$$E(\lambda) = \langle \Psi(\lambda) | \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 | \Psi(\lambda) \rangle$$

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial \Psi}{\partial \lambda} \right| \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 | \Psi(\lambda) \rangle +$$

$$\langle \Psi | \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 \left| \frac{\partial \Psi}{\partial \lambda} \right\rangle + \langle \Psi | P_1 + 2\lambda P_2 | \Psi \rangle$$

$$\left.\frac{\partial E}{\partial \lambda}\right|_{\lambda=0} = 2 \left\langle \frac{\partial \Psi}{\partial \lambda} \right| \hat{H}_0 | \Psi_0 \rangle + \langle \Psi_0 | P_1 | \Psi_0 \rangle$$

$$\frac{\partial \Psi}{\partial \lambda} = \frac{\partial \Psi}{\partial C} \frac{\partial C}{\partial \lambda} + \cancel{\frac{\partial \Psi}{\partial \chi} \frac{\partial \chi}{\partial \lambda}}$$

→ basis f-ns

↑ orbital coefs

$$\frac{\partial E}{\partial C} = \frac{\partial}{\partial C} \langle \Psi | \hat{H}_0 + \lambda \hat{P}_1 + \lambda^2 \hat{P}_2 | \Psi \rangle =$$

$$= 2 \left\langle \frac{\partial \Psi}{\partial C} \right| \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 | \Psi \rangle$$

$$\left.\frac{\partial E}{\partial C}\right|_{\lambda=0} = 2 \left\langle \frac{\partial \Psi}{\partial C} \right| \hat{H}_0 | \Psi_0 \rangle = 0$$

Br. theorem

true for variationally optimized wavefunctions: HF, DFT, MCSCF

not for MP, CC, ...

$$\frac{\partial}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} \right| H_0 + \lambda P_1 + \lambda^2 P_2 | \Psi \rangle =$$

$$= \left(\frac{\partial c}{\partial \lambda}\right) \left\langle \frac{\partial^2 \psi}{\partial c^2} \right| H_0 + \lambda P_1 + \lambda^2 P_2 \left| \psi \right\rangle +$$

$$+ \left(\frac{\partial c}{\partial \lambda}\right) \left\langle \frac{\partial \psi}{\partial c} \right| H_0 + \lambda P_1 + \lambda^2 P_2 \left| \frac{\partial \psi}{\partial c} \right\rangle +$$

$$+ \left\langle \frac{\partial \psi}{\partial c} \right| P_1 + 2\lambda P_2 \left| \psi \right\rangle$$

$$\frac{\partial}{\partial \lambda} \left\langle \frac{\partial \psi}{\partial c} \right| H_0 + \lambda P_1 + \lambda^2 P_2 \left| \psi \right\rangle \Big|_{\lambda=0} =$$

$$= \left(\frac{\partial c}{\partial \lambda}\right) \left\langle \frac{\partial^2 \psi}{\partial c^2} \right| H_0 \left| \psi \right\rangle + \left(\frac{\partial c}{\partial \lambda}\right) \left\langle \frac{\partial \psi}{\partial c} \right| H_0 \left| \frac{\partial \psi}{\partial c} \right\rangle$$

$$+ \left\langle \frac{\partial \psi}{\partial c} \right| P_1 \left| \psi_0 \right\rangle = 0$$

$$\left[\left\langle \frac{\partial^2 \psi}{\partial c^2} \right| \hat{H}_0 \left| \psi_0 \right\rangle + \left\langle \frac{\partial \psi}{\partial c} \right| \hat{H}_0 \left| \frac{\partial \psi}{\partial c} \right\rangle \right] \left(\frac{\partial c}{\partial \lambda}\right) =$$

$$= - \left\langle \frac{\partial \psi}{\partial c} \right| P_1 \left| \psi_0 \right\rangle$$

$$\sim \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle - \delta_i \delta_j E_0$$

$$\sim \langle \Phi_i^a | \hat{H}_0 | \Phi_j^b \rangle$$

$$\sim \langle \Phi_i^a | P_1 | \Phi_0 \rangle$$

property gradient

both excitations & deexcitations are included

both real & imaginary variations

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} = - \begin{bmatrix} P \\ P^* \end{bmatrix}$$

Y, Z – vector representing real & im. parts of first-order response

$$A_{ij}^{ab} = \langle \Phi_i^a | H_0 | \Phi_j^b \rangle - E_0 \delta_{ij} \delta_{jb} =$$

$$= \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + \langle ij | ab \rangle - \langle ia | jb \rangle$$

$$B_{ij}^{ab} = \langle \Phi_0 | H_0 | \Phi_{ij}^{ab} \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$$

$$P_i^a = \langle i | P | a \rangle$$

exchange integrals

$$\left(\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} - \omega \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right) \begin{bmatrix} Y \\ Z \end{bmatrix} = - \begin{bmatrix} P \\ P^* \end{bmatrix}$$

for dynamic properties

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} Y \\ Z \end{bmatrix}$$

generalized eigenvalue problem

$\pm \omega \rightarrow$ excitation & deexcitation energies

TDHF equations

if $B=0$ Tamm-Dancoff appr.
TDA

then TDHF $\rightarrow$ CIS

B: correction term allowing de-excitations, provides correlation for the reference state.

also can be obtained using Random Phase Approximation in Response theory (RPA)

full RPA .. eqn with exchange integrals — TDHF

direct RPA (or simply RPA) – exchange integrals are neglected)

TDDFT

$$A_{ij}^{ab} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + \langle ij|ab\rangle + \langle ij|f_{xc}|ab\rangle$$

$$B_{ij}^{ab} = \langle ij|ab\rangle + \langle ij|f_{xc}|ab\rangle$$

f_{xc} XC kernal

$$f_{xc}(r,t,r',t') = \frac{\delta V_{xc}[\rho](r,t)}{\delta \rho(r',t')}$$

adiabatic approximation:

$$f_{xc}^{adiab}(r,r') = \frac{\delta V[\rho](r)}{\delta \rho(r')} = \frac{\delta^2 E_{xc}[\rho]}{\delta \rho(r)\, \delta \rho(r')}$$

TDA (neglect of B) – good approximation

TDDFT is significant improvement over TDHF due to better orbital energy differences in matrix A

Cost: A and B : occ x vir

in TDA cost ~ CIS (N^5)

in full TDDFT is several times higher

HF model

$$\hat{f}_i \chi_i(x) = \varepsilon_i \chi_i(x)$$

$$\hat{f}_i = \hat{h}_i + \sum_{j=1}^{N_{elec}} \left(\hat{J}_i(j) - \hat{K}_i(j) \right)$$

for occupied orbital k:

$$\hat{f}_k = \hat{h}_k + \sum_{j=1}^{N} \left(\hat{J}_j(k) - \hat{K}_j(k)\right) =$$

$$\left(\hat{J}_k(k) - \hat{K}_k(k) = 0\right)$$

$$= \hat{f}_k + \hat{h}_k + \sum_{j \neq k}^{N} \left(\hat{J}_j(k) - \hat{K}_j(k)\right)$$

electron on occ. k expierience field from $(N-1)$ electrons

for virtual orbital a:

$$\hat{f}_a = \hat{h}_a + \sum_{j=1}^{N_{elec}} \left(\hat{J}_j(a) + \hat{K}_j(a)\right)$$

electron on vir. a sees field from N electrons

ε_a corresponds to electron attachment to orb. a

$$(\varepsilon_a - \varepsilon_i) \neq \omega_{ia}$$

KS model:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \hat{v}_{eff}(r)\right)\chi_i(r) = \varepsilon_i\,\chi_i(r)$$

$$\hat{v}_{eff}(r) = \hat{v}_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}\,dr' + v_{xc}(r)$$

$$v_{xc} = \frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$$

Same field is felt by electron placed on occ. orb. or vir. orb. – field of $(N-1)$

ε_a corresponds to exc. energy

$$(\varepsilon_a - \varepsilon_i) \approx \omega_{ia}$$

true for non-hybrid functionals