

- 1 Introduction
- 2 Configuration interaction single
- 3 Time-dependent Hartree-Fock
- 4 Time-dependent density-functional theory
- 5 Multiconfigurational self-consistent field methods
- 6 Green's function methods

Time-dependent density-functional theory (TDDFT)

The Runge-Gross theorem

The **Runge-Gross theorem** can be seen as the time-dependent analogue of the first **Hohenberg-Kohn theorem** and constitutes the cornerstone of the formal foundation of the **time-dependent Kohn-Sham (KS) formalism**

TDDFT equations

$$\mathbf{F}_{\text{KS}}(\mathbf{r}, \textcolor{red}{t}) |\Psi_{\text{KS}}(\mathbf{r}, \textcolor{red}{t})\rangle = i \frac{\partial}{\partial \textcolor{red}{t}} |\Psi_{\text{KS}}(\mathbf{r}, \textcolor{red}{t})\rangle$$

How to solve the TDDFT equations?

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$\mathbf{A}_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ia|jb) + (ia|f_{\text{xc}}|jb)$$

$$\mathbf{B}_{ia,jb} = (ia|bj) + (ia|f_{\text{xc}}|bj)$$

TDDFT equations

$$(ia|f_{xc}|jb) = \iint \phi_i(\mathbf{r}_1) \phi_a(\mathbf{r}_1) \frac{\delta^2 E_{xc}}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \phi_j(\mathbf{r}_2) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Tamm-Danoff approximation

- ① In the Tamm-Danoff approximation (TDA), we set $\mathbf{B} = \mathbf{0}$:
 $\Rightarrow \mathbf{TDA/TDDFT}$
- ② It's a very good approximation & it makes the problem Hermitian

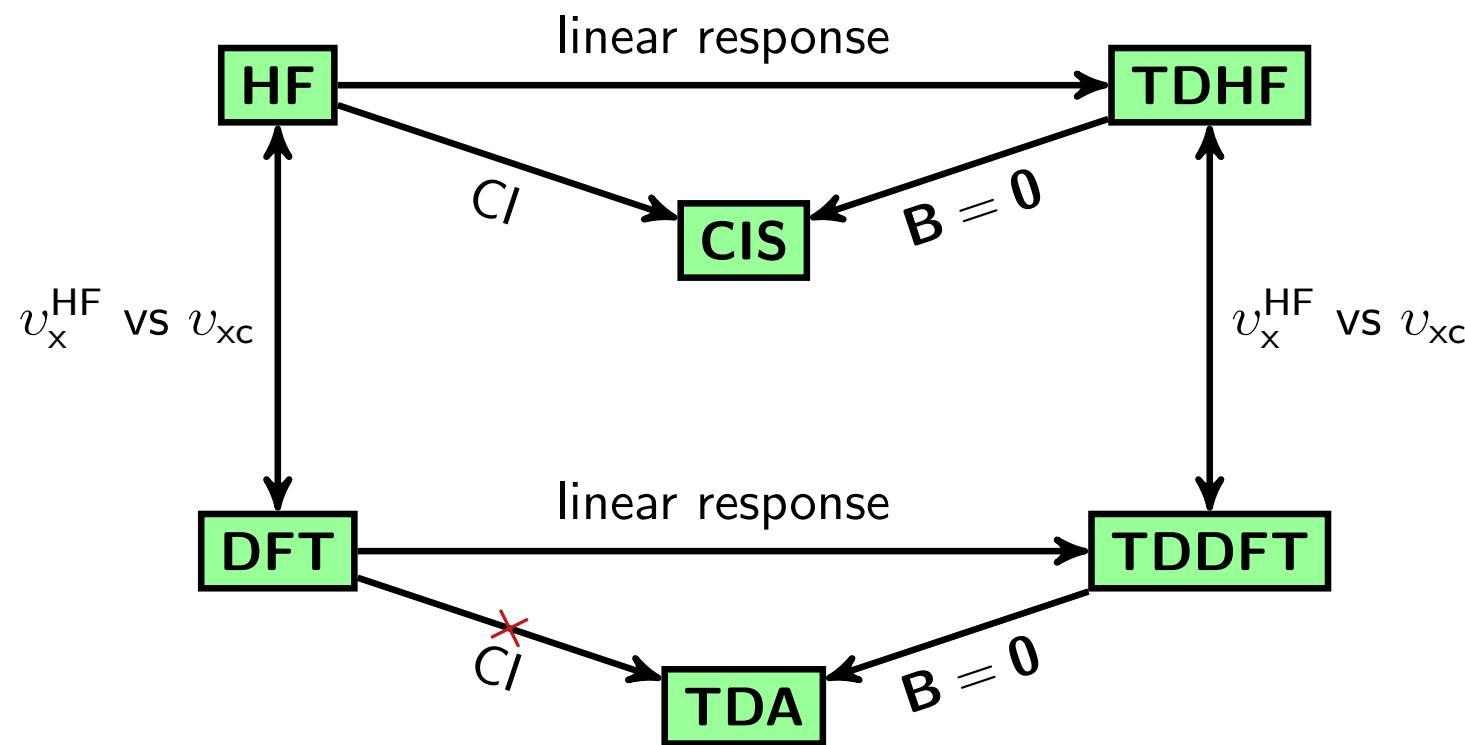
Hybrid functionals

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + (ia|jb) - c_{HF}(ij|ab) + (1 - c_{HF})(ia|f_{xc}|jb)$$

$$B_{ia,jb} = (ia|bj) - c_{HF}(ib|aj) + (1 - c_{HF})(ia|f_{xc}|bj)$$

where c_{HF} is the fraction of HF exchange in the hybrid functional

Relationship between CIS, TDHF, DFT and TDDFT



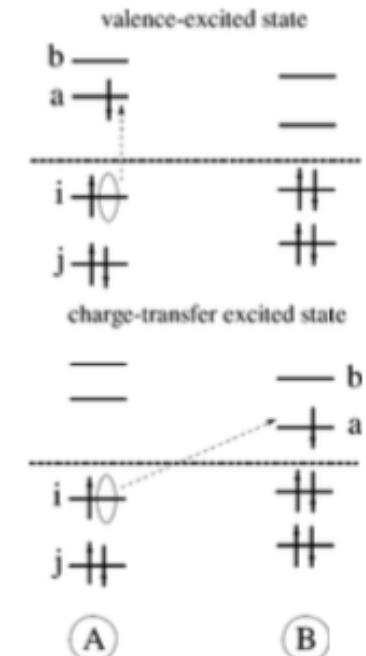
Comments on TDDFT

Properties

- Although **standard functionals** are developed for ground states, they are also employed in TDDFT
- Results are **very sensitive** to the choice of the xc functional
- TDDFT is accurate for **valence-excited states** (error of 0.1-0.5 eV)
⇒ It can be as good as EOM-CCSD or CASPT2
- TDDFT has **troubles** with
 - 1 Rydberg states
 - 2 Valence states of molecules exhibiting extended π -systems
 - 3 Doubly excited states
 - 4 Charge-transfer (CT) excited states
 - 5 Core-excited states

Failures of TDDFT

- **Rydberg states and extended π -systems:** wrong long-range behaviour of standard xc functionals (faster than $1/r$)
- **Doubly-excited states:** cannot be treated within linear response theory (only contains singly excited states)
- **CT excited states:** excitation energies are drastically underestimated due to wrong asymptotic behaviour of xc functionals. It can be fixed using range-separated functionals (CAM-B3LYP, etc).
- In these cases, we can have errors of several eV and incorrect curvature of PES



Examples for TDDFT: model complex for heme

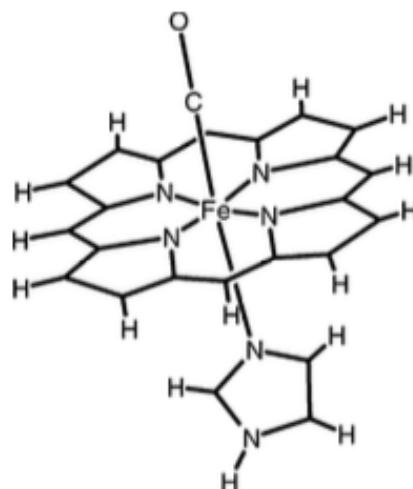


Figure 5. Model complex used for the theoretical investigation of CO-ligated heme.

Table 1. Calculated Geometrical Parameters (Å) of the CO-Ligated Heme Model Complex in Comparison with Experimentally Determined Values for the Complete System

	BLYP	B3LYP	expt
Fe–CO	1.81	1.80	1.73–1.93
Fe–N _P	2.01	2.03	1.98–2.06
Fe–N _{Im}	1.98	2.04	2.06–2.20
C–O	1.21	1.16	1.07–1.12

Table 2. Excitation Energies (eV) of the Q and B States of the Model Complex Compared with the Experimentally Observed Values

	SVWN		BLYP		B3LYP		expt
	LANL2DZ	6-31G*	LANL2DZ	6-31G*	LANL2DZ	6-31G*	
Q _y	1.515	1.396	1.833	1.573	2.404	2.403	2.18
Q _x	1.537	1.418	1.843	1.593	2.418	2.413	2.30
B _x	3.009	2.909	3.049	2.927	3.347	3.314	2.96
B _y	3.020	2.927	3.056	2.943	3.359	3.325	3.16

Drew & Head-Gordon, Chem Rev 105 (2005) 4009

Zincbacteriochlorin-Bacteriochlorin Complexes

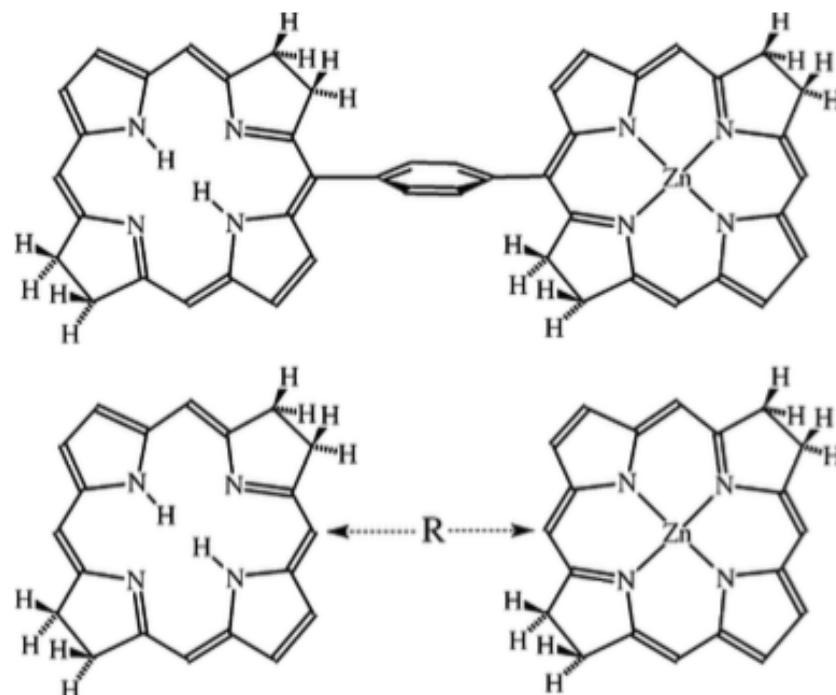


Figure 8. Molecular structure of the (1,4)-phenylene-linked zincbacteriochlorin–bacteriochlorin complex, as well as of the model complex used in some calculations. The distance coordinate R is here defined as the distance between the formerly linked carbon atoms.

Table 3. Comparison of the Energies of the Ten Lowest Singlet Excited States of the Full Phenylene-Linked ZnBC–BC Complex as Well as of the Model Complex without the Phenylene Bridge with the Individually Calculated and Experimentally Determined Excitation Energies of the Q States of the Monomers^a

state	ZnBC–BC complex			monomers	
	full	model	transition	calcd	expt
1	1.33 (0.000)	1.32 (0.000)	ZnBC → BC CT		
2	1.46 (0.000)	1.47 (0.000)	BC → ZnBC CT		
3	1.86 (0.000)	1.90 (0.000)	BC → ZnBC CT		
4	1.94 (0.001)	1.96 (0.000)	ZnBC → BC CT		
5	2.05 (0.393)	2.07 (0.266)	$\pi-\pi^*$ ZnBC (Q_x)	2.07 (0.231)	1.65 ^b
6	2.09 (0.131)	2.12 (0.170)	$\pi-\pi^*$ BC (Q_x)	2.10 (0.187)	1.6 ^c
7	2.38 (0.059)	2.40 (0.038)	$\pi-\pi^*$ BC (Q_y)	2.39 (0.034)	2.3 ^c
8	2.42 (0.019)	2.46 (0.018)	$\pi-\pi^*$ ZnBC (Q_y)	2.44 (0.026)	2.2 ^b
9	2.43 (0.022)	2.42 (0.000)	ZnBC → BC CT		
10	2.58 (0.000)	2.66 (0.000)	BC → ZnBC CT		

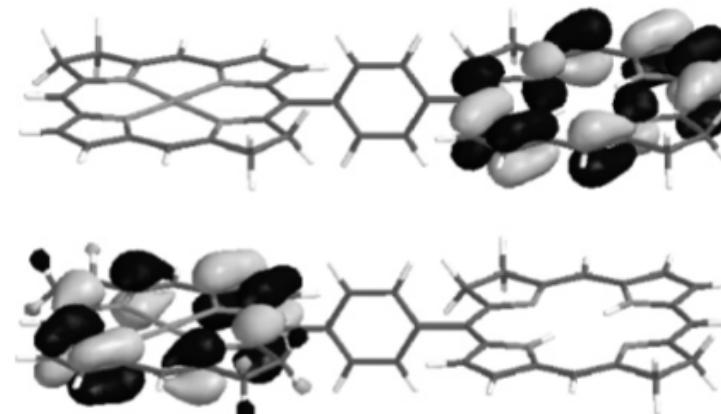


Figure 9. Highest occupied molecular orbital (HOMO, bottom) and lowest unoccupied molecular orbital (LUMO, top) of the ZnBC–BC complex. In the lowest excited CT state, an electron is transferred from the HOMO to the LUMO, and thus, this transition corresponds to an electron transfer from ZnBC to BC.

