



# Applications of TDDFT

## TDDFT for excited states dynamics

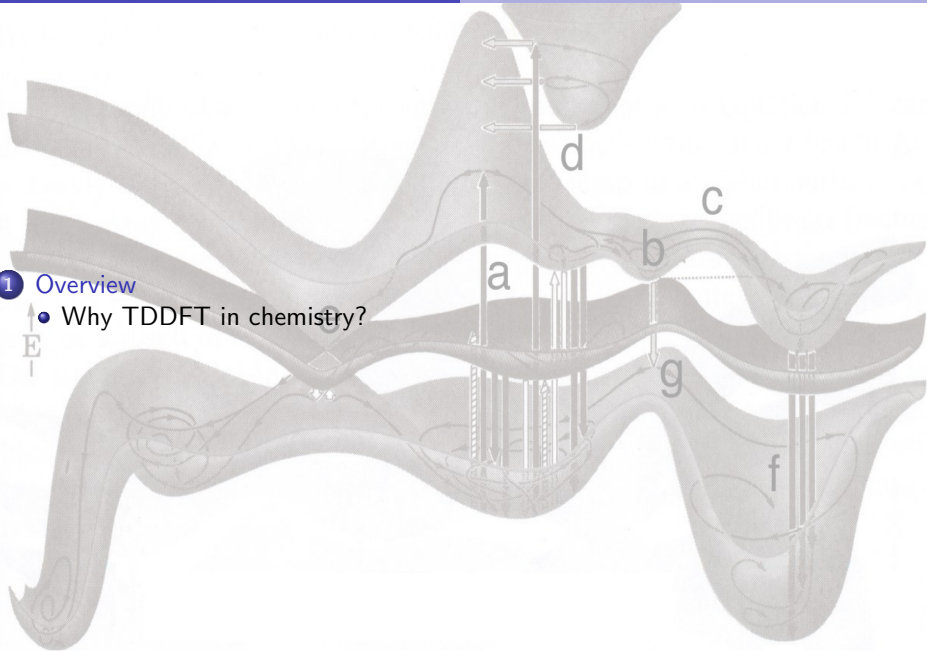
Ivano Tavernelli

IBM Research - Zurich

7th TDDFT SCHOOL  
BENASQUE 2016

# 1 Overview

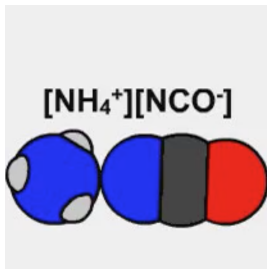
- Why TDDFT in chemistry?



# Chemistry is about atomic rearrangements

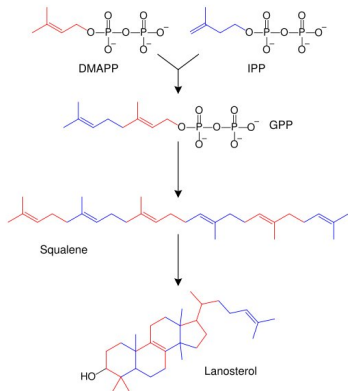
From Wikipedia:

**Chemistry** (from Egyptian keme (chem), meaning "earth") is the science concerned with the composition, structure, and properties of matter, as well as the **changes** it undergoes during **chemical reactions**. Historically, modern chemistry evolved out of alchemy following the chemical revolution (1773). Chemistry is a physical science related to studies of various atoms, molecules, crystals and other aggregates of matter whether in **isolation or combination**, which incorporates the concepts of **energy and entropy** in relation to the spontaneity of chemical processes.



# Chemistry is about atomic rearrangements

We need dynamics to model chemical reactions ...

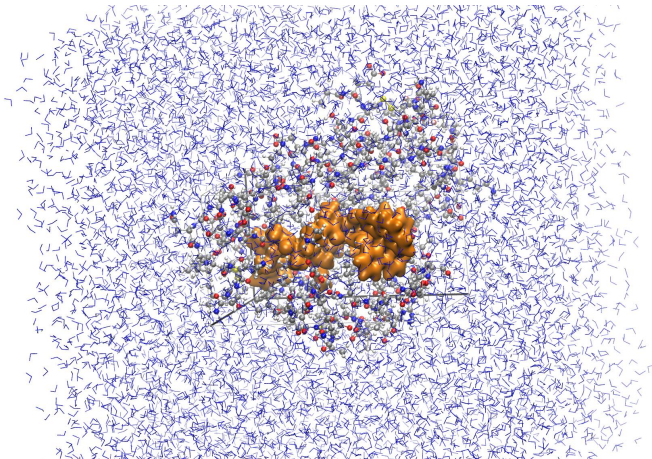


(Sterol synthesis)



# Chemistry is about atomic rearrangements

... and a way to describe the interaction with the environment.



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A theoretical/computational approach will therefore need:

- theoretical model for matter in the energy range [0 to few hundred of eV]
- description of chemical reactions (structural changes)
- description of the interaction with the environment (condensed phase)

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... which translate into:

- theory of electronic structure and ways to solve the corresponding equations
- solution of the equations of motion for atoms and electrons + statistical mechanics (from the microcanonical to the canonical ensemble)
- approximate solutions for the description of the interactions with the rest of the universe

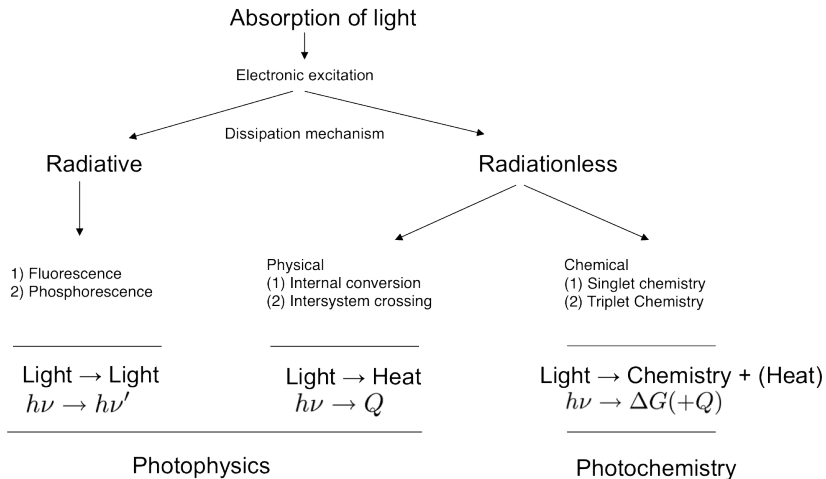
# Photochemistry is about atomic rearrangements

From Wikipedia:

**Photochemistry**, a sub-discipline of chemistry, is the study of the interactions between atoms, small molecules, and light (or electromagnetic radiation). [...] Photochemistry may also be introduced to laymen as a **reaction** that proceeds with the **absorption of light**. Normally a reaction (not just a photochemical reaction) occurs when a molecule gains the necessary activation energy to undergo change. A simple example can be the combustion of gasoline (a hydrocarbon) into carbon dioxide and water. This is a chemical reaction where one or more molecules/chemical species are converted into others. For this reaction to take place activation energy should be supplied. The activation energy is provided in the form of heat or a spark. **In case of photochemical reactions light provides the activation energy.**

Interesting there are no entries for **Photophysics** (2016).

# Photochemistry is about atomic rearrangements





# Why TDDFT in chemistry?

# Wavefunction-based methods for excited states properties

Most of the wavefunction-based methods in quantum chemistry are **more** accurate than TDDFT (using the *standard* exchange and correlation functionals) **but** their use is limited to small systems (up to 10-20 atoms).

The ZOO of quantum chemical methods

WF-based methods	SR	MR
CI	CIS(D)	Full CI (CISD, QCISD)
CC	CCSD, CCSD(T), CC2	MRCC
SCF	-	MCRCF, CASSCF, CASPT2
MP <sub>n</sub>	MP2, MP4, ...	MRMP <sub>n</sub>

In red are methods for excited states.

# TDDFT for excitation energies of large molecules

Among the single reference (SR) (plus perturbation) methods:

- **CIS** : is practically no longer used in the calculation of excitation energies in molecules.  
The error in the correlation energy is usually very large and give qualitatively wrong results.  
STILL good to gain insights into CT states energies.  
Largely replaced by TDDFT.
- **CC2** : Is a quite recent development and therefore not widely available.  
Accurate and fast, is the best alternative to TDDFT.  
Good energies also for CT states.



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Multi reference (MR) *ab initio* methods are still computationally too expensive for large systems (they are limited to few tenths of atoms) and for mixed-quantum classical dynamics. However, there are many interesting new developments (MR-CISD, G-MCQDPT2).

# TDDFT for excitation energies of large molecules

TDDFT :

- is formally exact and improvements of the xc-functionals is still possible.
- is still computationally more efficient and scales better than WF-based methods.
- can be used for large systems (up to thousand atoms).
- can be easily combined with MD (mixed quantum classical MD)
- **BUT is not a black box !**

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JOURNAL OF CHEMICAL PHYSICS

VOLUME 117, NUMBER 12

22 SEPTEMBER 2002

## **Failure of density-functional theory and time-dependent density-functional theory for large extended $\pi$ systems**

Zheng-Li Cai, Karina Sendt, and Jeffrey R. Reimers<sup>a)</sup>

*School of Chemistry, The University of Sydney, New South Wales, 2006 Australia*

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Chemical Physics Letters 461 (2008) 338–342

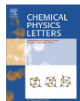


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Chemical Physics Letters

journal homepage: [www.elsevier.com/locate/cpllett](http://www.elsevier.com/locate/cpllett)



Failure of time-dependent density functional theory for excited state surfaces in case of homolytic bond dissociation

K.J.H. Giesbertz, E.J. Baerends \*

*Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

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J|A|C|S

A R T I C L E S

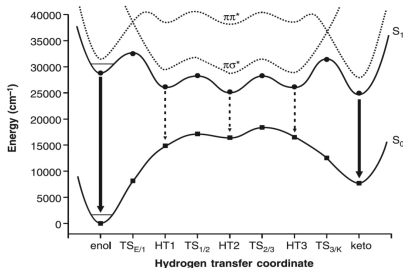
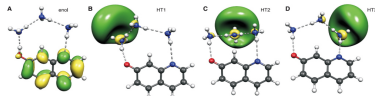
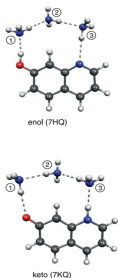
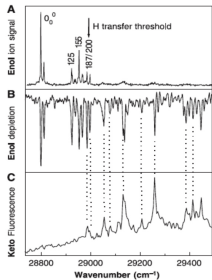
Published on Web 03/08/2004

**Failure of Time-Dependent Density Functional Theory for  
Long-Range Charge-Transfer Excited States: The  
Zincbacteriochlorin–Bacteriochlorin and  
Bacteriochlorophyll–Spheroidene Complexes**

Andreas Dreuw<sup>\*,†</sup> and Martin Head-Gordon<sup>‡</sup>

# TDDFT can easily be combined with molecular dynamics

Ultrafast tautomerization of 4-hydroxyquinoline·(NH<sub>3</sub>)<sub>3</sub>  
 Hydrogen or proton transfer along this molecular wire?

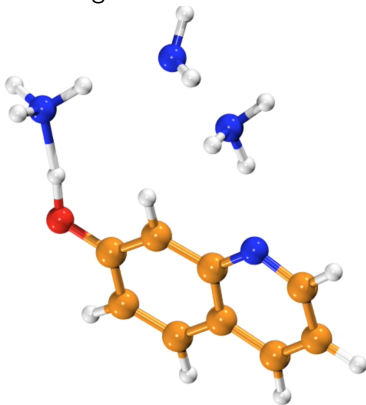


CIS/CASSCF for the in-plane geometry  $\rightarrow \pi\pi^*/\pi\sigma^*$  crossing leads to a hydrogen atom transfer.

S. Leutwyler *et al.*, Science, 302, 1736 (2003)

# TDDFT can easily be combined with molecular dynamics

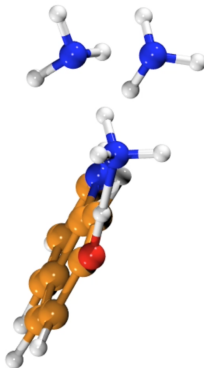
Ultrafast tautomerization of 4-hydroxyquinoline·(NH<sub>3</sub>)<sub>3</sub>  
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What about TDDFT combined with nonadiabatic dynamics?

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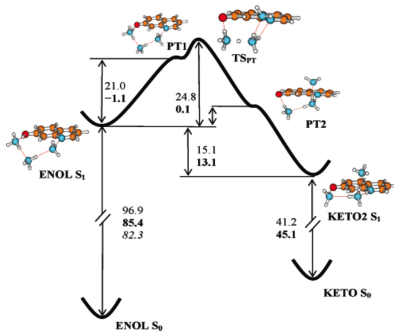
With TDDFT, we observe:

- Symmetry breaking.
- No crossing with the  $\pi\sigma^*$  state.
- Proton transfer instead of a hydrogen transfer.

Guglielmi *et al.*, PCCP, 11, 4549 (2009).

# TDDFT can easily be combined with molecular dynamics

Ultrafast tautomerization of 4-hydroxyquinoline·(NH<sub>3</sub>)<sub>3</sub>  
 Hydrogen or proton transfer along this molecular wire?  
 Similar observations with CASPT2 calculations:



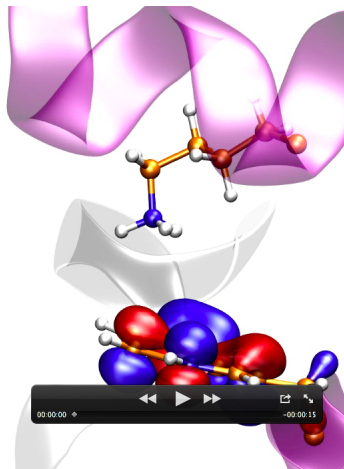
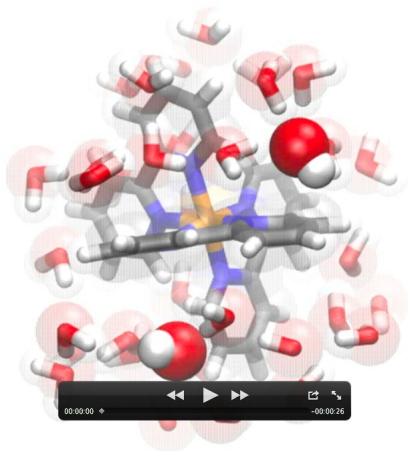
Forcing in-plane symmetry: hydrogen transfer.  
 Unconstrained geometry optimization leads to a proton transfer!  
 Fernandez-Ramos *et al.*, JPCA, 111, 5907 (2007).

# Main topics of this set of lectures

## Topics of this set of lectures

- 1 *Ab initio* molecular dynamics.
- 2 Nonadiabatic dynamics using LR-TDDFT.
- 3 Coupling with the environment (TDDFT/MM).

# Examples of photophysical and photochemical processes



Accuracy can become an issue