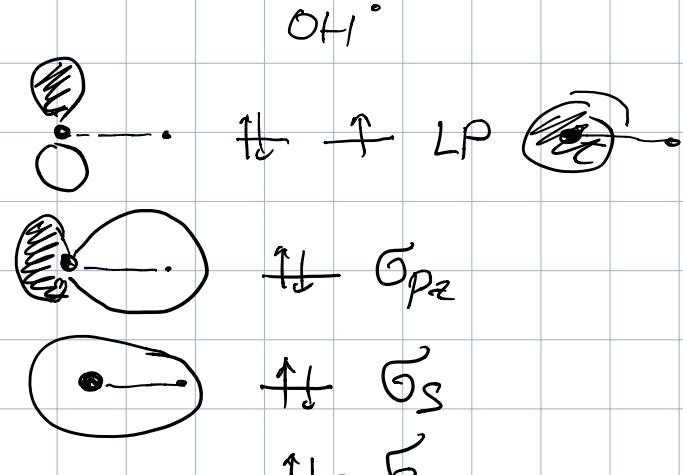


$\text{EOM-SF}$  : diradicals       $\pi \rightarrow \pi \uparrow\uparrow$   
 $\text{O}_2, \text{CH}_2, \dots$   
bond-breaking  


---

 $\text{EOM-IP}$       we start with  $N+1$  electrons

$\text{OH}^\bullet$  in water



doublet HF

calcs:

$\text{LP} \quad \frac{1}{2} \quad ?$   
 $\text{LP} \quad \frac{1}{2} \quad ?$   
 $\frac{1}{2}$   
 $\frac{1}{2}$   
 $\frac{1}{2}$

$\pi^*$  core

$N+1$  system (EOM-TP): reference

LP ↑↑ ↑↑ LP

↑↑  $\sigma_{p_z}$

↑↑  
⋮

↑↑

ground state of  
 $\text{OH}^-$ :  $2\pi$

$\text{OH}^-$   
LP ↑↑ ↑↑  
ground state  
of  $\text{OH}^-$   
LP ↑↑  
⋮  
↑↑

$\text{CT}$   $\text{H}_2\text{O}$  describes  $\text{CT}$

LP  
 $6_{p_y}$   
 $6_{p_z}$   
 $6_s$   
core

EOM-EA

$N-1$  system

benzene -  $\text{Li}^+$

benzene

$\text{CT}$

$\text{Li}^+$

$\pi^*$  — —

$\pi$  ↑↑ ↑↑

↑ 2s

↑↑ 1s

$\pi^*$  — —  
 $\pi$  ↑↑ ↑↑

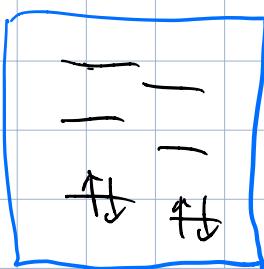
charge transfer state

$\text{N-1}$   
reference

EOM-CCSD robust  
give qualitatively correct picture  
of electronic states

$N^6$  scaling 500 b.f. - limit

MCSCF for excited states  
— frozen virtual orbs.



active space

all possible excitations allowed

frozen occupied orbs

- 1) Solve MCSCF eqns for the ground state. Ex. states - higher roots  
Problem: ground state is described much better than the excited states.  
Transition errors - high errors.

- 2) Optimize orbitals & coeffs. for the excited state

$$\psi^* = \sum_{L^*} C_{L^*} \phi_{L^*}$$

- variational collapse to lower state
- not possible to obtain transition properties (TDM, spin-orbit coupling)
- hard to achieve balance description for different exc. states

### 3) State-averaged procedure

$$\Psi = \sum_L C_L \Phi_L$$

$$\Psi^* = \sum_{L^*} C_{L^*} \Phi_{L^*}$$

use the same set of orbitals for both states

Minimize average energy of both states:

$$E = n_0 E_0 + n^* E^* = n \langle \Psi | \hat{H} | \Psi \rangle$$

weights' +  $n^* \langle \Psi^* | \hat{H} | \Psi^* \rangle$

- weights are arbitrary and affect the results
- both states are described poorly (orbitals do not fit any of the states)

but transition properties can be obtained

- different results for different # of included states

Improvements when PT is added

or CI from active space

MRPT /cc-pVTZ  $\sim$  1 kcal/mol for excited state

### TD-DFT methods

$$i\frac{\partial}{\partial t} \hat{\Psi}(r,t) = \hat{H}\hat{\Psi}(r,t)$$

$$\hat{H}(r,t) = \hat{H}_0(r) + \hat{V}_{\text{ext}}(r,t)$$

time-dependent  
external  
electric potential

Runge-Gross theorem (1984)

analogue of H.-K. for time-dependent density & potential

time-independent SE: energy is conserved  
(Var. principles)

time-dependent SE: action is conserved

$$S[\Psi] = \int_{t_0}^t \langle \Psi | (i\frac{\partial}{\partial t}, -\hat{H}) | \Psi \rangle dt'$$

$t_0$  - initial time to turn-on perturbation

$\nabla S = 0$  is not used

weak perturbation limit

For DFT:

$$i\frac{\partial}{\partial t} \phi_i(r,t) = (\hat{F} + \hat{V}_{\text{ext}}(t)) \phi_i(r,t)$$

$$\hat{F} + \hat{V}_{\text{ext}}(t) = \hat{T}(t) + \hat{V}_{\text{ne}}(t) + \hat{J}(t) + \hat{k}(t) +$$

$$\hat{K}(r,t)\phi_i(r,t) = \left( \sum_{j=1}^N \int \frac{\hat{V}_{ext}(t)}{|r-r'|} \phi_j(r',t) dr' \right) \phi_j(r,t)$$

Similar to TI case

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad \text{for TI case}$$

$$V_{xc}(r,t) = \frac{\delta S_{xc}[\rho]}{\delta \rho(r,t)} \quad \begin{matrix} \text{depends on} \\ \text{density starting} \\ \text{from time } t \end{matrix}$$

$\Rightarrow$  Solution to TD KS eqns should have memory and solved self-consistently in time domain as well.

Effectively, in TDDFT time-memory

$$\text{is ignored, } V_{xc}(r,t) \approx V_{xc}(r)$$

$\Rightarrow$  adiabatic appr.  $\Leftrightarrow$

density is slow varying in time

We use weak perturbation limit:

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

$$\text{e.g. } \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0} = \langle \psi_0 | P_1 | \psi_0 \rangle + 2 \left( \frac{\partial \psi}{\partial \lambda} | H_0 | \psi_0 \right)$$