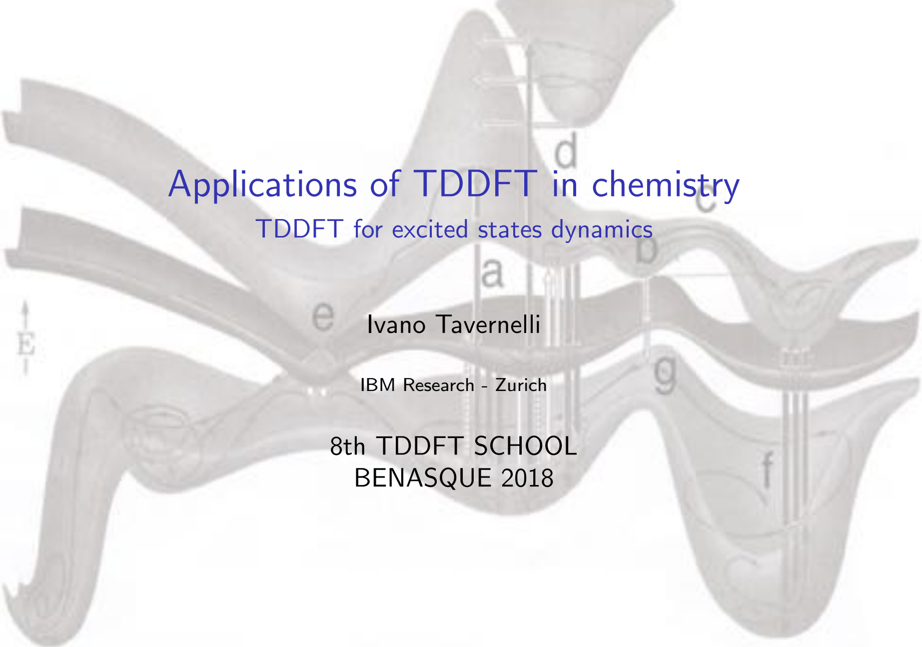


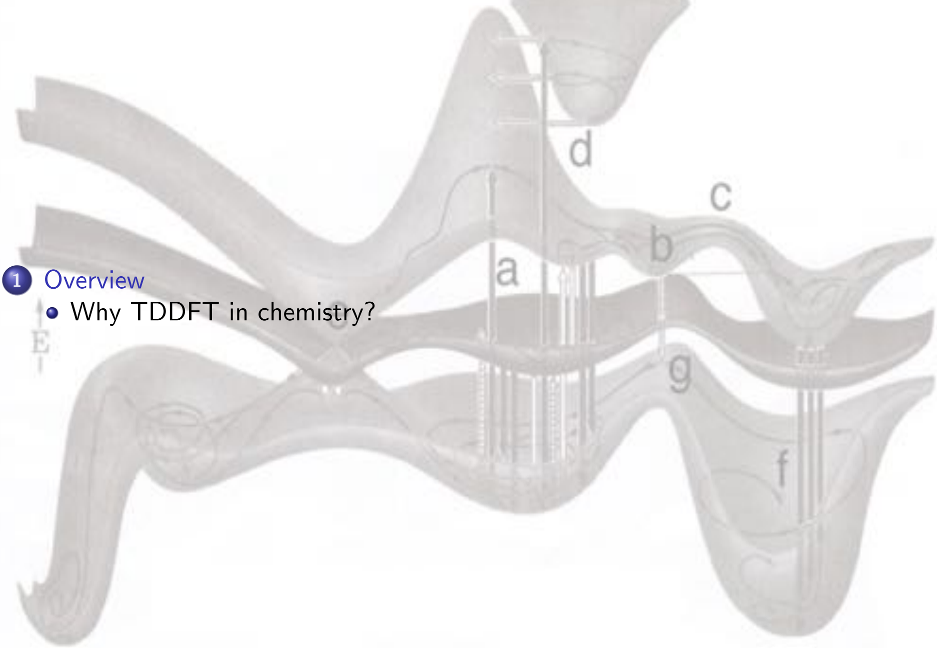
Applications of TDDFT in chemistry

TDDFT for excited states dynamics

Ivano Tavernelli

IBM Research - Zurich

8th TDDFT SCHOOL
BENASQUE 2018

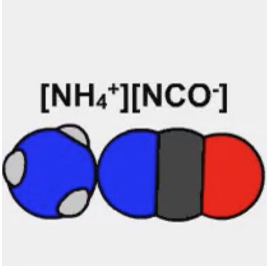


1. Overview
    - Why TDDFT in chemistry?

Chemistry is about atomic rearrangements

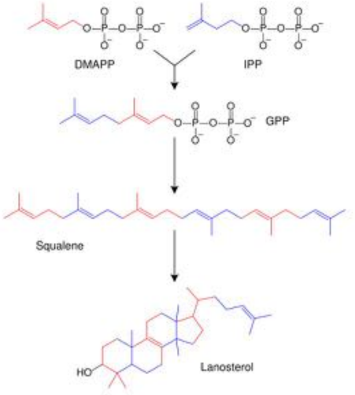
From Wikipedia:

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

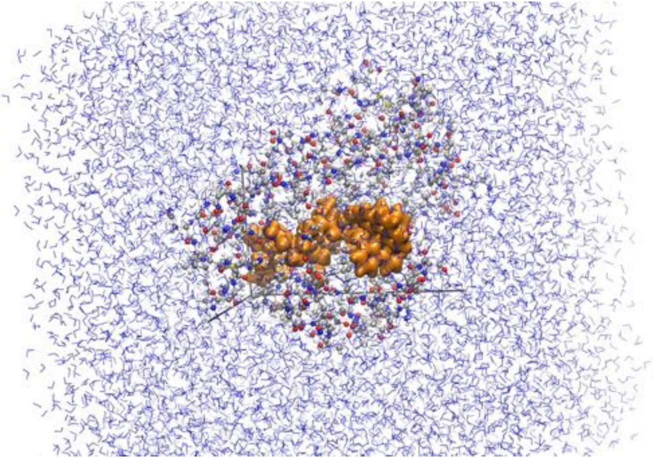
We need dynamics to model chemical reactions ....



(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

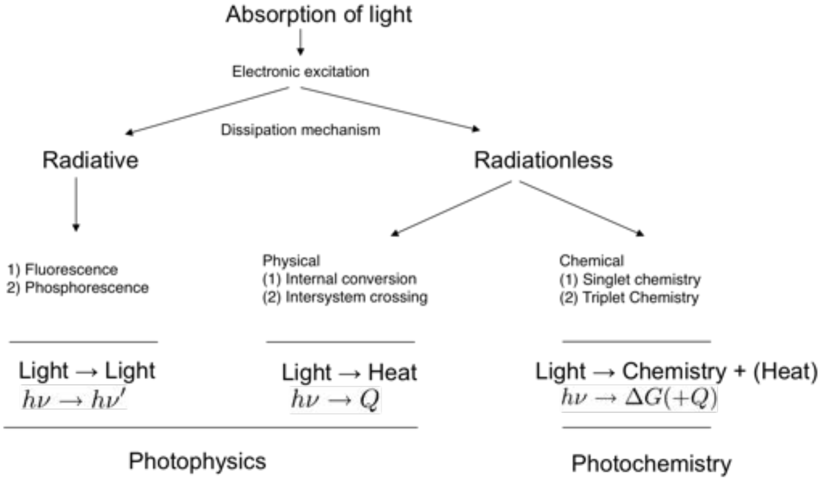
Photochemistry is about atomic rearrangements

From Wikipedia:

Photochemistry, is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400 -750 nm) or infrared radiation (750 -2500 nm). In nature, photochemistry is of immense importance as it is the basis of photosynthesis, vision, and the formation of vitamin D with sunlight. Photochemical reactions proceed differently than temperature-driven reactions. Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes. Photochemistry is also destructive, as illustrated by the photodegradation of plastics.

Interesting there are no entries for **Photophysics** (2018).

Photochemistry is about atomic rearrangements



Absorption of light

Electronic excitation

Dissipation mechanism

Radiative

Radiationless

1) Fluorescence
2) Phosphorescence

Physical
(1) Internal conversion
(2) Intersystem crossing

Chemical
(1) Singlet chemistry
(2) Triplet Chemistry

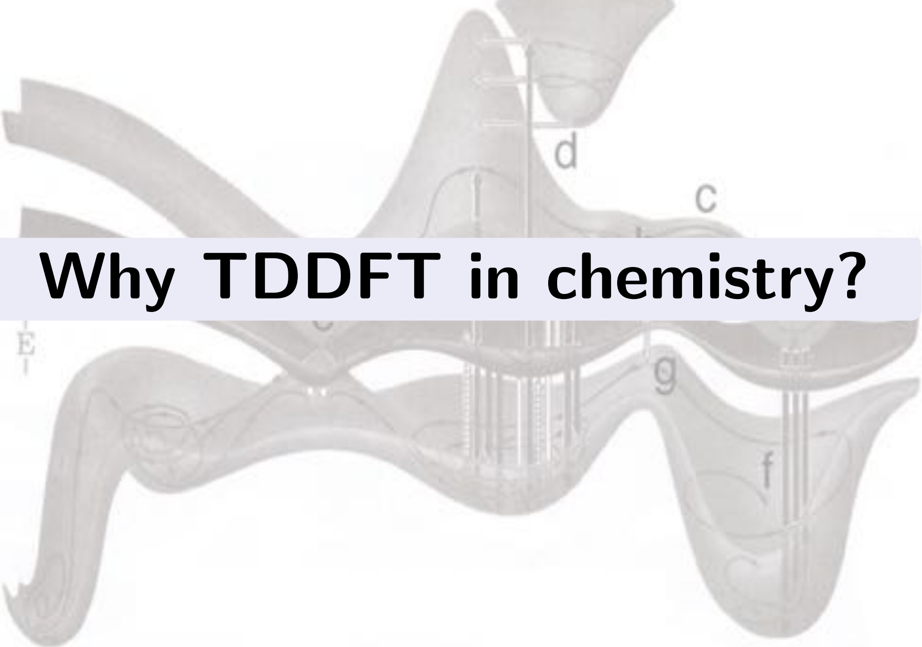
Light → Light
$h\nu \rightarrow h\nu'$

Light → Heat
$h\nu \rightarrow Q$

Light → Chemistry + (Heat)
$h\nu \rightarrow \Delta G(+Q)$

Photophysics

Photochemistry



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"
MPn	MP2, MP4, ...	MRMPn

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 : s a quite recent development together with ADC2. 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 π systems

Zheng-Li Cai, Karina Sendt, and Jeffrey R. Reimers[a]

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

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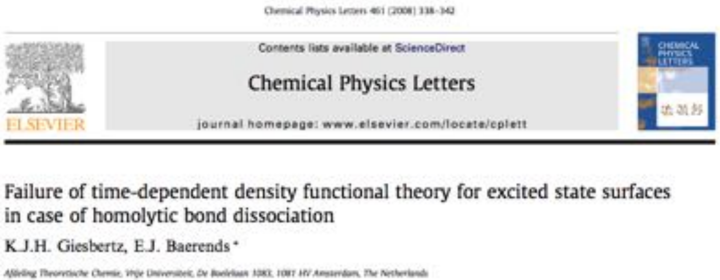

Chemical Physics Letters 461 (2008) 338–342

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

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

TDDFT for excitation energies of large molecules

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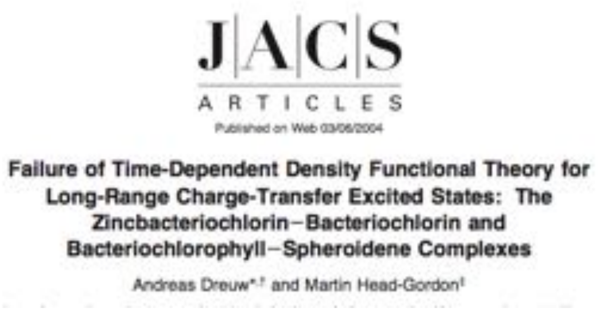


JACS

ARTICLES

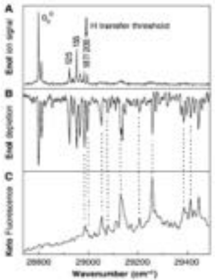
Published on Web 03/06/2004

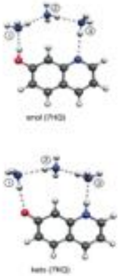
Failure of Time-Dependent Density Functional Theory for Long-Range Charge-Transfer Excited States: The Zincbacteriochlorin−Bacteriochlorin and Bacteriochlorophyll−Spheroidene Complexes

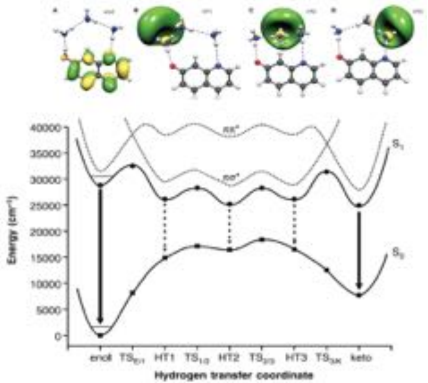
Andreas Dreuw*,[†] and Martin Head-Gordon[†]

TDDFT can easily be combined with molecular dynamics

Ultrafast tautomerization of 4-hydroxyquinoline$\cdot(NH_3)_3$
Hydrogen or proton transfer along this molecular wire?







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

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

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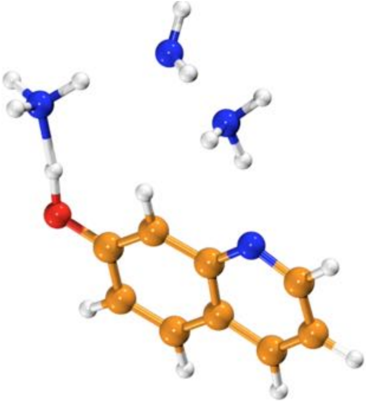

What about TDDFT combined with nonadiabatic dynamics?

TDDFT can easily be combined with molecular dynamics

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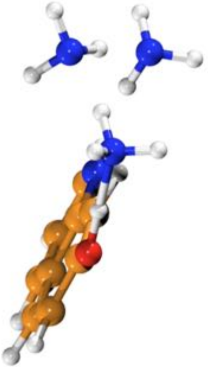


What about TDDFT combined with nonadiabatic dynamics?

TDDFT can easily be combined with molecular dynamics

Ultrafast tautomerization of 4-hydroxyquinoline·$(NH_3)_3$
Hydrogen or proton transfer along this molecular wire?

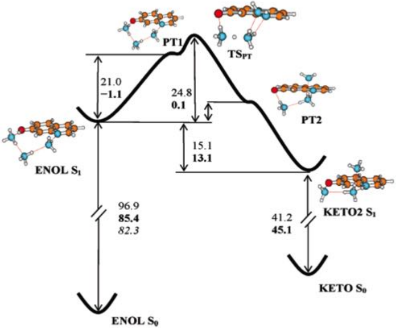
With TDDFT, we observe:

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

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

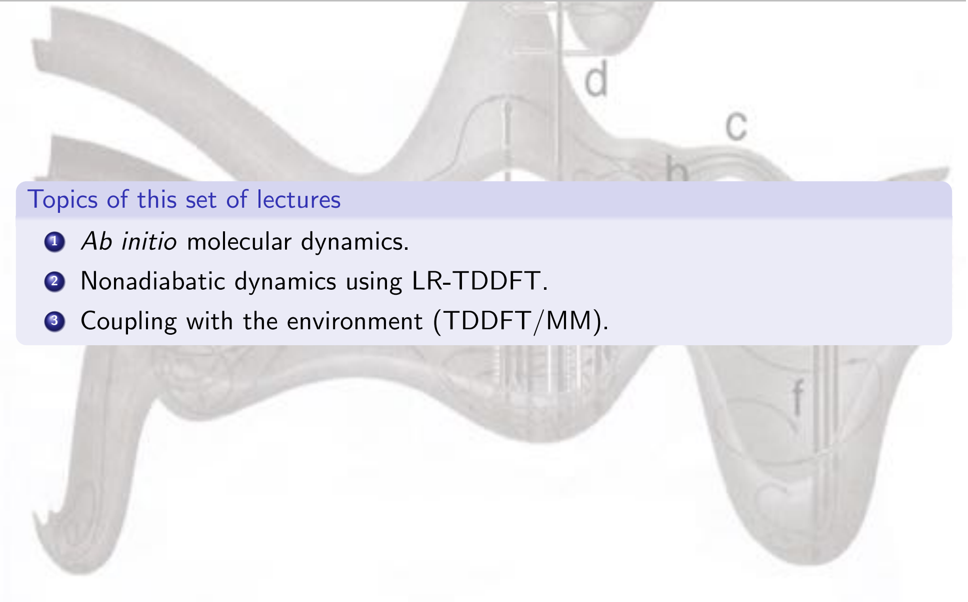
TDDFT can easily be combined with molecular dynamics

Ultrafast tautomerization of 4-hydroxyquinoline$\cdot(NH_3)_3$
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).

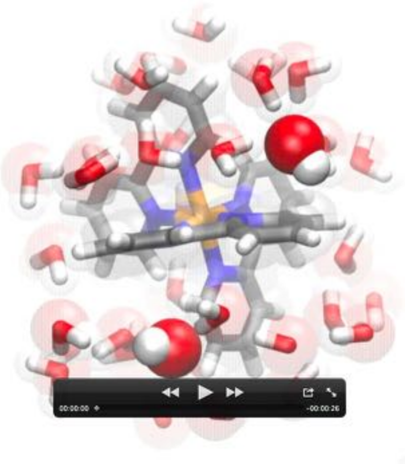
Main topics of this set of lectures

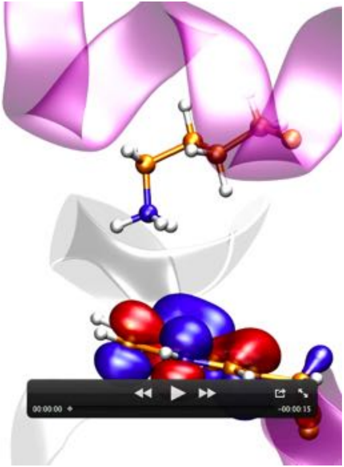


Topics of this set of lectures

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