Applied TDDFT - I: a Chemist's Perspective

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Outline

- Chemist’s Interests ?
  - What’s is chemistry?
  - GS chemistry = Thermochemistry
  - ES chemistry = photochemistry

- Theoretical Methods for Excited State in Chemistry

- Optical Properties from TDDFT:
  - Linear Response Theory
  - LRTDDFT : CASIDA Equations, TDA
  - Real-Time Propagation TDDFT

- Failures of TDDFT
  - Charge-Transfer excitations
  - PES topology

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Chemist's Interests

From Wikipedia:

Chemistry is a branch of physical science that studies the composition, structure, properties and change of matter. Chemistry includes topics such as the properties of individual atoms, how atoms form chemical bonds to create chemical compounds, the interactions of substances through intermolecular forces that give matter its general properties, and the interactions between substances through ***chemical reactions to form different substances.***

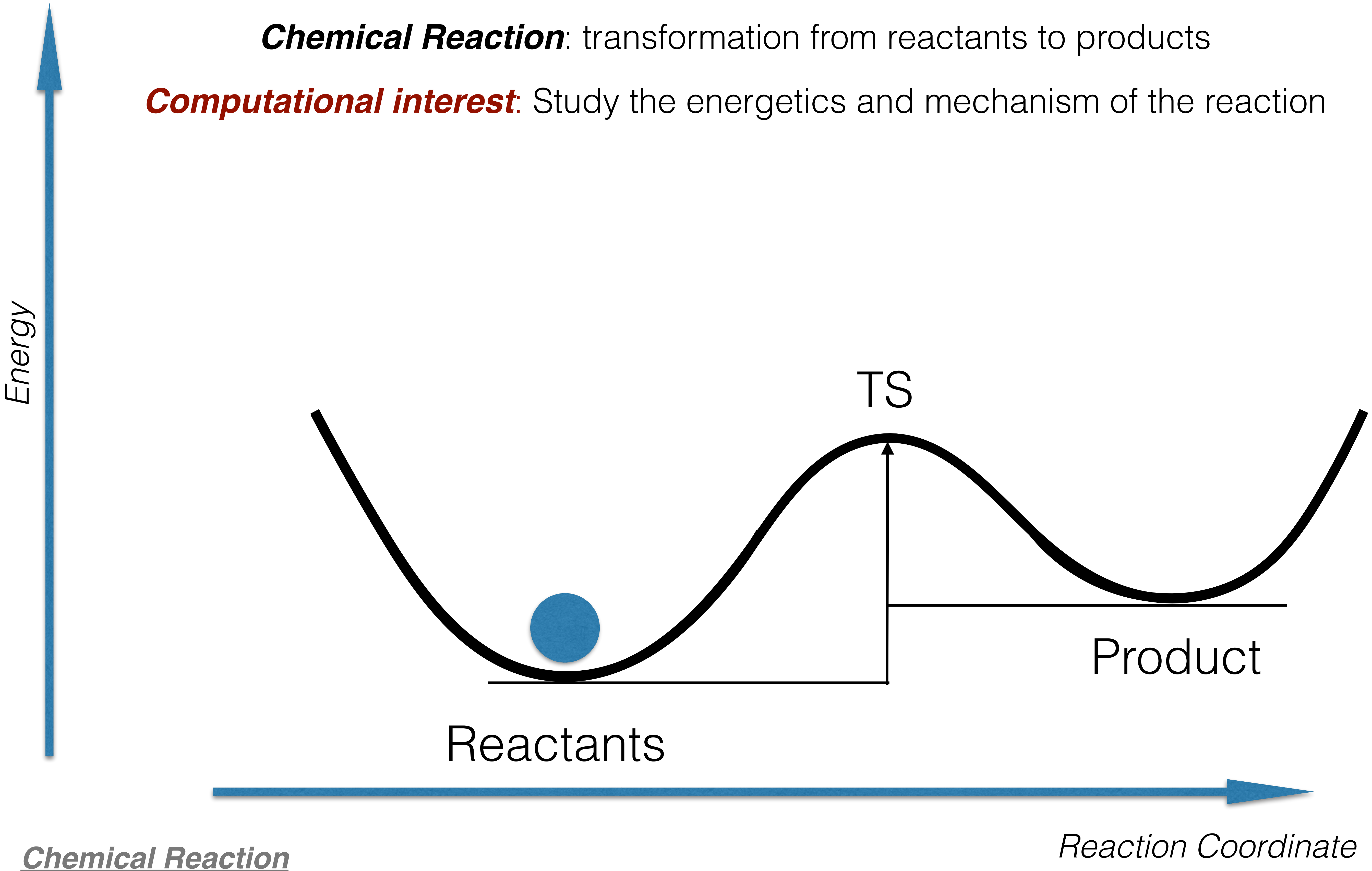
Chemistry is sometimes called the central science because it bridges other natural sciences, including physics, geology and biology.

From Wikipedia:

A **chemical reaction** is a transformation of some substances into one or more different substances. The basis of such a chemical transformation is the rearrangement of electrons in the chemical bonds between atoms. Since a chemical transformation is accompanied by a change in one or more of these kinds of structures, it is invariably accompanied by an **increase or decrease of energy** of the substances involved. Some energy is transferred between the surroundings and the reactants of the reaction in the **form of heat or light**; thus the products of a reaction may have more or less energy than the reactants.

Chemical Reaction: transformation from reactants to products

Computational interest: Study the energetics and mechanism of the reaction



Chemist’s Interests

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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 the interaction with the environment (condensed phase)
- description of chemical reactions (structural changes)

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… which translates into:

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

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… and in practice:

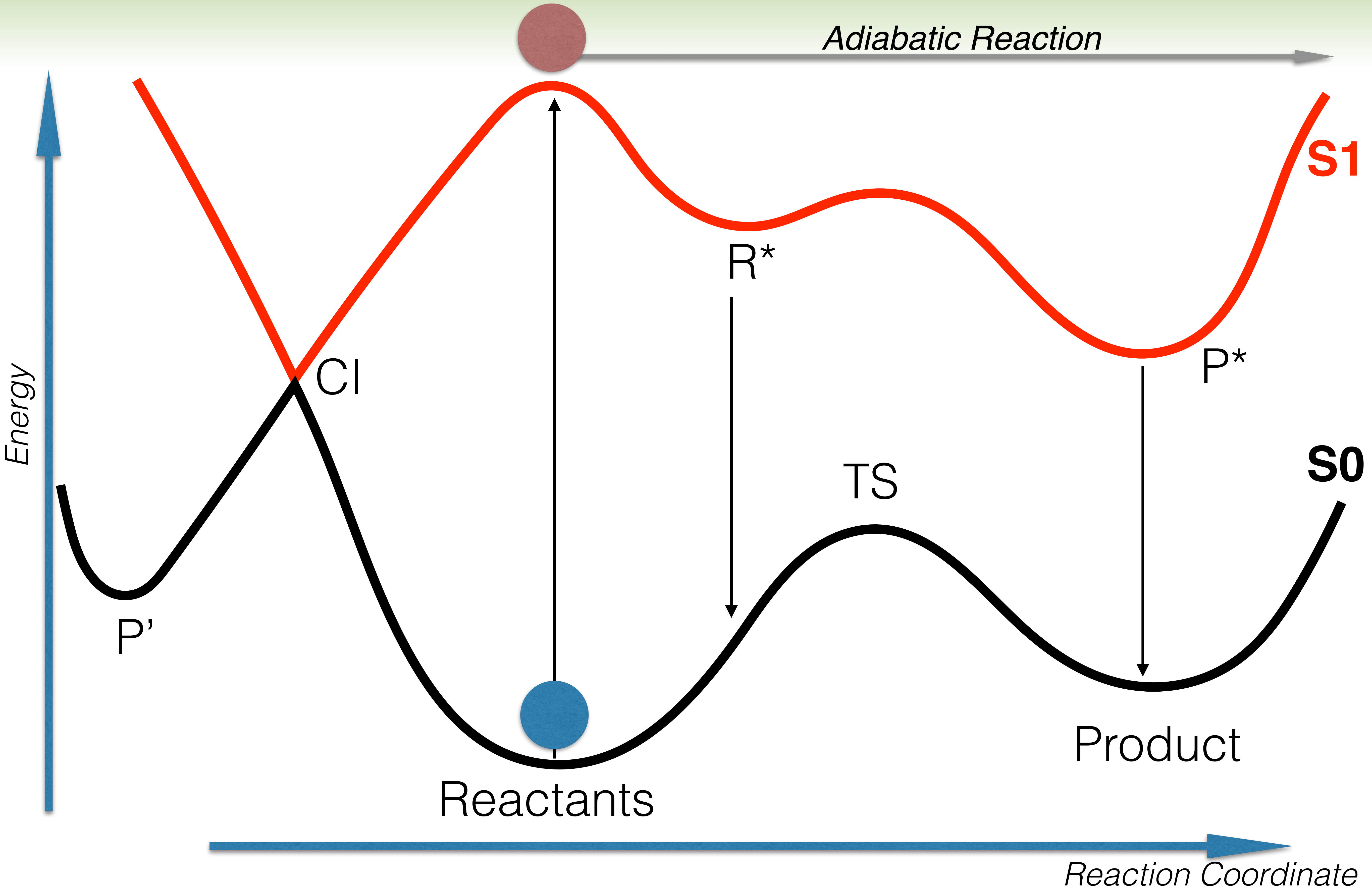
- HF, CI, MPn, CAS, ..., DFT and corresponding theories for excited states
- periodic boundary conditions, PBC, for homogeneous systems and hybrid schemes, for inhomogeneous systems: QM/MM, coarse grained, hydrodynamics, ...
- time dependent theories for adiabatic and non adiabatic dynamics of atoms and electrons: mixed-quantum classical molecular dynamics

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).

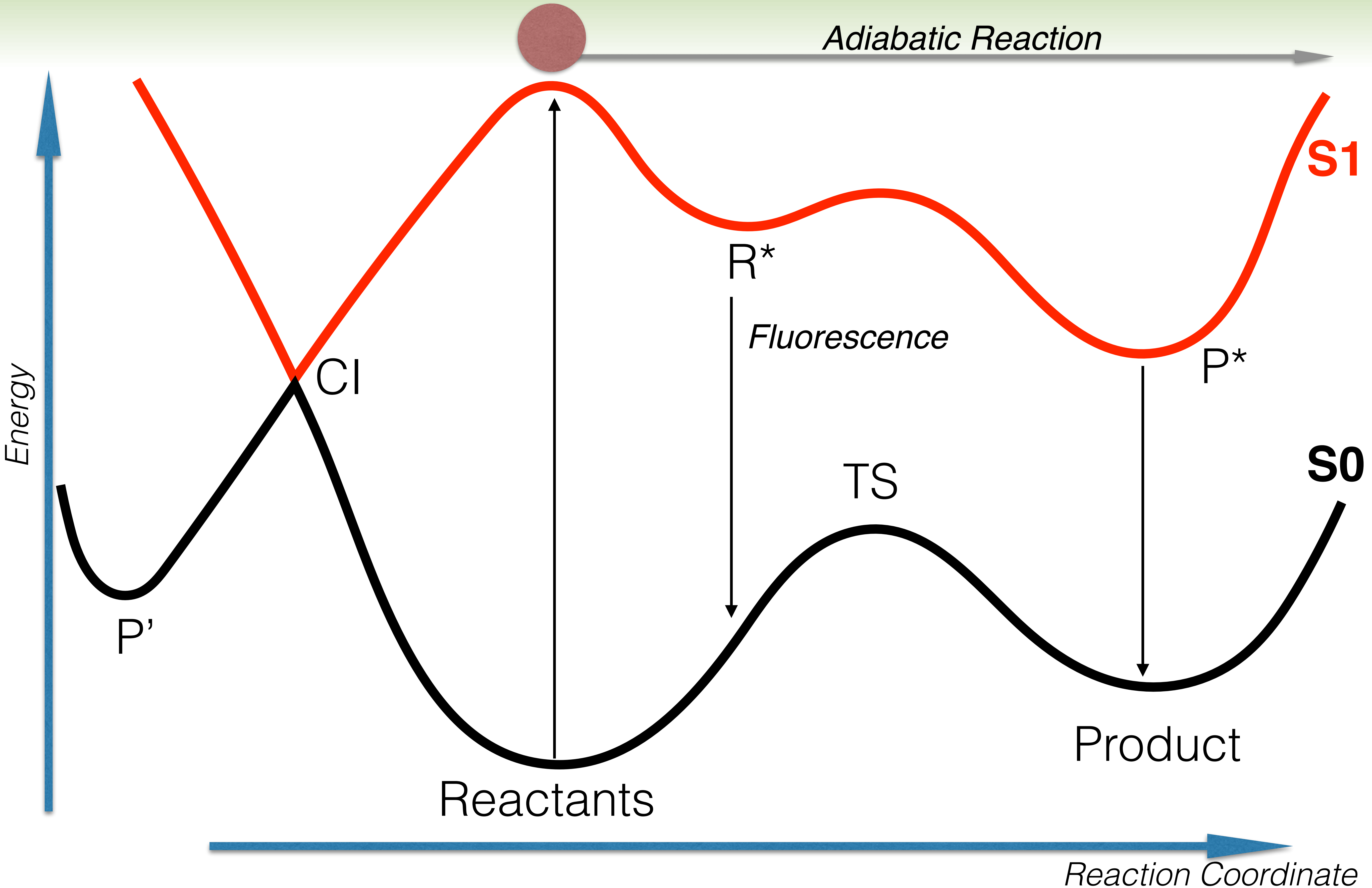
Photochemical reactions are mainly of only specialized value in organic and inorganic chemistry. In nature, photochemistry is of ***immense importance as it is the basis of photosynthesis, vision, and the formation of vitamin D with sunlight***. Photochemical reactions proceed differently than thermal 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.

Chemist's Interests



Photoschemical Reaction

Chemist's Interests



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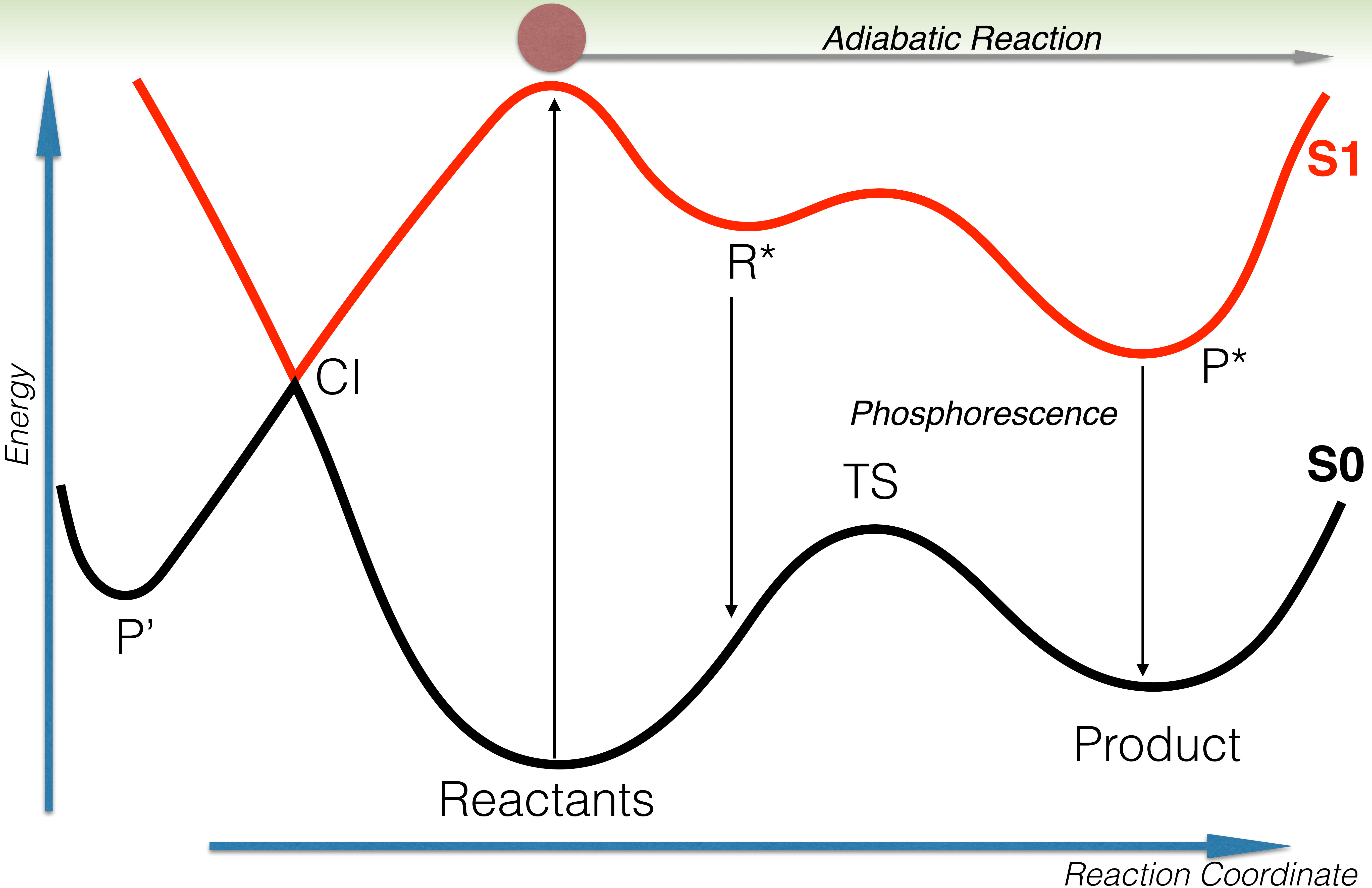

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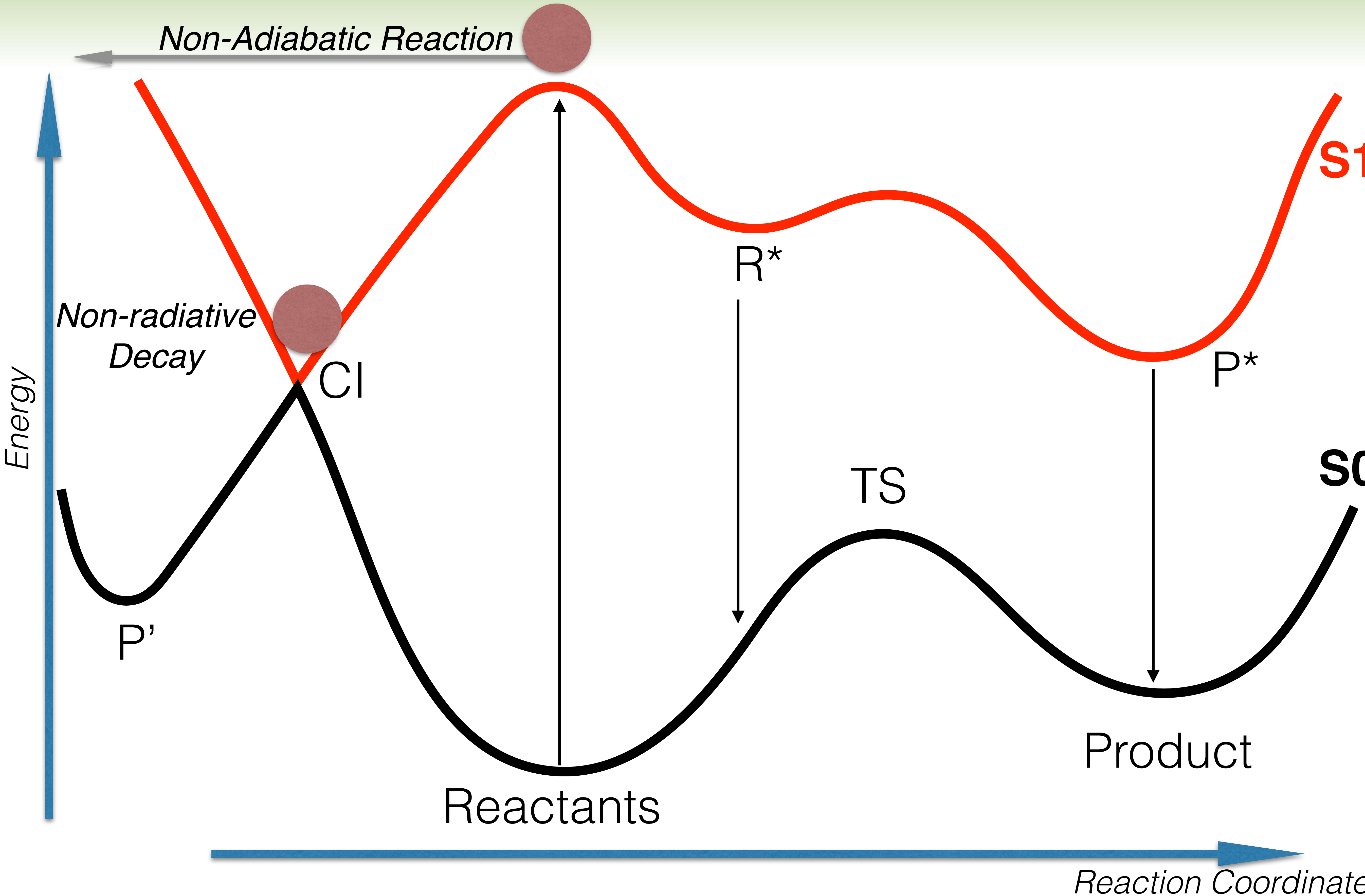

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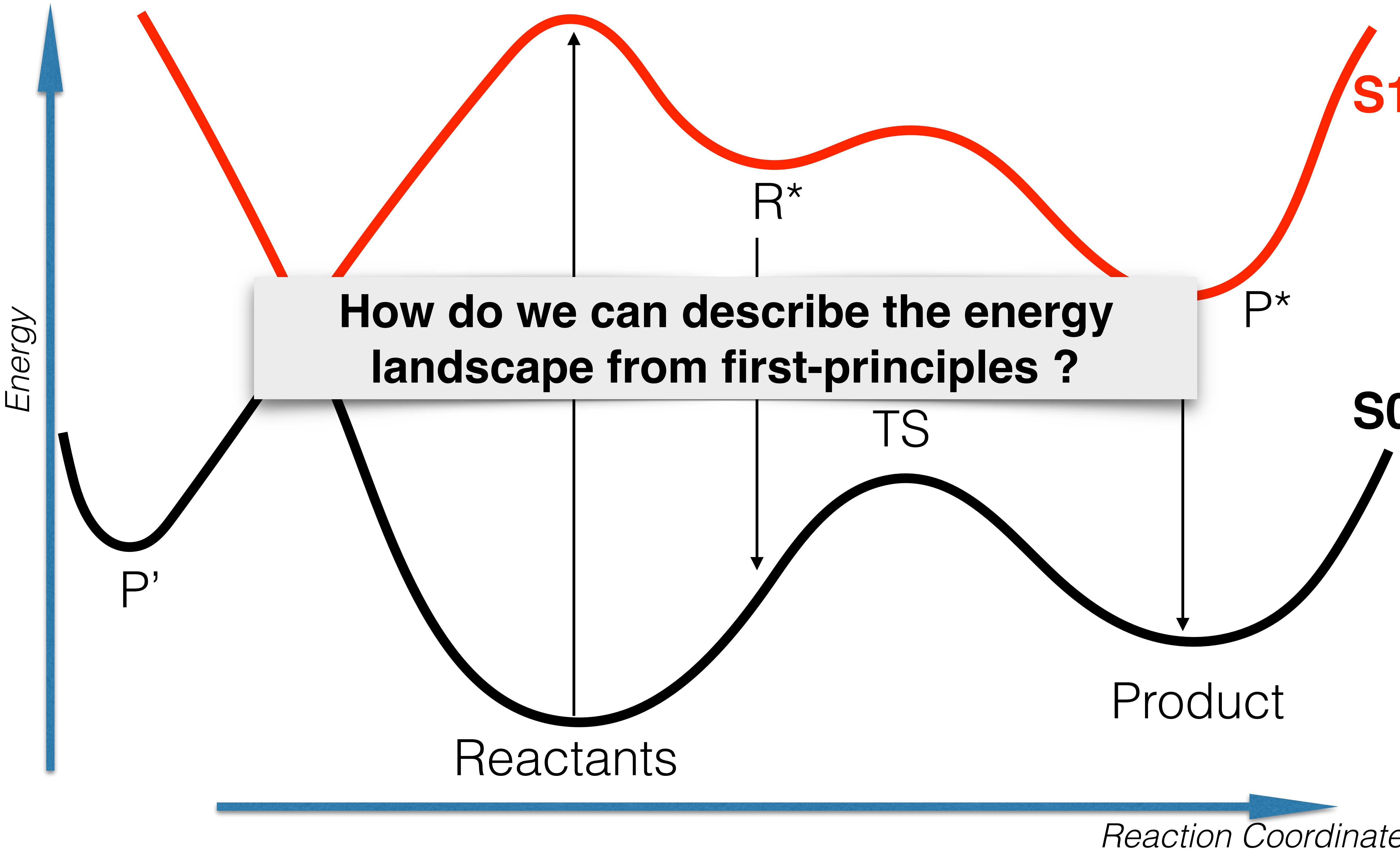

How do we can describe the energy landscape from first-principles ?

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Wavefunction-based methods

Wavefunction-based ab-initio methods are usually selected for **computational chemists** to solve the electronic Schrödinger equation in the excited states.

Most of the *ab-initio* methods used in quantum chemistry belongs to **the post Hartree-Fock** family group: e.g.

Wave function based methods suited for exited states	**SR** (single reference = 1 Slater determinant)	**MR** (multi reference > 1 Slater determinant weighted by de coefficient c_i))
CI (Configuration Interaction)	**CIS** (D) (CI Single and extension via perturbation theory)	Full CI, CISD, QCISD
CC (Coupled Cluster)	**CC2** (SRCC with approximated second order corrections)	MRCC, CCSD, CCSD(T)
SCF (self-consistent field. Orbitals optimised like in HF)	-	MCSCF, **CASSCF**, CASPT2
MPn (Møller-Plesset perturbational theory)	-	MP2 and MP4

All post Hartree-Fock methods are based on the expansion of the many-electron wavefunction in a linear combination of "excited" Slater determinants:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ia} c_i^a|\Phi_i^a\rangle + \sum_{\substack{i<j\\a<b}} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \sum_{\substack{i<j<k\\a<b<c}} c_{ijk}^{abc}|\Phi_{ijk}^{abc}\rangle + \cdots$$

In comparison of the HF method, these expansion **corrects** a hight percentage the so called electronic correlation (i.e. the difference between the exact energy and the HF energy)

The different quantum chemical methods for the electronic structure (ground and excited states) differ in the way this (infinite) sum is approximated.

In all cases, the results can always be **improved by increasing the number of allowed excitation** to expand the ansatz: singles(S), doubles (D), triples (T) …

Most of the **computational cost** rely on the evaluation of the large number of four-centre electron repulsion integrals

$$K_{ia,bj} = \int d^3r \int d^3r' \Phi_{ia}^*(\boldsymbol{r}) f_H \Phi_{jb}(\boldsymbol{r}'); \qquad \Phi_{ia}(\boldsymbol{r}) = \varphi_i^*(\boldsymbol{r})\varphi_a(\boldsymbol{r})$$

Practical Issues

Among the **single reference (SR) 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 gives 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.

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, RI-CC2, EOM-CC2).

Practical Issues

Alternative to wavefunction-based methods:

TDDFT for excitation energies of large systems:

- is formally exact and improvements of the xc-functionals are still possible.
- is computationally more efficient and scales better than *ab-initio* wavefunction-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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Brief Review of the time-dependent KS equations

The role played by the 2nd Hohenberg-Kohn theorem in the derivation of the time-dependent DFT equation is now "played" by a variational principle involving the action:

$$A[\Psi] = \int_{t_0}^{t_1} \langle \Psi(t) | i\frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle dt$$

Where the wavefunction is determined by the initial conditions up to a time-dependent phase factor:

$$\Psi(t) = \Psi[\rho, \Psi_0] \cdot e^{-i\phi(t)}$$

The effect of the phase-factor is simply to introduce an additive constant to the total action

$$\tilde{A}[\rho] = \int_{t_0}^{t_1} \langle \tilde{\Psi}(t) | i\frac{\partial}{\partial t} - \hat{H}(t) | \tilde{\Psi}(t) \rangle dt + \phi_1 - \phi_0 = A[\rho] + const.$$

Runge-Gross Theorem - II

Then the true density, which determine the action, is the one that make the action stationary,

$$0 = \frac{\delta A[\rho]}{\delta \rho(\boldsymbol{r}, t)} = \int_{t_0}^{t_1} \langle \frac{\delta \Psi(t')}{\delta \rho(\boldsymbol{r}, t)} | i\frac{\partial}{\partial t'} - \hat{H}(t') | \Psi(t') \rangle dt' + c.c.$$

Corrected action density functional (causality and symmetry paradox): R. van Leeuwen *PRL* **80**, 1280 (1998)

Optical properties from TDDFT

The density functional action can be re-written in terms of a universal density functional which does not depend on the external potential,

$$A[\rho] = B[\rho] - \int d\boldsymbol{r} \int_{t_0}^{t_1} v_{ext}(\boldsymbol{r}; \boldsymbol{R}, t)\rho(\boldsymbol{r}, t)dt$$

In analogy with the ground state density function theory, we may assume an independent particle system whose orbitals have the property:

$$\rho(\boldsymbol{r}, t) = \sum_i f_i |\varphi_i(\boldsymbol{r}, t)|^2$$

interacting density **non-interacting KS orbital**

Assuming that the effective potential exists (v-*representability problem*), the universal functional can be expressed as

$$B[\rho] = \sum_i f_i \int_{t_0}^{t_1} dt \langle \varphi_i(t)| i\frac{\partial}{\partial t} - \frac{1}{2}\nabla_i^2 |\varphi_i(t)\rangle$$
$$- \frac{1}{2}\int_{t_0}^{t_1} dt \int\int d\boldsymbol{r_1}\boldsymbol{r_2} \frac{\rho(\boldsymbol{r}_1, t)\rho(\boldsymbol{r}_2, t)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} - A_{xc}[\rho]$$

exchange-correlation action functional

Optical properties from TDDFT

Minimizing the action functional (variational principle),

$$A[\rho] = B[\rho] - \int d\boldsymbol{r} \int_{t_0}^{t_1} v_{ext}(\boldsymbol{r}; \boldsymbol{R}, t)\rho(\boldsymbol{r}, t)dt$$

we obtain the time-dependent KS equations:

$$\Big[-\frac{1}{2}\nabla^2 + v_{eff}(\boldsymbol{r}, t) \Big] \varphi_i(\boldsymbol{r}, t) = i\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r}, t)$$

where,

$$v_{eff}(\boldsymbol{r}, t) = v_{ext} + \int \frac{\rho(\boldsymbol{r}, t)}{|\boldsymbol{r} - \boldsymbol{r'}|} d\boldsymbol{r'} + v_{xc}(\boldsymbol{r}, t)$$

External **Hartree** **Exchange Correlation potential**

Where the unknown is now the time-dependent XC potential, defined as

$$v_{xc}(\boldsymbol{r}, t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\boldsymbol{r}, t)}$$

In analogy to the traditional time-independent Kohn-Sham scheme, **all exchange and correlation effects** in TDDFT are collected in to the $\delta A_{xc}[\rho]/\delta\rho(\boldsymbol{r}, t)$

In the formal derivation of the TDDFT equations no approximations are made, and therefore the theory is ***in principle exact***.

Adiabatic Approximation (AA).

Since the exact time-dependent exchange-correlation action functional is not known, **approximations** have to be done in order to perform numerical calculations on real systems.

Although the exchange-correlation action functional form is unknown, in the limit case where the external potential varies slowly in time, it can be expressed as

$$A_{xc}[\rho(\boldsymbol{r},t)] = \int_{t_0}^{t_1} E_{xc}[\rho_t(\boldsymbol{r})]$$

The Adiabatic Approximation is a **local approximation in time** (like LDA is local in space)
Notice that, whereas the XC action is a functional of the density over both space and time, the XC energy functional is a functional of a function over only space (since *t* is fixed).

In this approximation, the first derivative can be written as

$$v_{xc}[\rho](\boldsymbol{r},t) = \frac{\delta A_{xc}[\rho]}{\delta\rho(\boldsymbol{r},t)} \approx \left.\frac{\delta E_{xc}[\rho]}{\delta\rho_t(\boldsymbol{r})}\right|_{\rho_t=\rho(\boldsymbol{r},t)} = v_{xc}[\rho(t)](\boldsymbol{r})$$

The AA assumes instantaneous reaction of the exchange correlation potential when the electron density is changed in time ! No retardation effects !!

Optical properties from TDDFT

Practical Issues about the Adiabatic Approximation (AA).

Due to this approximation works well beyond its domain of rigorous justification, and to its relative simplicity, the AA approximation has become the work house of the TDDFT.

Within this approximation, **we can use all xc functionals, $v_{xc}(\boldsymbol{r})$,** derived for the time-independent DFT also for the time-dependent functionals $v_{xc}(\boldsymbol{r})|_t$ *and* $f_{xc}(\boldsymbol{r})|_t$ (including hybrid functionals)

Some known failures of the Adiabatic Approximation

We **neglect all retardation or memory effects**. This can easily be seen in AA *xc* kernel:

$$f_{xc}(\boldsymbol{r}t, \boldsymbol{r}'t') \cong \delta(t-t')\frac{\delta^2 E_{xc}[rho]}{\delta\rho_t(\boldsymbol{r})\rho_{t'}(\boldsymbol{r}')}$$

- Frequency-dependence in xc-kernel is essential for the description of double excited states.
- Rabi oscillation are not well reproduced.

Linear Response Theory

The basis of linear response formulation is the change of the density of a system under the influence of an external time dependent perturbation, δv_{ext}

$$\rho(\boldsymbol{r},t) = \rho_0(\boldsymbol{r},t) + \delta\rho(\boldsymbol{r},t)$$

The main quantity in LRT is the density-density response function

$$\chi(\boldsymbol{r},\boldsymbol{r}',t-t') = \left.\frac{\delta\rho(\boldsymbol{r},t)}{\delta v_{ext}(\boldsymbol{r}',t')}\right|_{v_0}$$

Notice that the response have to be zero at any time before t'.

which relates the first order density response with to the applied perturbation

$$\delta\rho(\boldsymbol{r},t) = \int_{t_0}^{t} dt' \int d\boldsymbol{r}' \chi(\boldsymbol{r},\boldsymbol{r}',t-t') \delta v_{ext}(\boldsymbol{r}',t')$$

where the total external potentials is given by the sum of the stationary initial state potential, usually GS, and the external perturbation potential

$$v_{ext}(\boldsymbol{r},t) = v_0(\boldsymbol{r}) + \delta v_{ext}(\boldsymbol{r},t)$$

Optical properties from TDDFT

For our purpose, it is convenient to **introduce the matrix formalism of the response density**, in second quantisation. Assuming a complete basis set of time-independent orthonormal orbitals, $\{\psi_i\}$, the linear response of the density matrix is defined by

$$\delta P_{ij} = \langle \delta\Psi_0(t)|\hat{a}_j^\dagger \hat{a}_i|\Psi_0(t)\rangle + \langle \Psi_0(t)|\hat{a}_j^\dagger \hat{a}_i|\delta\Psi_0(t)\rangle$$

Where $\hat{a}_j^\dagger, \hat{a}_i$ are the corresponding creation and annihilation operators.

The response of the density matrix can be also expressed in terms of the generalised susceptibility $\boldsymbol{\chi}$,

$$\delta P_{ij}(t) = \sum_{kl} \int_{-\infty}^{+\infty} \chi_{ij,kl}(t-t')\delta v_{kl}^{ext} dt'$$

After doing some algebra, we can write it as,

$$\delta P_{ij}(t_1) = \sum_{kl} \int_{-\infty}^{+\infty} \Bigg\{ -i\Theta(t_1 - t) \sum_{I\neq 0} \Big[\langle \Psi_0|\hat{a}_j^\dagger \hat{a}_i|\Psi_I\rangle \langle \Psi_0|\hat{a}_k^\dagger \hat{a}_l|\Psi_I\rangle e^{-i(E_I - E_0 - i\eta)(t_1 - t)}$$
$$- \langle \Psi_0|\hat{a}_k^\dagger \hat{a}_l|\Psi_I\rangle \langle \Psi_I|\hat{a}_j^\dagger \hat{a}_i|\Psi_0\rangle e^{-i(E_0 - E_I - i\eta)(t_1 - t)} \Big] \Bigg\} \delta v_{kl}^{ext}(t) dt$$

Optical properties from TDDFT

Then, taking the Fourier Transform gives the **sum-over-states representation of the generalised susceptibility** (Lehmann representation)

$$\chi_{ij,kl}(\omega) = \sum_{I\neq 0} \left\{ \frac{\langle \Psi_0 | \hat{a}_j^\dagger \hat{a}_i | \Psi_I \rangle \langle \Psi_0 | \hat{a}_k^\dagger \hat{a}_l | \Psi_I \rangle}{\omega - \Omega_I + i\eta} - \frac{\langle \Psi_0 | \hat{a}_k^\dagger \hat{a}_l | \Psi_I \rangle \langle \Psi_I | \hat{a}_j^\dagger \hat{a}_i | \Psi_0 \rangle}{\omega + \Omega_I + i\eta} \right\}$$

accounts for excitations and relaxation contributions

A special case is that of a single particle systems with the Schrödinger equation

$$\hat{h}\psi_i = \epsilon_i \psi_i$$

for such systems, and keeping in the second quantisation notation, the generalised susceptibility reads,

$$\chi_{ij,kl}(\omega) = \delta_{i,k}\delta_{j,l} \frac{f_j - f_i}{\omega - (\epsilon_i - \epsilon_j)}$$

being f_i the occupation of the orbital i.

(notice that all reference to the spin components has been avoided for simplicity)

Optical properties from TDDFT

The sum-over-states expressions can also be derived for particular response properties. Of particular interest in *molecular spectroscopy* is the computation of the **dynamics polarisability**, $\alpha(\omega)$, which is the response function that relates an electric external potential to the change of the dipole.

$$\mu_\nu(t) = \mu_\nu(t_0) + \int_{-\infty}^{+\infty} \alpha_{\nu\lambda}(t-t')\mathcal{E}_\lambda(t')dt'$$

Exercise: Derive the expression of the dynamics polarisability, knowing

dipole moment operator $\hat{\mu}_\nu = q\hat{r}_\nu$

external electric field $\delta v_\lambda^{ext}(t) = \hat{r}_\lambda \mathcal{E}(t)$

dynamic polarizability $\alpha_{\nu\lambda}(t-t') = -i\Theta(t-t')\langle\Psi_0|[\hat{\mu}_\nu(t-t'), \hat{r}_\lambda]|\Psi_0\rangle$

Optical properties from TDDFT

<u>Exercise:</u> Derive the expression of the dynamics polarisability, knowing

$$\hat{\mu}_\nu = q\hat{r}_\nu \qquad \delta v^{ext}_\lambda(t) = \hat{r}_\lambda \mathcal{E}(t) \qquad \alpha_{\nu\lambda}(t-t') = -i\Theta(t-t')\langle\Psi_0|[\hat{\mu}_\nu(t-t'),\hat{r}_\lambda]|\Psi_0\rangle$$

dipole operator — external electric field — dynamic polarisability

We consider a complete set of eigenfunctions $\{\Psi_n\}$, n = 0, 1, 2 …, of the unperturbed system, and the completeness relation $1 = \sum_{n=0}^{\infty} |\Psi_n\rangle\langle\Psi_n|$

$$\alpha_{\mu\lambda}(\omega) = -\lim_{\eta\to 0^+}\sum_{n=1}^{\infty}\left\{\frac{\langle\Psi_0|\hat{r}_\nu|\Psi_n\rangle\langle\Psi_n|\hat{r}_\lambda|\Psi_0\rangle}{\omega-\Omega_n+i\eta} - \frac{\langle\Psi_0|\hat{r}_\lambda|\Psi_n\rangle\langle\Psi_n|\hat{r}_\nu|\Psi_0\rangle}{\omega+\Omega_n+i\eta}\right\}$$

take into account the negative charge of the electron density

Making use of the fact that

$$\langle\Psi_0|\hat{r}_\nu|\Psi_n\rangle\langle\Psi_n|\hat{r}_\lambda|\Psi_0\rangle = \langle\Psi_0|\hat{r}_\lambda|\Psi_n\rangle\langle\Psi_n|\hat{r}_\nu|\Psi_0\rangle$$

and arranging terms, we obtain

$$\alpha_{\mu\lambda}(\omega) = \sum_{n=1}^{\infty}\left\{\frac{2\Omega_n\langle\Psi_0|\hat{r}_\nu|\Psi_n\rangle\langle\Psi_n|\hat{r}_\lambda|\Psi_0\rangle}{\Omega_n^2-\omega^2}\right\}$$

Optical properties from TDDFT

The general expression of the dynamic polarisability is then written as

$$\alpha_{\mu\lambda}(\omega) = \sum_{n=1}^{\infty} \left\{ \frac{2\Omega_n \langle \Psi_0 | \hat{r}_\nu | \Psi_n \rangle \langle \Psi_n | \hat{r}_\lambda | \Psi_0 \rangle}{\Omega_n^2 - \omega^2} \right\}$$

This result is interesting because it shows that excitation energies

$$\Omega_n = E_n - E_0$$

and the spectroscopic oscillator strength,

$$f_n = \frac{2\Omega_n}{3} \sum_{\mu=1}^{3} |\langle \Psi_n | \hat{r}_\mu | \Psi_0 \rangle|^2$$

are the poles and residues of the mean polarisability

$$\bar{\alpha}(\omega) = \frac{1}{3} \mathrm{tr} \boldsymbol{\alpha}(\omega) = \sum_{n=1}^{\infty} \frac{f_n}{\Omega_n^2 - \omega^2}$$

And then, the optical spectrum is defined by the photoabsorption cross-section:

$$\sigma(\omega) = \frac{4\pi\omega}{3c} \Im\mathrm{m}[\alpha(\omega)]$$

Optical properties from TDDFT

Summary:

$$\bar{\alpha}(\omega) = \frac{1}{3}\mathrm{tr}\boldsymbol{\alpha}(\omega) = \sum_{n=1}^{\infty} \frac{f_n}{\Omega_n^2 - \omega^2}$$

The response of an interacting system with an external electric field can be obtained if we know the excitation energies and oscillator strength.

However, considering the difficulty of calculating accurate transition energies and oscillator strength (which requires knowing the continuum states as well as bound states), it is usually **much easier to compute the polarisability** directly, using its matrix representation

$$\alpha_{\nu\lambda}(\omega) = \frac{\delta\mu_\nu(\omega)}{\mathcal{E}_\lambda(\omega)} = -\sum_{ij,kl} r_{ji}^{\nu}\chi_{ij,kl}(\omega)r_{kl}^{\lambda} \qquad (r_{ab}^{\eta} = \langle\psi_a|\hat{r}_\eta|\psi_b\rangle)$$

density-density response function

The poles of the response function of the physical system will correspond to the pole of the dynamic polarisability.

Now the problems becomes into the computation of the response function for an interacting system. Here is when **TDDFT takes its important role**.

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Linear Response in Khon-Sham Realm (LR-TDDFT)

LR-TDDFT aims to obtain the response function of a physical system from the fact that is it possible to obtain the **real time-dependent electron density** if we know an effective potential of a **non-interacting electron system**.

The response function of the physical system of interacting electrons can be computed from the Dyson-like equation

$$\chi(\omega) = \chi_s(\omega) + \chi_s(\omega) \star f_{Hxc}(\omega) \star \chi(\omega)$$

where the space dependence has been omitted for simplicity, the ★ indicates integrals over space, and the Hartree and Exchange correlation functional is the Fourier transform of:

$$f_{Hxc}(\boldsymbol{r_1}t, \boldsymbol{r_2}t') = \frac{\delta(t-t')}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} + \frac{\delta v_{xc}[\rho](\boldsymbol{r}, t)}{\delta\rho(\boldsymbol{r}', t')}$$

And the non-interacting response function in a base of Kohn-Sham orbitals reads as

$$\chi_s(\boldsymbol{r}, \boldsymbol{r}', \omega) = \lim_{\eta\to 0^+} \sum_{k,j} (f_k - f_j)\delta_{\sigma_k\sigma_j} \frac{\varphi_k^{(0)*}(\boldsymbol{r})\varphi_j^{(0)}(\boldsymbol{r})\varphi_j^{(0)*}(\boldsymbol{r}')\varphi_k^{(0)}(\boldsymbol{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$

Optical properties from TDDFT

Now, integrating both sides of Dyson-like equation agains the external perturbation potential, we obtain

$$\left[\hat{1} - \chi_s(\omega) \star f_{Hxc}(\omega)\right] \star \delta\rho(\omega) = \chi_s(\omega) \star \delta v_{ext}(\omega)$$

The exact density-response has poles at the true excitation energies. However, these are not identical to the KS excitation energies. The true excitation energies are therefore those frequencies where the eigenvalue of the integral operator (left h.s.) vanishes.

Different solutions have been proposed to find the poles of the true response function:

· **Casida's Equation**: matrix formulation of the TDDFT linear response (M. E. Casida 1995, 1996)
· **Tamm-Dancoff approximation in TDDFT**: neglects backwards transitions (S. Hiarta & M. Head-Gordon 1999)
· *Single-Pole Approximation*: expand all quantities around one particular KS energy difference (Petersilka 1999)
· *Sternheimer method*: apply time-dependent perturbation theory, often applied to extended systems (ref?)

Casida´s Equations

The first matrix formulation of the TDDFT linear response was derived by M.E. Casida. He showed that the excitation energies of a physical system can be obtained by solving the system of equations

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B}^* & \mathbb{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -\mathbb{I} & 0 \\ 0 & \mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

where

$$A_{ia,jb} = \delta_{ia}\delta_{jb}(\epsilon_a - \epsilon_i) + 2\int d^3r \int d^3r' \Phi^*_{ia}(\boldsymbol{r}) f_{Hxc} \Phi_{jb}(\boldsymbol{r}')$$

$$B_{ia,jb} = 2\int d^3r \int d^3r' \Phi^*_{ia}(\boldsymbol{r}) f_{Hxc} \Phi_{bj}(\boldsymbol{r}')$$

$$\Phi_{ia}(\boldsymbol{r}) = \varphi^*_i(\boldsymbol{r})\varphi_a(\boldsymbol{r})$$

Notice that the frequency dependence of the matrices A and B has been dropped assuming the Adiabatic Approximation of the Hartree-Exchange Correlation kernel.

Casida´s Equations

Once the Casida's equations are solved (i.e. knowing excitation energies and **X**,**Y** matrices), we can also obtain the oscillator strength function as

$$f_\Omega = \frac{2}{3}\sum_{\nu=1}^{3}|\mathbf{x}_\nu^{\mathbf{T}}(\mathbb{A}-\mathbb{B})^{(\mathbf{1/2})}\boldsymbol{Z}_{\boldsymbol{\Omega}}|^{\mathbf{2}};$$

$$\boldsymbol{Z}_\Omega = (\mathbb{A}-\mathbb{B})^{(1/2)}(\mathbf{X}-\mathbf{Y})$$

$$\mathrm{x}_{ia}^{\nu} = \int d\boldsymbol{r} x_\nu \Phi_{ia}$$

And assuming that GS is a single determinant of KS orbitals, and the two orbital products are linearly independent (which is reasonable when the basis set is no too large), then it is possible to expand the excited states as

$$\Psi_I = \sum_{ia} c_{ia}^I \hat{a}_a^\dagger \hat{a}_i \Phi_{ia} + \ldots$$

$$c_{ia}^I = \sqrt{\frac{\epsilon_a - \epsilon_i}{\Omega_I}} Z_{ij}^I$$

Casida´s Equations in Adiabatic Approximation

Since also f_{xc} becomes frequency independent, the number of solutions of the LR-TDDFT equations is just equal to **the dimensions of Casida's matrices**.

This corresponds exactly to the number of **possible one-electron excitations** in the system. Hence we conclude that, although the AA does include important correlations effects, **it is essentially a one-electron (CIS-like) theory.**

LR-TDDFT within the AA has become the most widely used implementation of TDDFT. This theory is known to work **well for low-lying excitations of primarily single electron character**, which do not involve too large charge density relaxations and which are at least somewhat localized in space.

Tamm-Dancoff approximation (TDA)

The TDA consists of setting the matrices **B** equal to 0 in the Casida's equations. Hence, we obtain:

$$\mathbf{A}\overrightarrow{X}_I = \omega_I \overrightarrow{X}_I$$

which is comparable to the CIS equation (TDA on the TDHF equations), with the difference that in LR-TDDFT the elements of the matrix **A** depend on the exchange-correlation kernel, (i.e. includes dynamic correlation effects)

Physically, setting **B** = 0 means neglecting all contributions to the excitation energies coming from the de-excitation of the correlated ground state. Even though an approximation, the **TDA can improve the stability** of the TDDFT calculations with most of the standard (approximated) functionals.

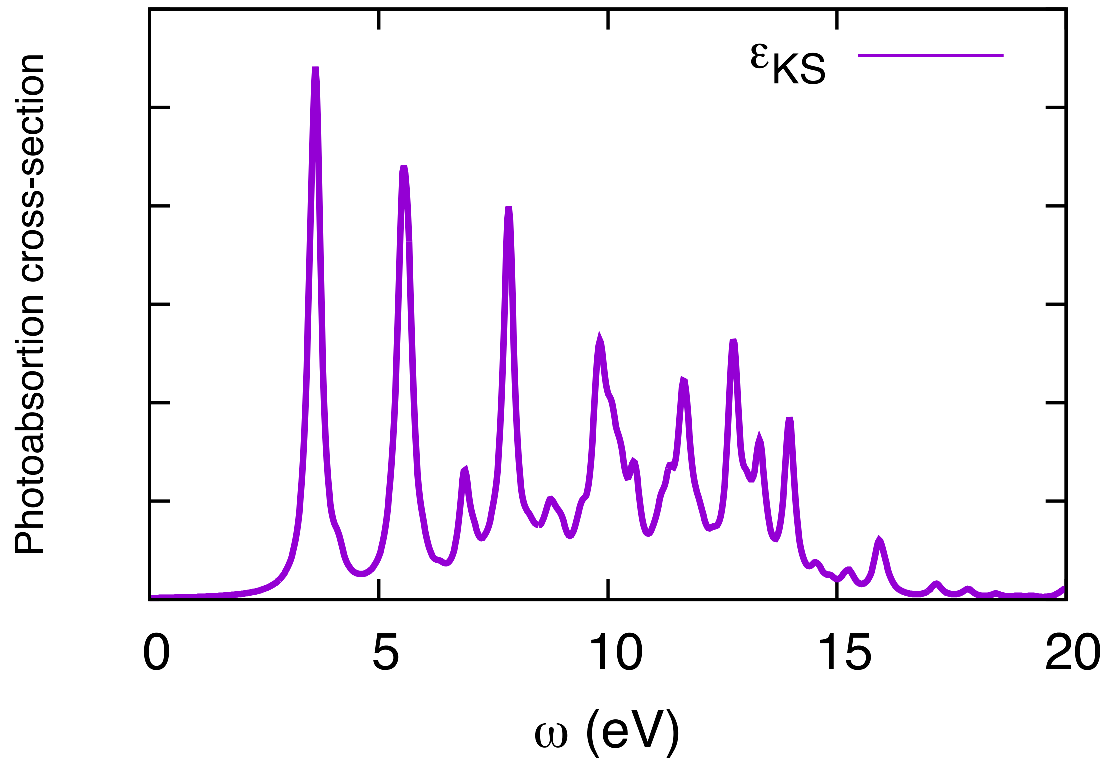
Although TDA gives good values for the excitation energies, it gives poor transition dipole moment values because TDA *violates the oscillator strength sum-rule*.

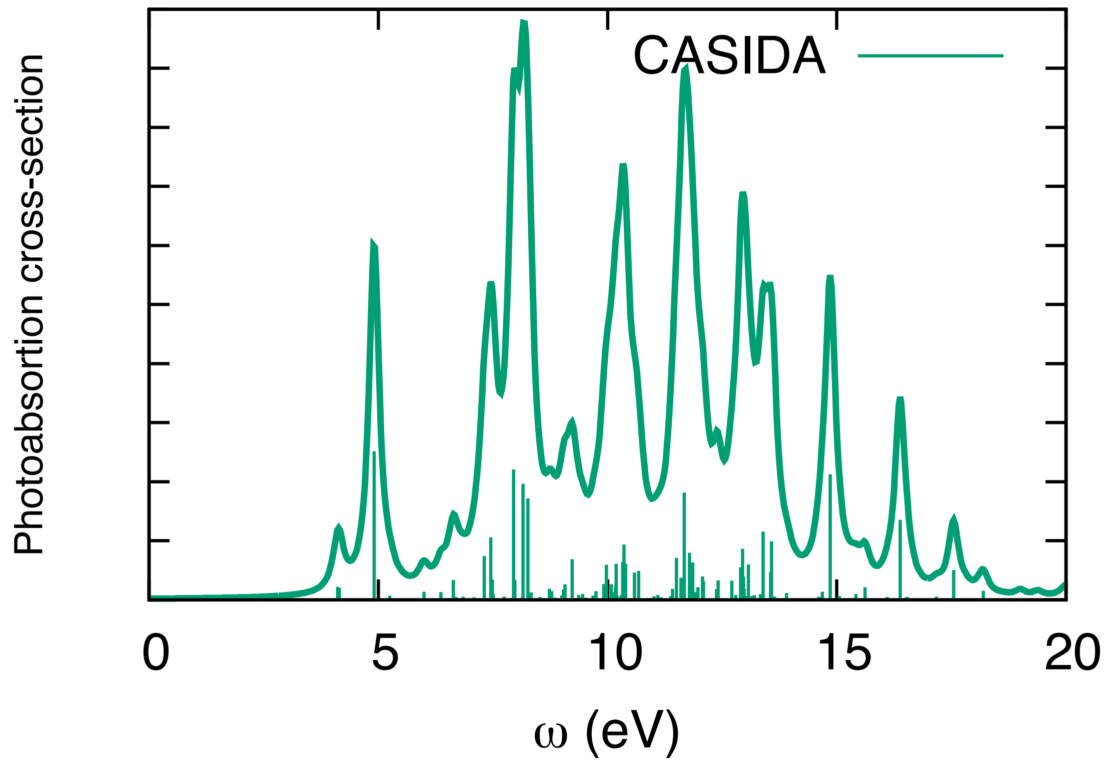
Practical procedure of LR-TDDFT equations in Casida's form

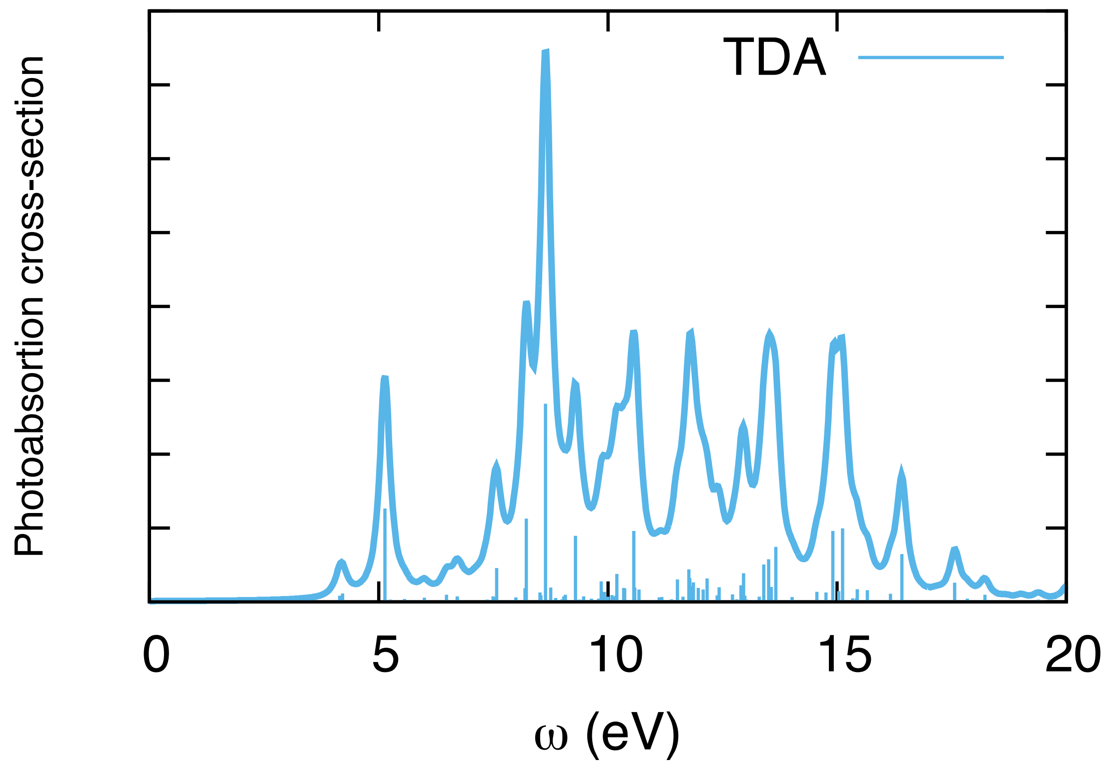
- 1 Do a ground state Kohn-Sham calculation: obtain $\{\varphi_i\}$ and the corresponding $\{\epsilon_i\}$.
- 2 Form the matrices **A** (and **B** if TDA is not used).
- 3 Diagonalize the full matrices or used specific algorithm to extract the first roots: obtain $\{\Omega_{\mathrm{I}}\}$ and f_{I} .
- 4 Informations about the character of the excited states can be obtained from the vectors $\mathbf{X}_I$ and $\mathbf{Y}_I$ (interpretation).

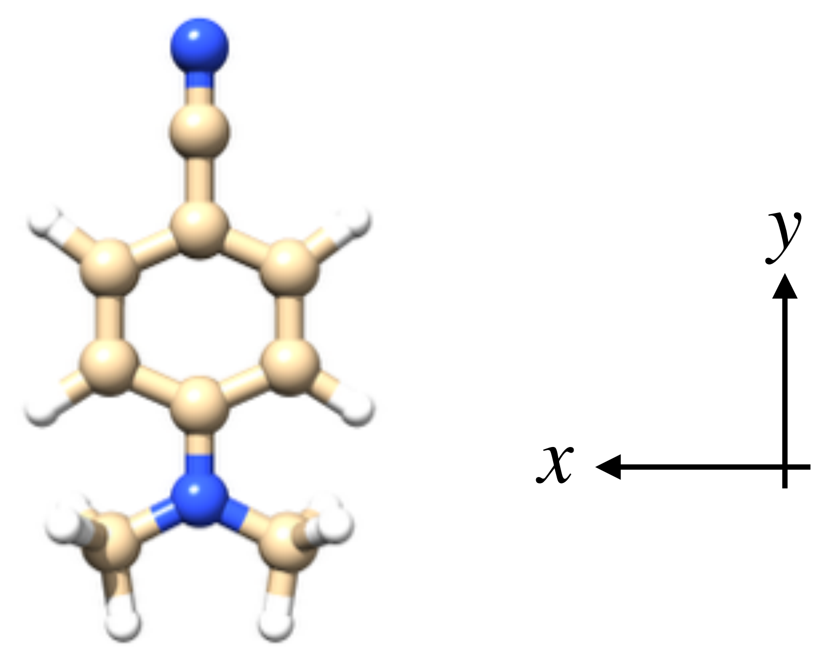
Notice that in this form, a large set of virtual orbitals have to be computed !!!

Example: (DMABN) N,N-dimethylaminobenzonitrile









Outline

- Chemist's Interests ?
    - What's is chemistry?
    - GS chemistry = Thermochemistry
    - ES chemistry = photochemistry

- Theoretical Methods for Excited State Chemistry

- Optical Properties from TDDFT:
    - Linear Response Theory
    - LRTDDFT : CASIDA Equations, TDA
    - **Real-Time Propagation TDDFT**

- Failures of TDDFT
    - Charge-Transfer excitations
    - PES topology

Real-Time Propagation

Spectral information about a system can be alternatively extracted from the real time-propagation.

As mentioned before, **the response density has poles at the true excitation energies**, i.e. an electronic excitation at a frequency **Ω is associated with a specific charge-density fluctuation**, which can be seen as an electronic eigenmode of the system. The eigenmode can be obtained from solving Casida's equation:

$$\delta\rho(\boldsymbol{r},\Omega) = \sum_{ia}[\Phi^*_{ia}(\boldsymbol{r})X_{ia}(\Omega) + \Phi_{ia}(\boldsymbol{r})Y_{ia}(\Omega)]$$

If **an eigenmode were set in motion**, it would keep oscillating forever at that precise frequency, with the time-dependent response density:

$$\delta\rho(\boldsymbol{r},t) = \delta\rho(\boldsymbol{r},\Omega)e^{-i\Omega t}$$

And the photoabsortion **spectrum has a sharp peak at this frequency**.

$$\sigma(\omega) = \frac{4\pi\omega}{3c}\Im\mathrm{m}[\int_{-\infty}^{\infty}\alpha(t)e^{-i\omega t}dt]$$

Optical properties from TDDFT

In other words, if we let evolve the stimulated system over a sufficiently long time interval that we **can accurately calculate the FT of the dipole moment**, we can go back an obtain the associated energy of the system.

The argument is also valid when the system is in a state where several (all) excitation are present simultaneously:

$$\delta\rho(\boldsymbol{r},t) = \sum_{i=1}^{\infty} C_i \delta\rho(\boldsymbol{r},\Omega_i) e^{-i(\Omega_i t + \alpha_i)}$$

Fourier transformation of the oscillating dipole moment produces discrete peaks at each excitation frequencies of the coexisting eigenmodes. If every possible eigenmode are present, we would be able to **get the complete excitation spectrum**.

Question: how do we prepare the system in a superposition of all eigenmodes?

Optical properties from TDDFT

Question: **what is the "hummer" in TDDFT ?**

Any sudden perturbation at time t=0, and let the system freely evolve.

Impulsive electric field: case of an external field that has the shape of a delta impulse in time.

$$v_{ext}(\boldsymbol{r},t) = -e\boldsymbol{r}\cdot\boldsymbol{K}\delta(t) = -e\boldsymbol{r}\cdot\boldsymbol{K}\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\,\exp(i\omega t)$$

An electric field with intensity $\boldsymbol{K}$ and polarised in $\boldsymbol{r}$.

The FT of this is the same for all frequencies and should therefore excite all electronic modes.

Assumes that we start from the GS at time t0=0-, infinitesimal before time t = 0. Using the **time evolution operator** at time t=0+ following excitation with the pulsed field, we obtain the TDKS orbitals infinitesimally later:

$$\varphi_k(\boldsymbol{r},t=0^+) = \exp\left\{\frac{-i}{\hbar}\int_{0^-}^{0^+}[\hat{H}^0_{KS} - e\boldsymbol{r}\cdot\boldsymbol{K}\delta(t')]dt'\right\}\varphi_k(\boldsymbol{r},t=0^-) =$$

$$\exp(ie\boldsymbol{r}\cdot\boldsymbol{K}/\hbar)\varphi_k(\boldsymbol{r},t=0^-)$$

all electrons experience an instantaneous boost at the initial time.

Optical properties from TDDFT

Then, the **dynamic polarisability tensor** can be calculated from the FT of the time dependent dipole moment:

$$\alpha_{\gamma\delta}(\omega) = \frac{1}{K_\delta}\int_0^\infty dt[\mu_\gamma(t) - \mu_\gamma(0)]e^{-i\omega t} \qquad \mu_\gamma(t) = \int \mathrm{r}_\gamma \cdot n(\boldsymbol{r},t)d\boldsymbol{r}$$

And the photo-absorption cross-section can be obtained from

$$\sigma(\omega) = \frac{4\pi\omega}{3c}\Im\mathrm{m}[\alpha(\omega)]$$

Then, starting from the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\varphi_k(\boldsymbol{r},t) = \hat{H}_{KS}[n](\boldsymbol{r},t)\varphi_k(\boldsymbol{r},t)$$

the issue reduces into how to propagate KS orbitals of the time-dependent KS equations:

$$\varphi_k(\boldsymbol{r},t) = \hat{U}(t,0)\varphi_k(\boldsymbol{r},0) = \mathcal{T}\exp\left\{-i\int_0^t d\tau \hat{H}_{KS}[n](\boldsymbol{r},\tau)\right\}\varphi_k(\boldsymbol{r},0)$$

the time evolution operator refers to the time-ordered exponential

In practice, one breaks [0,t] into smaller time intervals, then $\hat{U}(t,0) = \prod_{i=1}^{N-1} \hat{U}(t_i + \Delta t_i, t_i)$

$$\varphi_k(\boldsymbol{r}, t+\Delta t) = \hat{U}(t+\Delta t, t)\varphi_k(\boldsymbol{r}, t) = \mathcal{T}\exp\left\{ -i\int_t^{t+\delta t} d\tau \hat{H}_{KS}[n](\boldsymbol{r},\tau)\right\}\varphi_k(\boldsymbol{r}, t)$$

Many efforts has been devoted to construct **approximation of the time-propagator**, most of them referred to nuclear wave-packet propagation, but also applicable for solving the time-dependent KS equations.

The idea is to find and approximation of the $\varphi_k(t+\Delta t)$ from the knowledge of $\varphi_k(\tau)$ and $\hat{H}(\tau)$ for $0 \le \tau \le t$. Most method requires the evaluation of the hamiltonian in some points in time between $t \le \tau \le t+\Delta t$, and to be very precise one should proceed self-consistent. But, for small time steps, an extrapolation of the $\hat{H}(\tau)$ may be sufficient.

Most of the **approximate operators** use exponentials of the form $\exp(\hat{\mathrm{A}})$ as building blocks, then several algorithms have been proposed to evaluate the exponential of an operator.

For a very complete discussion, see A. Castro, M. A. L. Marques, and A. Rubio, J Chem Phys 121, 3425-3433 (2004).

Practical procedure of Real-Time Propagation TDDFT

- 1 Do a ground state Kohn-Sham calculation: obtain $\{\varphi_i\}$

$$\hat{H}_{KS}[n](\boldsymbol{r},t)\varphi_i(\boldsymbol{r},t) = \epsilon_i\varphi_k(\boldsymbol{r},t)$$

- 2 Time propagation of the KS orbitals (in 3 orthogonal directions)
  - Apply a short perturbative field (usually and instantaneous perturbation).
  - Propagate the KS orbitals for a long time (the longer the propagation, the higher the energy resolution.

- 3 Sample the dipole moment in time series.

$$\mu_\gamma(t) = \int \mathrm{r}_\gamma \cdot n(\boldsymbol{r},t)d\boldsymbol{r}$$

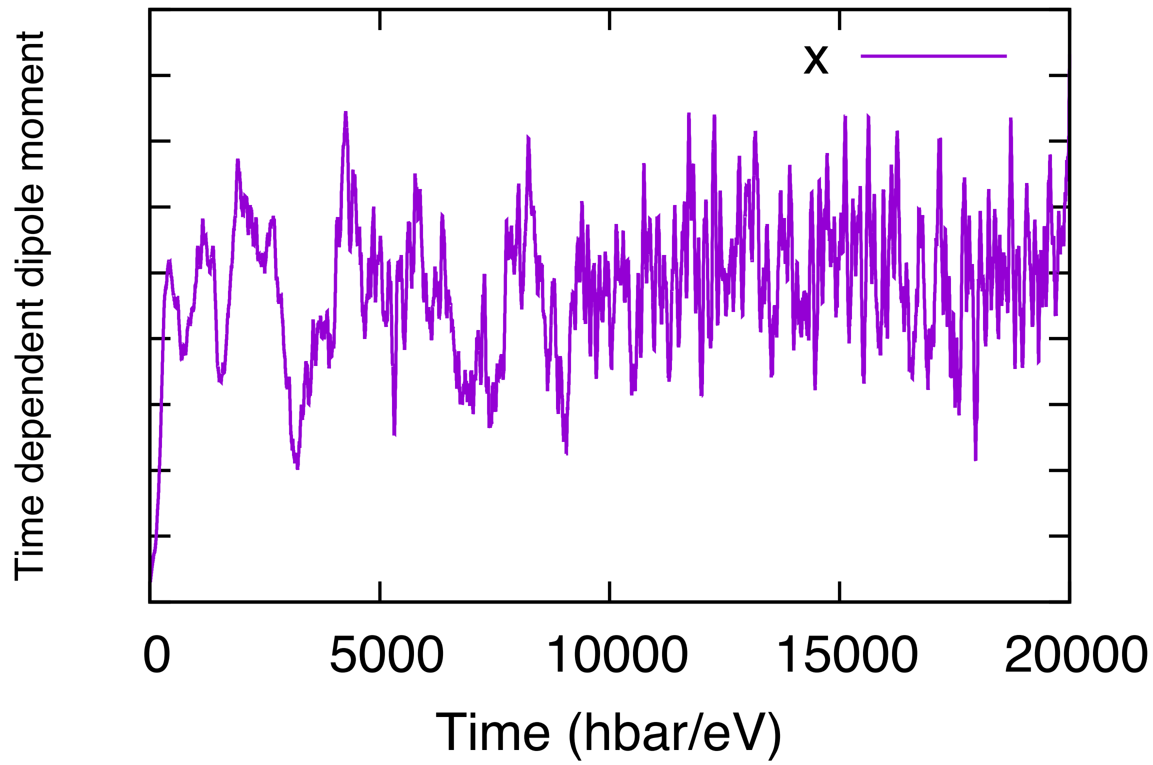
- 4 Fourier transform to obtain the dynamic polarisability

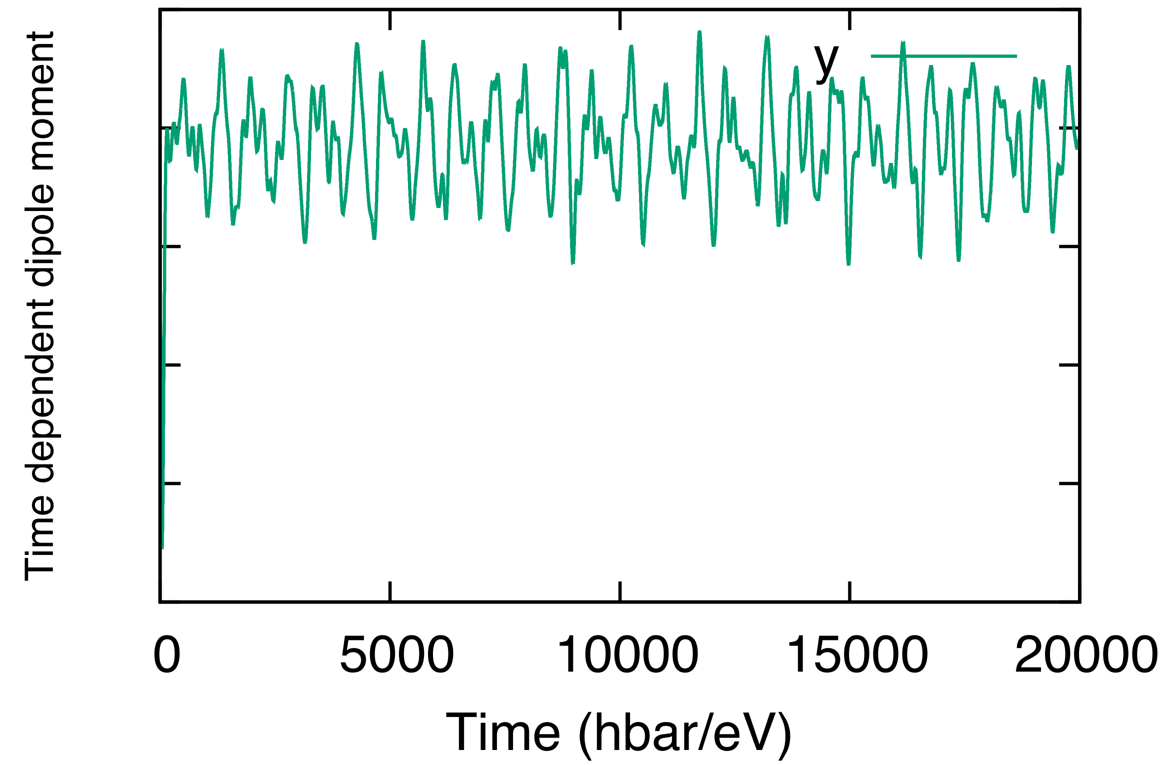
$$\alpha_{\gamma\delta}(\omega) = \frac{1}{K_\delta}\int_0^\infty dt[\mu_\gamma(t) - \mu_\gamma(0)]e^{-i\omega t}$$

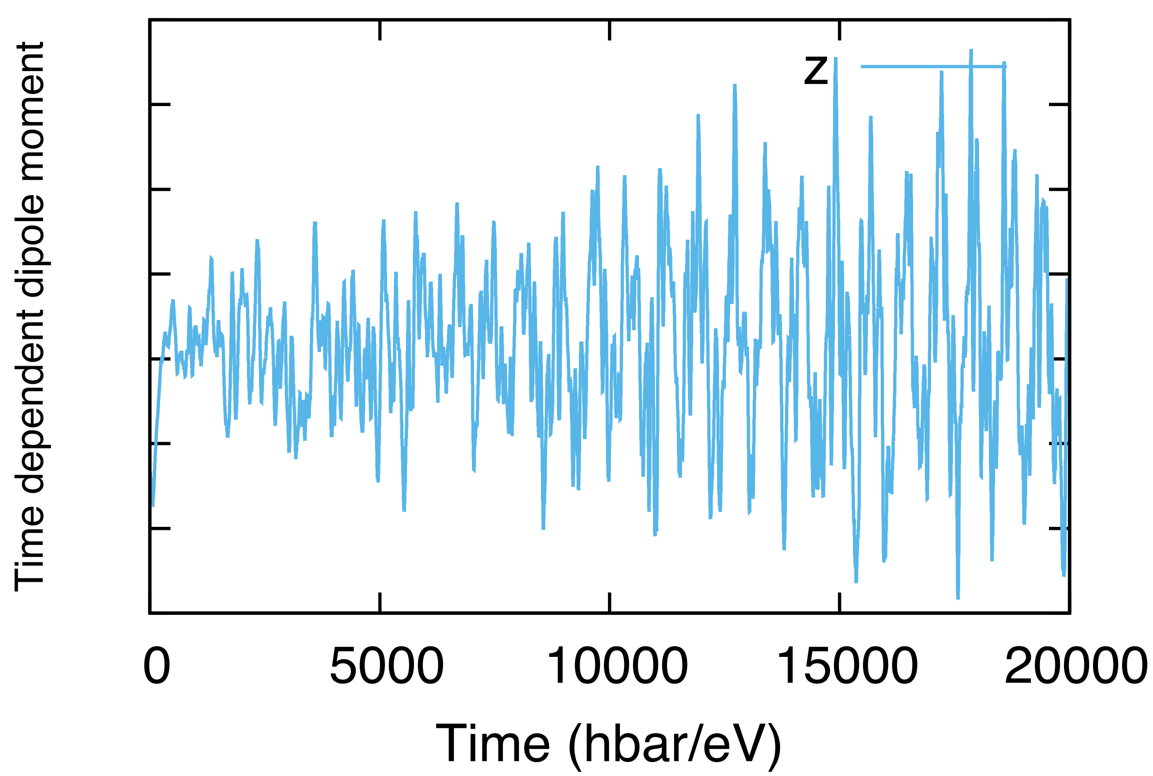
- 5 Spectrum can be obtained from the photo absorption cross-section:

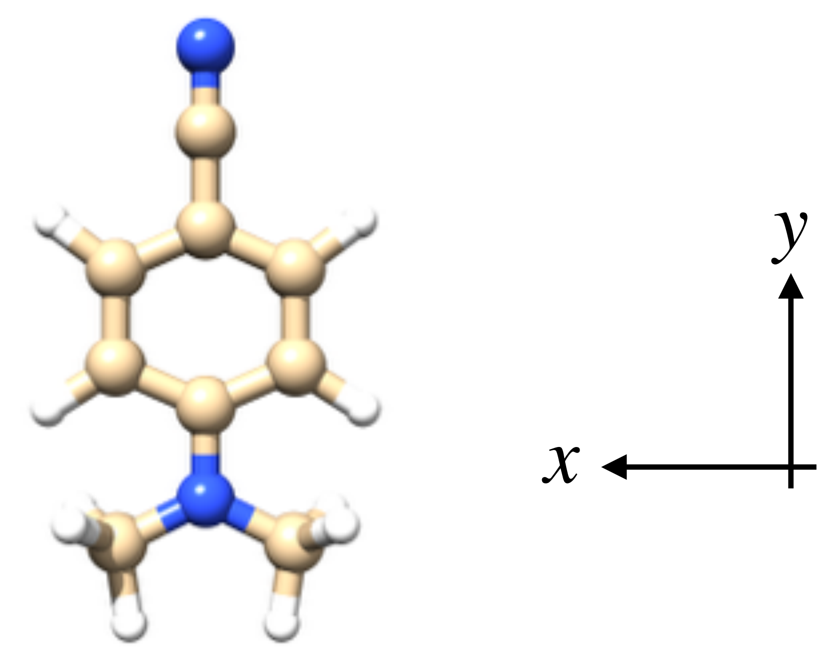
$$\sigma(\omega) = \frac{4\pi\omega}{3c}\Im\mathrm{m}[\alpha(\omega)]$$

Example: (DMABN) N,N-dimethylaminobenzonitrile

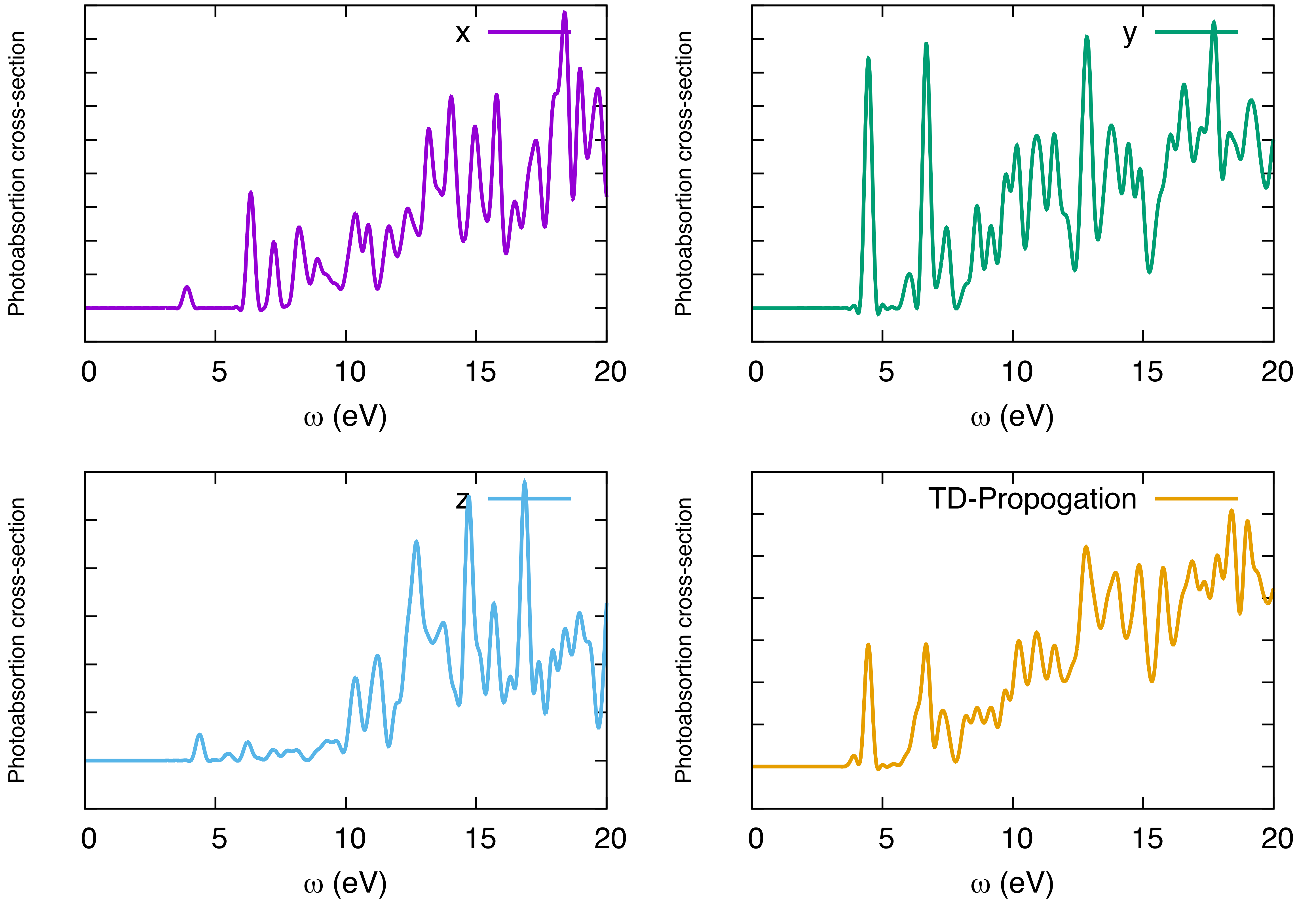








Example: (DMABN) N,N-dimethylaminobenzonitrile



Practical Issues

Let us ask: under what circumstances is it preferable to use **time propagations** as opposed to the **Casida equation** ?

- The **Casida equation** is generally the superior method for low-lying, well-separated excitation energies of molecular systems. Bottleneck: it depends on unoccupied states (low convergence with respect to the basis size)
- One can achieve a numerical scaling of TDDFT in the Casida formalism of N^2 to N^3. A substantial part of the **computational cost goes into building the K matrix**.

$$K_{ia,bj} = \int d^3r \int d^3r' \Phi^*_{ia}(\boldsymbol{r}) f_{Hxc} \Phi_{jb}(\boldsymbol{r}'); \qquad \Phi_{ia}(\boldsymbol{r}) = \varphi^*_i(\boldsymbol{r})\varphi_a(\boldsymbol{r})$$

- **Time propagation methods** are advantageous if they are carried out on real-space grid. These are more convenient if one wants an excitation or photoabsorption spectrum over a large spectral range (including the continuum and autoionization states)
- The numerical scaling is somewhere around N to N^2. However, since the real dynamics of the electrons has high frequencies, it requires a small time step (~10^-3 a.u.), which adds an **important cost factor**.

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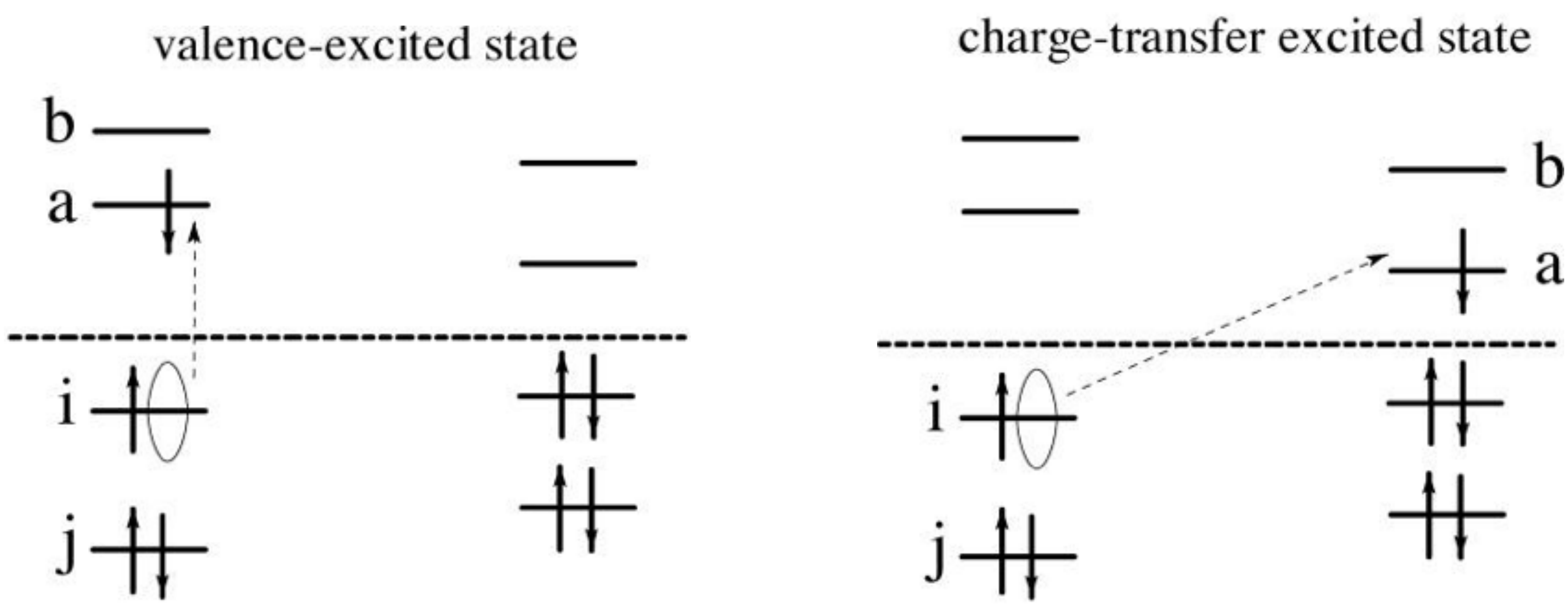
  - Charge-Transfer excitations
  - PES topology

Charge-Transfer (CT) Problem

Current xc-functionals usually underestimate dramatically charge transfer excitation state energies.

Charge transfer according to IUPAC
An electronic transition in which a large fraction of an electronic charge is transferred from one region of a molecular entity, called the electron donor, to another, called the electron acceptor (intramolecular CT) or from one molecular entity to another (intermolecular CT).



Some known failures of the TDDFT

Charge-Transfer (CT) Problem

Current xc-functionals usually underestimate dramatically charge transfer excitation state energies.

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

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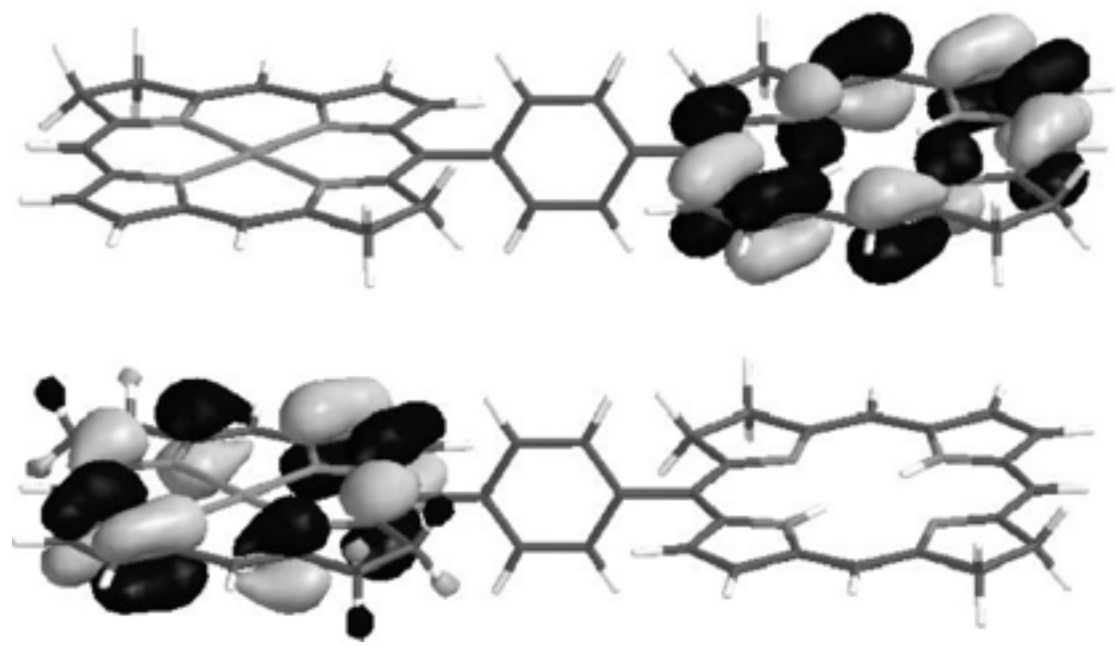
Contribution from the Institut für Physikalische und Theoretische Chemie, Johann Wolfgang Goethe-Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt, Germany, and Department of Chemistry, University of California, Berkeley, and Chemical Science and Physical Bioscience Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1470



Charge-Transfer (CT) Problem

Current xc-functionals usually underestimate dramatically charge transfer excitation state energies.

Exercise: Why does LR-TDDFT in AA fail to evaluate CT excitation energies?

$$\begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B}^* & \mathbb{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -\mathbb{I} & 0 \\ 0 & \mathbb{I} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia,jb} = \delta_{ia}\delta_{jb}(\epsilon_a - \epsilon_i) + K_{ia,jb}$$
$$B_{ia,jb} = K_{ia,bj}$$

where the Hartree-exchange-correlation matrix elements are defined as

$$K_{ia,jb} = \int d^3r \int d^3r' \Phi^*_{ia}(\boldsymbol{r}) f_{Hxc} \Phi_{jb}(\boldsymbol{r}'); \qquad \Phi_{ia}(\boldsymbol{r}) = \varphi^*_i(\boldsymbol{r})\varphi_a(\boldsymbol{r})$$

Then, if the *Adiabatic Approximation* if applied to the exchange-correlation kernel, in both time and space domain ($f_{xc}(\boldsymbol{r}, \boldsymbol{r}', \omega) \approx f_{xc}(\boldsymbol{r})\delta(\boldsymbol{r} - \boldsymbol{r}')$), the $\boldsymbol{K}$ matrix vanishes because the (i,a)-overlapping are zero.

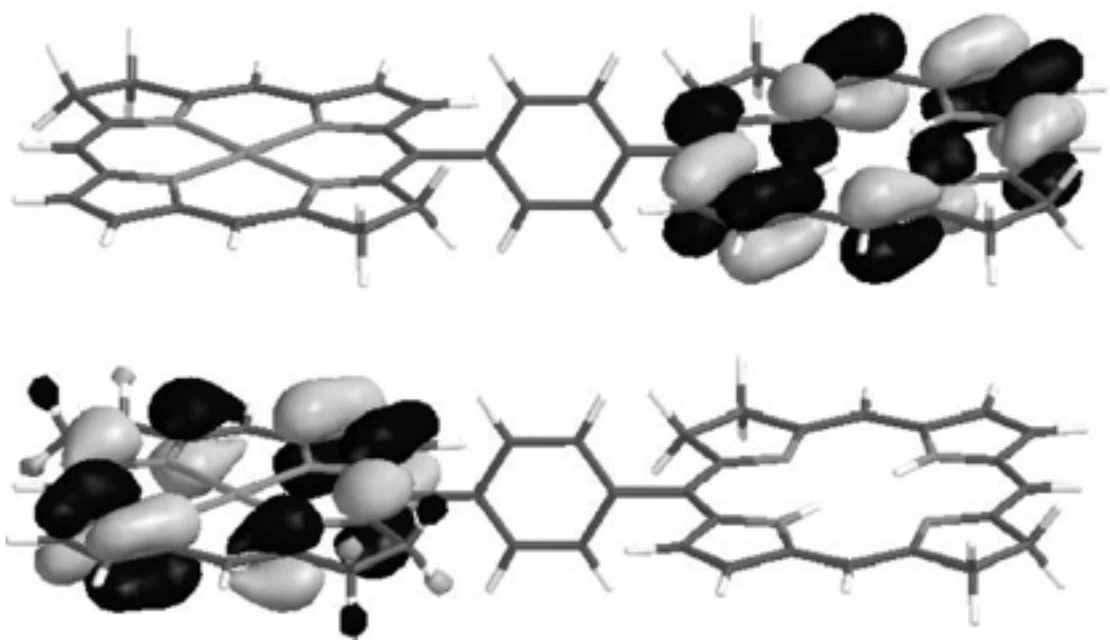
One solution: include the Fock-exchange term into the kernel (i.e. hybrid functionals)

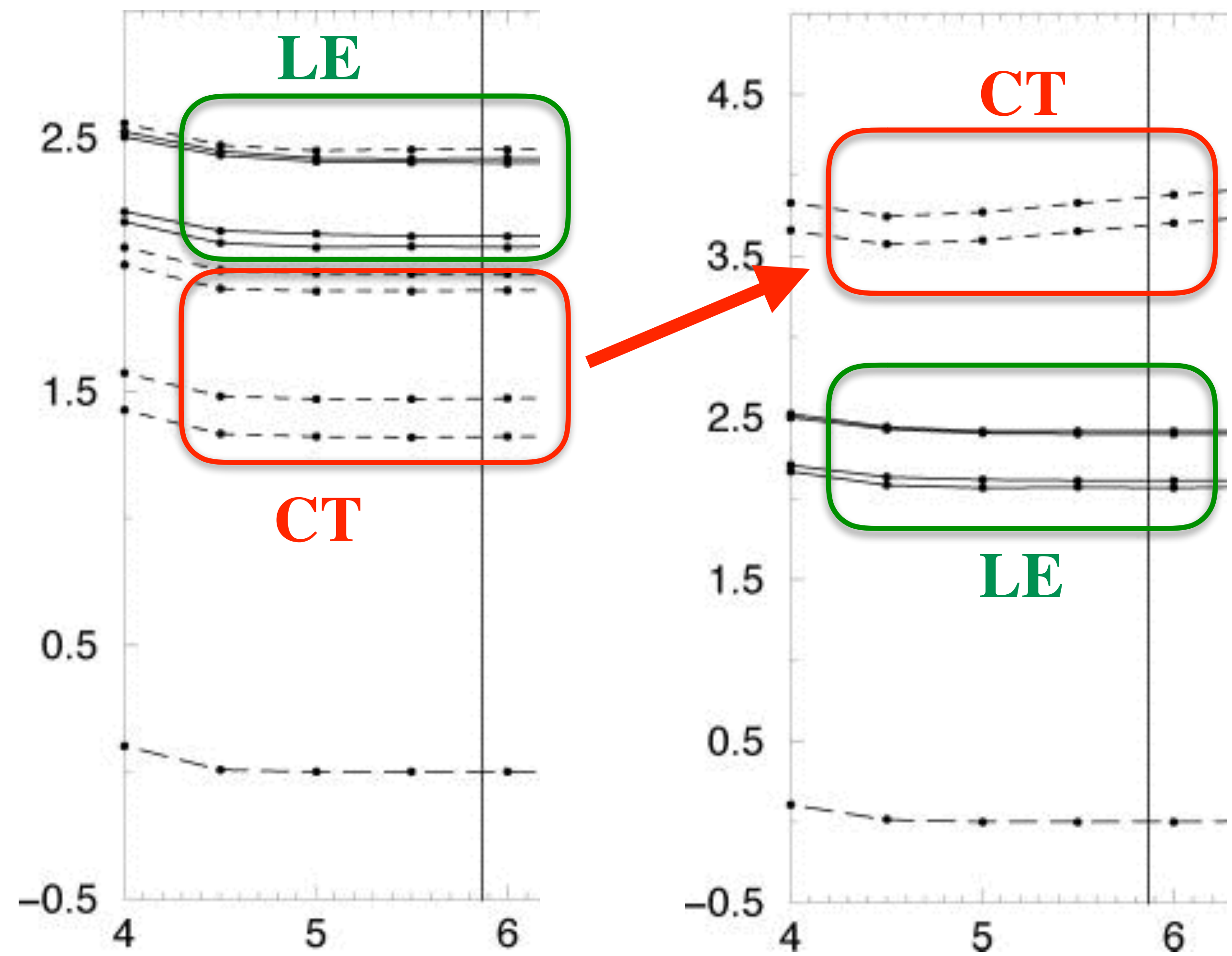
$$A_{ia,jb} = \delta_{ia}\delta_{jb}(\epsilon_a - \epsilon_i) + J_{ia,jb} - c_{\mathrm{HF}} J_{ij,ab} + (1 - c_{\mathrm{HF}})K'_{ia,jb}$$
$$B_{ia,jb} = J_{ia,bj} - c_{\mathrm{HF}} J_{ib,aj} + (1 - c_{\mathrm{HF}})K'_{ia,bj}$$

notice that the only non-zero term is due to the HF exact exchange term of the A matrix. All other terms are zero because the orbitals i,j are localised on molecule 1, and a,b in molecule 2.

Charge-Transfer (CT) Problem

Current xc-functionals usually underestimate dramatically charge transfer excitation state energies.





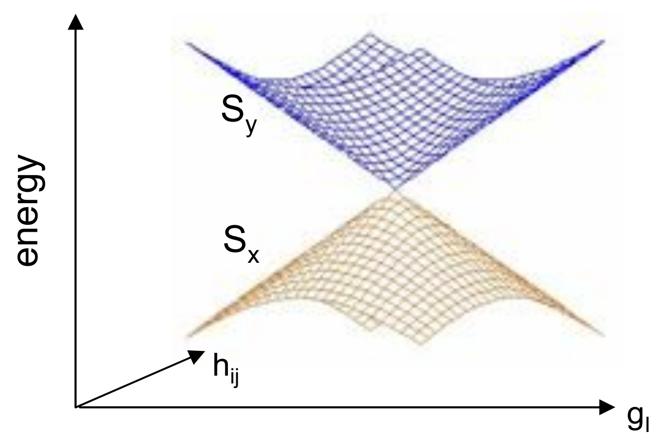
GGA+ALDA (BLYP) **HYBRID: B3LYP**

LUMO is generally more strongly bound in DFT, then the orbital energy difference corresponding to a CT state (pure TDDFT) is **usually a drastic underestimation** of its correct excitation energy.

Topology of the excited states

What about the topology of the TDDFT PESs close to a conical intersection?

Photochemistry/photophysics require a correct description of the topological properties of the most relevant potential energy surfaces involved. **Conical intersections** (CX) are now recognized to play a critical role in the reaction dynamics of electronic excited states.



CI topology is characterised by the "branching space"

difference gradient: $g_{ij} = \nabla_{\mathbf{R}}(E_j - E_i)$

non-adiabatic coupling vector: $h_{ij} = \langle \Psi_i | \nabla_{\mathbf{R}} | \Psi_j \rangle$

Some known failures of the TDDFT

Topology of the excited states

What about the topology of the TDDFT PESs close to a conical intersection?

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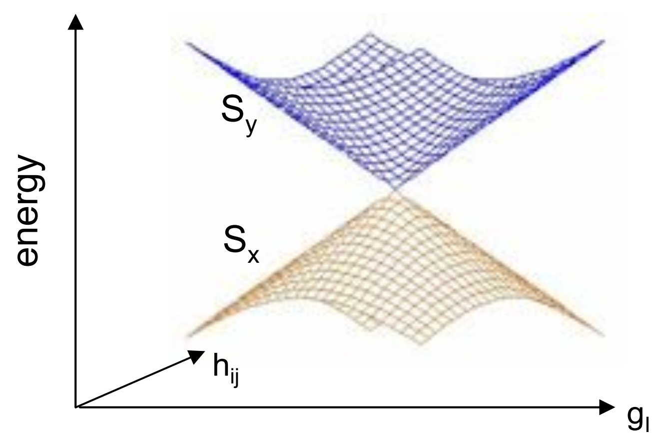
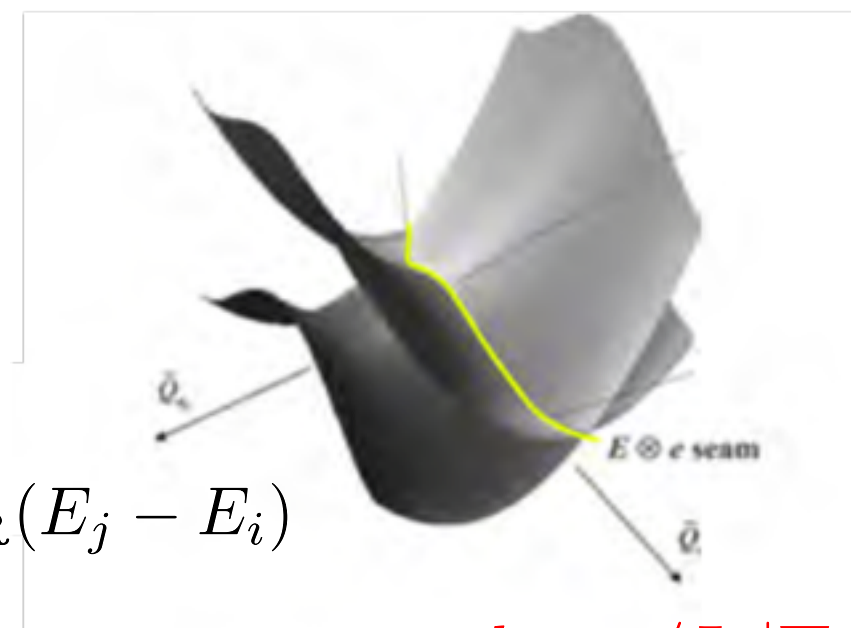


$$g_{ij} = \nabla_{\mathbf{R}}(E_j - E_i)$$



$$h_{ij} = \langle \Psi_i | \nabla_{\mathbf{R}} | \Psi_j \rangle = 0$$

By applying Brillouin's theorem, one can show that restricted CIS (for closed shell systems) has the wrong dimensionality for the intersection with the S0 PES: **f – 1 (a seam of intersections instead of a conical intersection).**
Therefore, it is believed that CXs should not normally exist at the **configuration interaction singles** (CIS) level when the ground state is a closed-shell singlet

Topology of the excited states

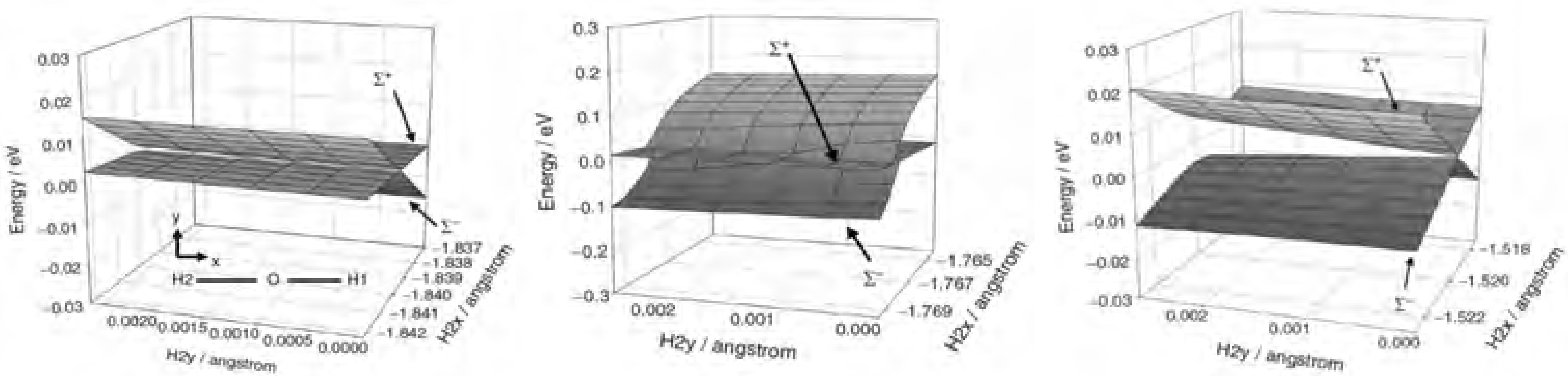
Concerning the coupling between S0 and S1, the main issue is to understand **if LR-TDDFT** in the usual approximations (adiabatic TDA with standard GGA functionals) **can correctly predict the dimensionality** of the intersection between the two surfaces.

Although the structure of the LR-TDDFT/TDA equations in the matrix formulation (Casida's equations) is similar to CIS, the Brillouin's theorem, does not hold in TDDFT and the question about the existence of CXs in DFT/LR- TDDFT remains open.

Some examples:

S0/S1 intersection in linear water (Mol. Phys., 104, 1039 (2006))

CIS **TDDFT** **CASSCF**



Usual approximation of TDDFT fails on the CI description.

Some known failures of the TDDFT

Topology of the excited states

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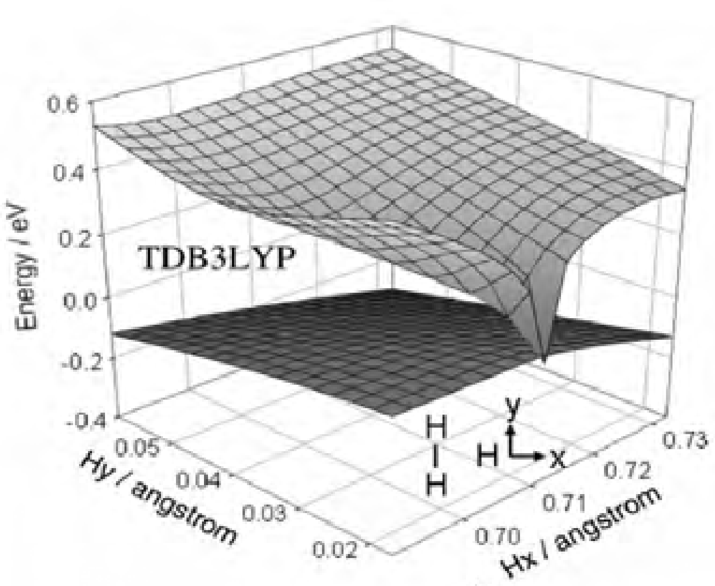
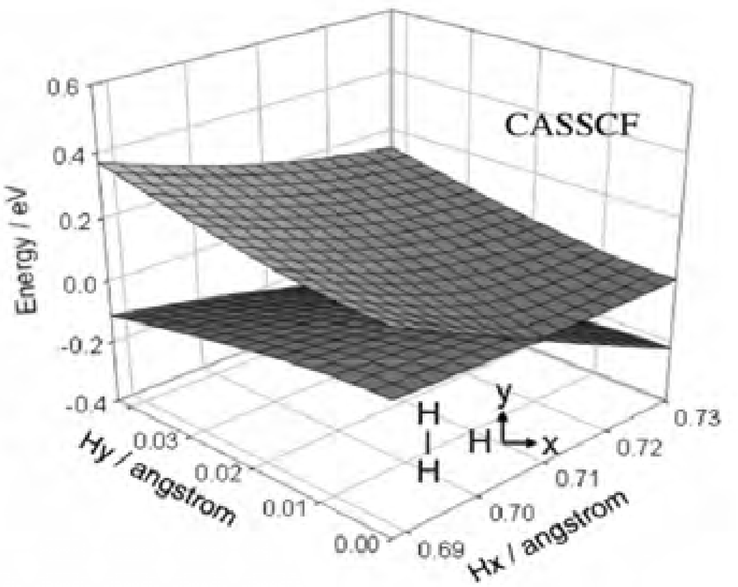
Some examples:

S0/S1 for H2 + H (Mol. Phys., 104, 1039 (2006))

TDDFT



CASSCF



Usual approximation of TDDFT gives a qualitatively description of the CI
(slope around the CI is much steeper)

Some known failures of the TDDFT

Topology of the excited states

Concerning the coupling between S0 and S1, the main issue is to understand **if LR-TDDFT** in the usual approximations (adiabatic TDA with standard GGA functionals) **can correctly predict the dimensionality** of the intersection between the two surfaces.

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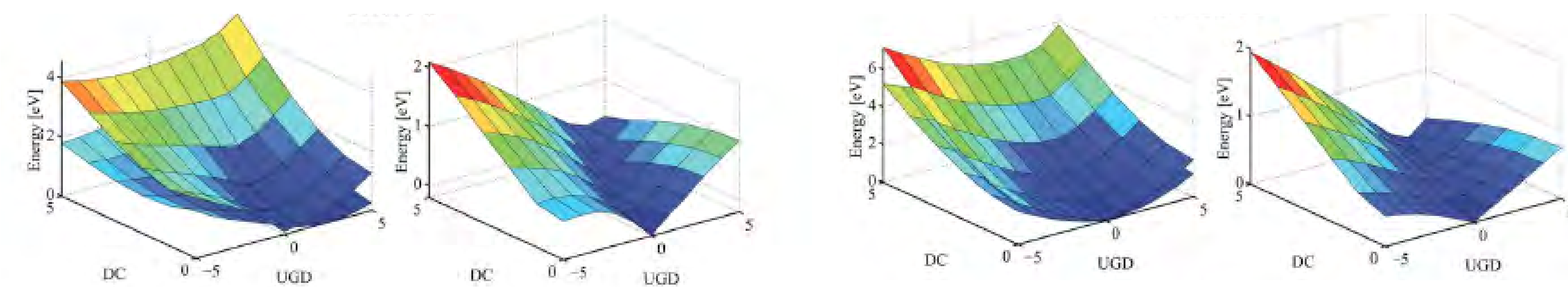
Some examples:

S0/S1 for C2H4O (J. Chem. Phys. 129, 124108 (2008))

TDDFT **CASSCF**



but it is not always the case !!!

Short-Summary for LR-TDDFT for Excitation energies

Applicability of TDDFT

- For valence excited states well below the ionization potential—> error between 0.2 and 0.6 eV (0.1 eV ≈ 10 kJ/mol).
- Good ordering and relative energies of the excited states (except for CT states). Good also for transition metals (difficult for wavefunction based methods).
- Scales ~ like $O(n^2)$ with n the number of electrons: can deal with very large systems up to many hundreds of atoms.

- Many times, TDDFT properties are bad because the underlying DFT is inaccurate (bond dissociations, biradicals, self-interaction error, . . .).
- Topology of the excited surfaces is not always correct.
- Problems to describe double excitations, Rydberg excited states, large π systems.
- Standard xc functionals fail in the case of CT states.
  Errors in the ordering of the excited PESs is deleterious for excited states MD.

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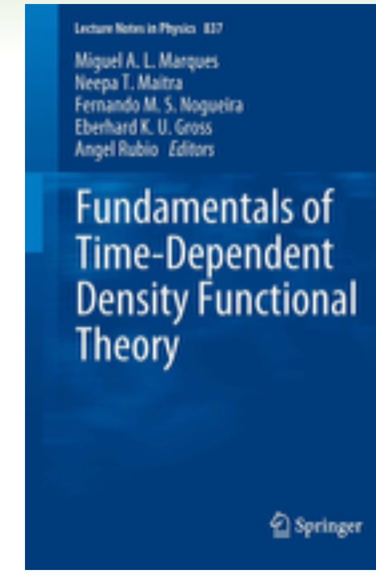
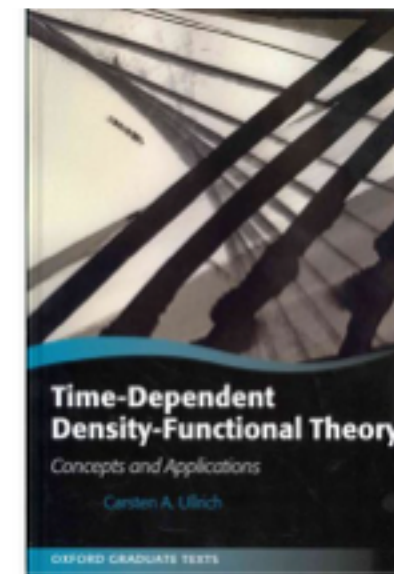


- *Time-dependent density-functional theory : concepts and applications* Author:Carsten Ullrich Publisher: Oxford ; New York : Oxford University Press, 2012.



- *TDDFT for excitation energies: TDDFT for ultrafast electronic dynamics Ivano Tavernelli and Basile Curchod. (http://benasque.org/2014tddft/talks_contr/103_Ivano1.pdf)*

- *Time Dependent Density Functional Response Theory for Molecules* Mark E. Casida . *Recent Advances in Density Functional Methods: pp. 155-192.(1995). DOI: http://dx.doi.org/10.1142/9789812830586_0005*