CHM 673
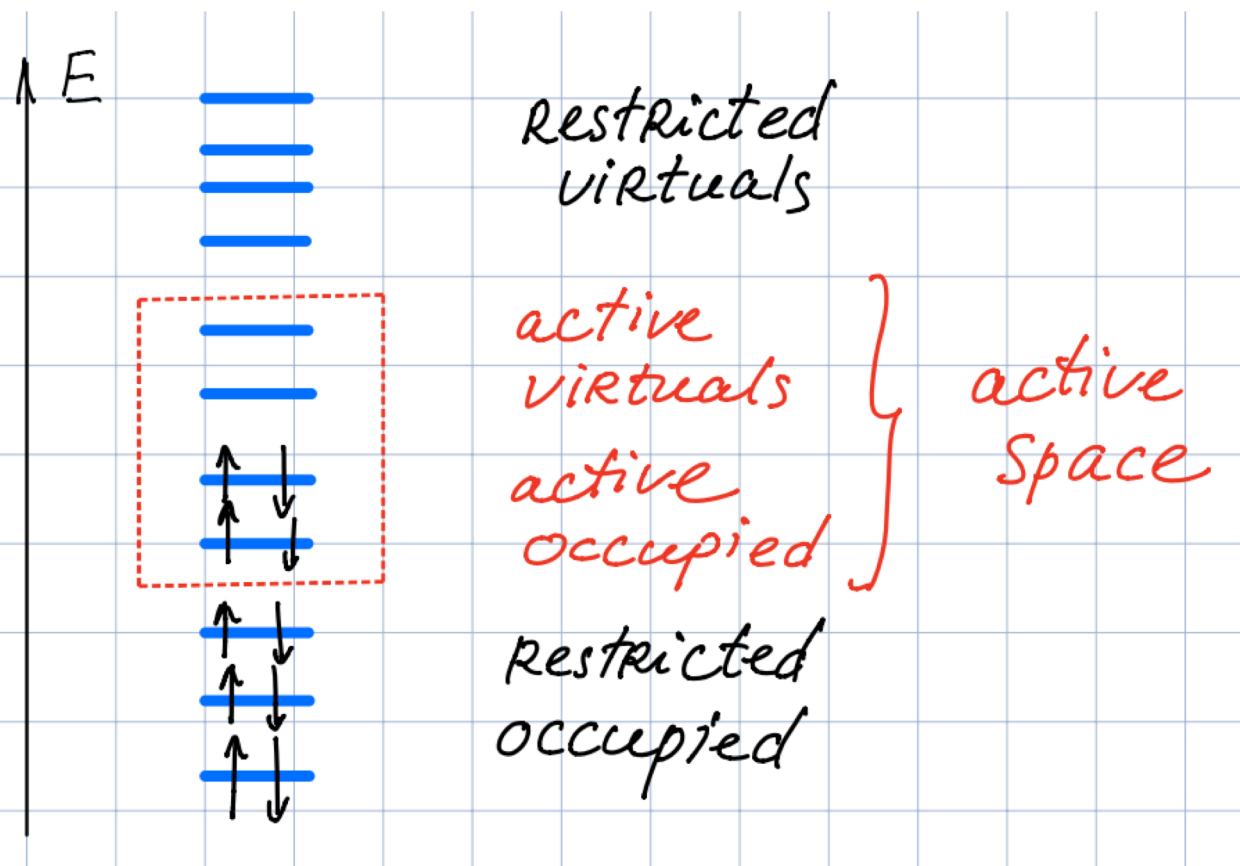## Lecture 21: Electronic excited states, part 3

Suggested reading:

Chapter 4.14, 6.9, 11.3, 11.6, 11.10 from Jensen

MCSCF for electronic excited states

Solution: both orbitals and CI coefficients are optimized variationally at the same time to give the lowest energy for the wave function

$$\Psi = \sum_i c_i \Phi_i$$

How to describe electronic excited states with MCSCF?

1. Solve MCSCF equations for the ground state

(i.e., optimize molecular orbitals and expansion coefficients to minimize the energy of the ground state). Excited states are found as higher CI roots.

Cons:

-orbitals are optimized for the ground state → the ground state is described much better than excited states → errors in transition energies

How to describe electronic excited states with MCSCF?

2. Optimize orbitals and coefficients for a particular electronic state:

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

Cons:
- Variational collapse to lower state
- Different set of orbitals for different states → no way to calculate transition properties such as transition dipole moments, non-adiabatic and spin-orbit couplings
- Arbitrariness in configuration selection: excited states often involve mixing with non-valence (Rydberg) states. Balanced description – impossible

How to describe electronic excited states with MCSCF?

3. State-averaged procedure

Use same set of orbitals for all considered states (e.g., the ground and one excited state)

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

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

Minimize average energy of both states:

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

Pros: No problems with non-orthogonal orbitals

Cons:
- both states are described equally poorly
- weights are arbitrary and affect the results
- different results for different number of included states

Beyond MCSCF

Similar to the ground state, for accurate results, dynamical correlation should be included :

- Perturbation theory – MRPT, CASPT2 etc
- Configuration interaction – MRCI, CASCI, etc

MRPT/cc-pVTZ → accuracy of ~1 kcal/mol for excited states

Time-dependent SE

Start from time-dependent SE (TI SE) with time-dependent external electric potential:

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

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

Time-independent SE: energy is conserved (variational principle)

Time-dependent SE: action S is conserved

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

For example, time-dependent Hartree-Fock equations are:

$$i\frac{\partial}{\partial t}\phi_i(r,t) = \left(\hat{T}(r,t) + \hat{V}_{eN}(r,t) + \hat{J}(r,t) + \hat{K}(r,t) + \hat{V}_{ext}(r,t)\right)\phi_i(r,t)$$

Time-dependent DFT

Runge-Gross theorem (1984) is an analogue of the Hohenberg-Kohn theorem for the time-dependent density and external potential

Then, time-dependent DFT equations are:

$$i\frac{\partial}{\partial t}\phi_i(r,t) = \left(\hat{T}(r,t) + \hat{V}_{eN}(r,t) + \hat{J}(r,t) + \hat{V}_{xc}(r,t,\Psi_0) + \hat{V}_{ext}(r,t)\right)\phi_i(r,t)$$

$$\hat{J}(r,t) = \int \frac{\rho(r',t)}{|r-r'|}dr' \qquad \text{Time-dependent Coulomb operator}$$

$$\hat{V}_{xc}(r,t,\rho_0) = \frac{\delta S_{xc}[\rho(r,t)]}{\delta\rho(r,t)} \qquad \text{time-dependent exchange-correlation potential}$$

V_{xc} depends on density starting from initial time t_0!

→ Solution to TDKS equations should have memory and solved self-consistently also in time domain

Time-dependent DFT

$$\hat{V}_{xc}(r, t, \rho_0) = \frac{\delta S_{xc}[\rho(r,t)]}{\delta \rho(r,t)}$$

time-dependent exchange-correlation potential

V_{xc} depends on density starting from initial time t_0!

Practically, in TDDFT time-memory is ignored

This is adiabatic approximation, i.e. we assume that the density is slowly varying in time

Derivative techniques in a weak perturbation limit

How to obtain working TDDFT equations?

Let's use derivative techniques:

- Write energy of a system in a presence of perturbation
- Compute n-order analytic derivatives to compute n-order property
- Let perturbation be 0

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

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

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

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

Derivative techniques in a weak perturbation limit

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

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

← Basis functions

Let's assume this term is 0

↑
orbital coefficients

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

0 for variationally optimized wave functions

Derivative techniques in a weak perturbation limit

Let's consider the following derivative:

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

$$\left. \frac{\partial E}{\partial C} \right|_{\lambda=0} = 2 \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 | \Psi \right\rangle = 0 \qquad \textcolor{red}{\text{True for variationally optimized wave functions}}$$

$$\left. \frac{\partial}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 | \Psi \right\rangle \right|_{\lambda=0}$$

$$= \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial^2 \Psi}{\partial C^2} | \hat{H}_0 | \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial C} | \hat{P}_1 | \Psi \right\rangle + \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 | \frac{\partial \Psi}{\partial C} \right\rangle = 0$$

Wave function response

$$\frac{\partial}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 \middle| \Psi \right\rangle \Bigg|_{\lambda=0}$$

$$= \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial^2 \Psi}{\partial C^2} \middle| \hat{H}_0 \middle| \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{P}_1 \middle| \Psi \right\rangle + \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{H}_0 \middle| \frac{\partial \Psi}{\partial C} \right\rangle = 0$$

$$\rightarrow \quad \left[\left\langle \frac{\partial^2 \Psi}{\partial C^2} \middle| \hat{H}_0 \middle| \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{H}_0 \middle| \frac{\partial \Psi}{\partial C} \right\rangle \right] \left(\frac{\partial C}{\partial \lambda} \right) = - \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{P}_1 \middle| \Psi \right\rangle$$

Second derivatives of the energy with respect tot the wave function parameters

Change (response) of wave function to perturbation

Property gradient

Wave function response

$$\left[\left\langle \frac{\partial^2 \Psi}{\partial C^2} \middle| \hat{H}_0 \middle| \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{H}_0 \middle| \frac{\partial \Psi}{\partial C} \right\rangle \right] \left(\frac{\partial C}{\partial \lambda} \right) = - \left\langle \frac{\partial \Psi}{\partial C} \middle| \hat{P}_1 \middle| \Psi \right\rangle$$

For a single Slater determinant wave function:

$$\left\langle \frac{\partial^2 \Phi}{\partial \chi_i^a \partial \chi_j^b} \middle| \hat{H}_0 \middle| \Psi \right\rangle \propto \left\langle \Phi_{ij}^{ab} \middle| \hat{H}_0 \middle| \Psi \right\rangle - \delta_{ij} \delta_{ab} E_0 \qquad \left\langle \frac{\partial \Phi}{\partial \chi_i^a} \middle| \hat{P}_1 \middle| \Phi \right\rangle \propto \left\langle \Phi_i^a \middle| \hat{P}_1 \middle| \Phi \right\rangle$$

$$\left\langle \frac{\partial \Phi}{\partial \chi_i^a} \middle| \hat{H}_0 \middle| \frac{\partial \Phi}{\partial \chi_j^b} \right\rangle \propto \left\langle \Phi_i^a \middle| \hat{H}_0 \middle| \Phi_j^b \right\rangle$$

- Both excitations and deexcitations are included
- Both real and imaginary variations are allowed