigma P^*_{pq\sigma} H^{core}_{pq\sigma} + \frac{1}{2}\sum_{p,q,r,s}^{all}\sum_{\sigma,\tau} P^*_{pq\sigma} P_{rs\tau}\,(p_\sigma q_\sigma | s_\tau r_\tau) + E_{xc}[\rho]$$

$$\rho = \sum_{p,q}\sum_\sigma P^*_{pq\sigma}\,\varphi^*_{p\sigma}\varphi_{q\sigma}$$

Kohn-Sham Hamiltonian

$$H^{KS}_{pq\sigma} = \frac{\partial E_{DFT}}{\partial P^*_{pq\sigma}} = H^{core}_{pq\sigma} + \sum_{r,s}\sum_\tau P_{rs\tau}\,(p_\sigma q_\sigma | s_\tau r_\tau) + \underbrace{\int \frac{\partial \rho}{\partial P^*_{pq\sigma}} \overbrace{\left(\frac{\delta f}{\delta \rho}\right)}^{V_{xc}} d1}_{\int \varphi^*_{p\sigma}(1)\, V_{xc}[\rho](1)\, \varphi_{q\sigma}(1)\, d1}$$

(2.5) Density matrix formalism revisited

Usual Fock eq.

$$\sum_q F_{pq\sigma} C_{qi\sigma} = \epsilon_{i\sigma} C_{pi\sigma}$$

or

$$\sum_q F^*_{pq\sigma} C^\dagger_{qi\sigma} = \epsilon^*_{i\sigma} C^*_{pi\sigma}$$

$$\sum_i \sum_q F_{pq\sigma} \underbrace{C_{qi\sigma} C^*_{ri\sigma}}_{P_{qr\sigma}} = \sum_i \epsilon_{i\sigma} \underbrace{C_{pi\sigma} C^*_{ri\sigma}}_{P_{pr\sigma}}$$

eq. $\updownarrow$

$$\sum_i \sum_q \underbrace{F^*_{pq\sigma}}_{F_{qp\sigma}} \underbrace{C^*_{qi\sigma} C_{ri\sigma}}_{P_{rq\sigma}} = \sum_i \epsilon^*_{i\sigma} \underbrace{C^*_{pi\sigma} C_{ri\sigma}}_{P_{rp\sigma}}$$

equal (swap 'p' and 'r' in the second eq)

$$\mathbb{F}\mathbb{P} = \mathbb{P}\mathbb{F}$$

$$\left[\begin{array}{c|c} \epsilon_i & 0 \\ \hline 0 & \epsilon_a \end{array}\right] \left[\begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array}\right] = \left[\begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array}\right] \left[\begin{array}{c|c} \epsilon_i & 0 \\ \hline 0 & \epsilon_a \end{array}\right]$$

Time-dependent case

$C_{pi\sigma}(0)e^{-i\epsilon_{i\sigma}t}$ $\quad$ $C^*_{ri\sigma}(0)e^{i\epsilon_{i\sigma}t}$

$$\sum_q \{F_{pq\sigma}P_{qr\sigma} - P_{pq\sigma}F_{qr\sigma}\} = \sum_i \Big\{ \underbrace{(\epsilon_{i\sigma} C_{pi\sigma})}_{i\frac{\partial C_{pi\sigma}}{\partial t}} C^*_{ri\sigma} - C_{pi\sigma} \underbrace{(\epsilon^*_{i\sigma} C^*_{ri\sigma})}_{i\frac{\partial C^*_{ri\sigma}}{\partial t}} \Big\}$$

$$= \underbrace{\left(i\frac{\partial}{\partial t}\right)}_{\text{energy op.}} P_{pr\sigma}$$

$$\mathbb{F}\mathbb{P} - \mathbb{P}\mathbb{F} = i\frac{\partial \mathbb{P}}{\partial t}$$