

CHM 673

Lecture 25: Time-dependent DFT

Suggested reading:

Chapter 6.9, 11.3, 11.6, 11.10 from Jensen

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-independent 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:

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

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

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

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

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

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

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

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

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

Derivative techniques in a weak perturbation limit

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

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

↑
orbital coefficients

← Basis functions

← Let's assume this term is 0

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

0 for variationally optimized wave functions

Derivative techniques in a weak perturbation limit

Let's consider the following derivative:

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

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

$$\begin{aligned} & \left. \frac{\partial}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 | \Psi \right\rangle \right|_{\lambda=0} \\ &= \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial^2 \Psi}{\partial C^2} | \hat{H}_0 | \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial C} | \hat{P}_1 | \Psi \right\rangle + \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 | \frac{\partial \Psi}{\partial C} \right\rangle = 0 \end{aligned}$$

Wave function response

$$\frac{\partial}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 + \lambda P_1 + \lambda^2 P_2 | \Psi \right\rangle \bigg|_{\lambda=0}$$
$$= \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial^2 \Psi}{\partial C^2} | \hat{H}_0 | \Psi \right\rangle + \left\langle \frac{\partial \Psi}{\partial C} | \hat{P}_1 | \Psi \right\rangle + \frac{\partial C}{\partial \lambda} \left\langle \frac{\partial \Psi}{\partial C} | \hat{H}_0 | \frac{\partial \Psi}{\partial C} \right\rangle = 0$$

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

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

Change (response) of wave function to perturbation

Property of gradient

Wave function response

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

For a single Slater determinant wave function:

$$\left\langle \frac{\partial^2 \Phi}{\partial \chi_i^a \partial \chi_j^b} | \hat{H}_0 | \Psi \right\rangle \propto \langle \Phi_{ij}^{ab} | \hat{H}_0 | \Psi \rangle$$

$$\left\langle \frac{\partial \Phi}{\partial \chi_i^a} | \hat{H}_0 | \frac{\partial \Phi}{\partial \chi_j^b} \right\rangle \propto \langle \Phi_i^a | \hat{H}_0 | \Phi_j^b \rangle - \delta_{ij} \delta_{ab} E_0$$

$$\frac{\partial C}{\partial \lambda} \propto Y + Z^* \quad \text{real and imaginary variations are allowed!}$$

$$\left\langle \frac{\partial \Phi}{\partial \chi_i^a} | \hat{P}_1 | \Phi \right\rangle \propto \langle \Phi_i^a | \hat{P}_1 | \Phi \rangle$$

both excitations and de-excitations are included

Wave function response

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

 vector representing real & imaginary parts of the first-order response

$$A_{ij}^{ab} = \langle \Phi_i^a | \hat{H}_0 | \Phi_j^b \rangle - E_0 \delta_{ij} \delta_{ab} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + \langle ij | ab \rangle - \langle ia | jb \rangle$$

$$B_{ij}^{ab} = \langle \Phi_0 | \hat{H}_0 | \Phi_{ij}^{ab} \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$$

$$P_i^a = \langle \Phi_0 | \hat{P}_1 | \Phi_i^a \rangle = \langle i | \hat{P}_1 | a \rangle$$

Dynamic (time-dependent) properties

For dynamic (time-dependent) properties $\frac{\partial C}{\partial \lambda} \propto Y \exp(-i\omega t) + Z^* \exp(i\omega t)$

Then the same strategy leads to the following equation:

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

ω is the frequency of the perturbing field

Generalized eigen-value problem (by setting P to 0):

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

+/- ω are excitation and de-excitation energies


Time-dependent Hartree-Fock (TDHF)

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

$$A_{ij}^{ab} = \langle \Phi_i^a | \hat{H}_0 | \Phi_j^b \rangle - E_0 \delta_{ij} \delta_{ab} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + \langle ij | ab \rangle - \langle ia | jb \rangle$$

$$B_{ij}^{ab} = \langle \Phi_0 | \hat{H}_0 | \Phi_{ij}^{ab} \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$$

Exchange integrals



B matrix allows de-excitations; provides correlation for the reference state

If $B = 0 \rightarrow$ Tamm-Dancoff approximation (TDA)

TDHF with TDA is analogous to CIS

The same set of equations can be produced using Random Phase Approximation (RPA) in response theory

Full-RPA or RPAX = TDHF

Direct RPA or RPA \rightarrow exchange integrals are neglected

Time-dependent DFT (TDDFT)

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

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

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

 XC kernel

Exchange-correlation kernel:
$$f_{xc}(r, t, r', t') = \frac{\delta V_{xc}[\rho](r, t)}{\delta \rho(r', t')} = \frac{\delta^2 S_{xc}[\rho]}{\delta \rho(r, t) \delta \rho(r', t')}$$

In adiabatic approximation:
$$f_{xc}^{adiab}(r, r') = \frac{\delta V_{xc}[\rho](r)}{\delta \rho(r')} = \frac{\delta^2 E_{xc}[\rho]}{\delta \rho(r) \delta \rho(r')}$$

TDDFT RPA \rightarrow f_{xc} is neglected

TDDFT TDA \rightarrow B matrix is neglected : often a good approximation

TDDFT vs TDHF/CIS

TDDFT is a significant improvement over TDHF/CIS for valence states due to a better description of orbital energies in A matrix

TDHF:

$$A_{ij}^{ab} = \langle \Phi_i^a | \hat{H}_0 | \Phi_j^b \rangle - E_0 \delta_{ij} \delta_{ab} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + \langle ij | ab \rangle - \langle ia | jb \rangle$$

TDDFT:

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

TDDFT vs TDHF/CIS

CIS

TDDFT

accuracy:

~1 eV error

0.1 - ? eV (functional dependent)

computational scaling:

N^5

N^5

(bigger pre-factor)

single excitations only

Potential trouble with charge-transfer states & Rydberg states →

use long-range corrected & hybrid functionals

different multiplets:

high-spin states too low in energy

high-spin states too high in energy →
use long-range corrected & hybrid functionals