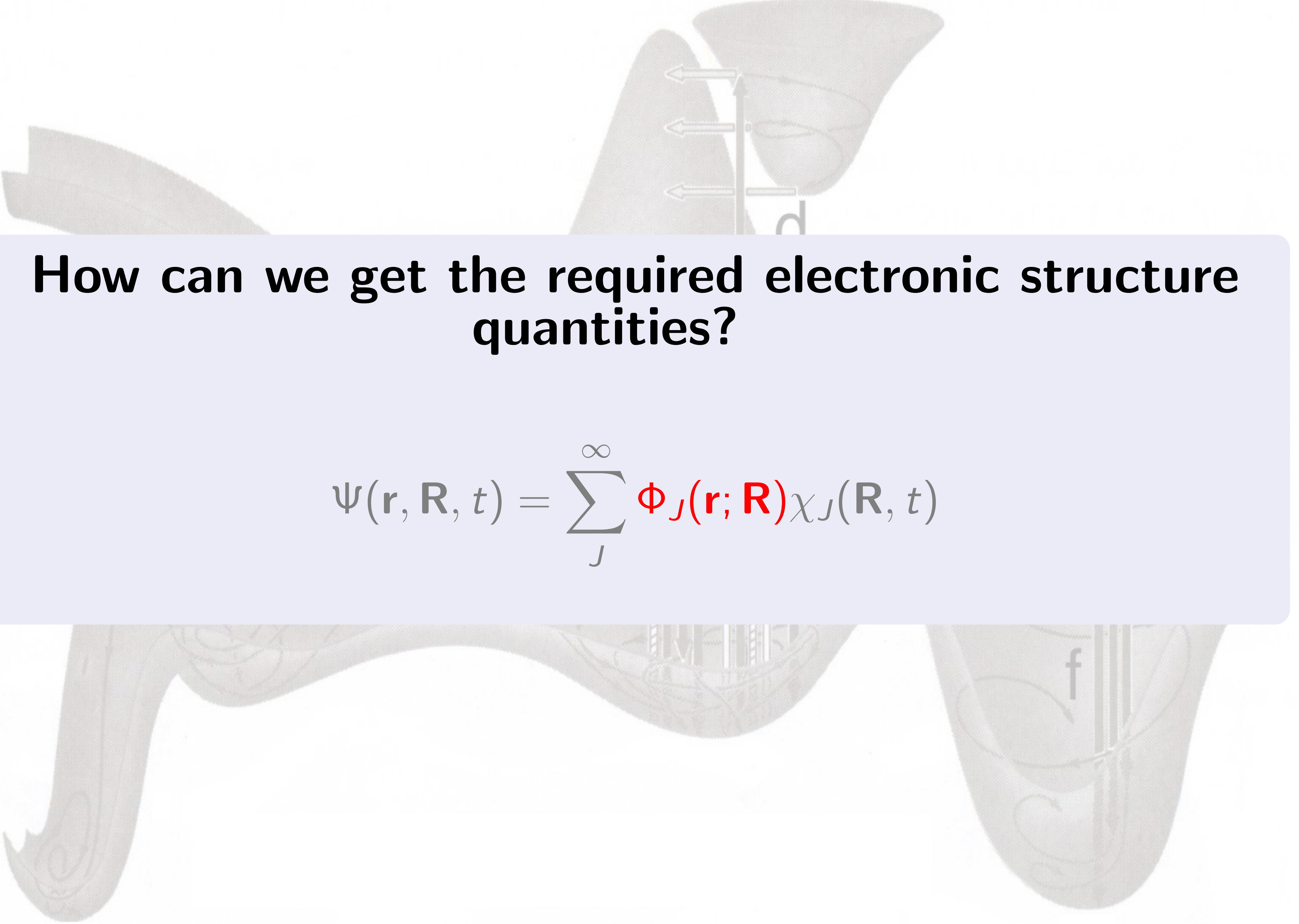
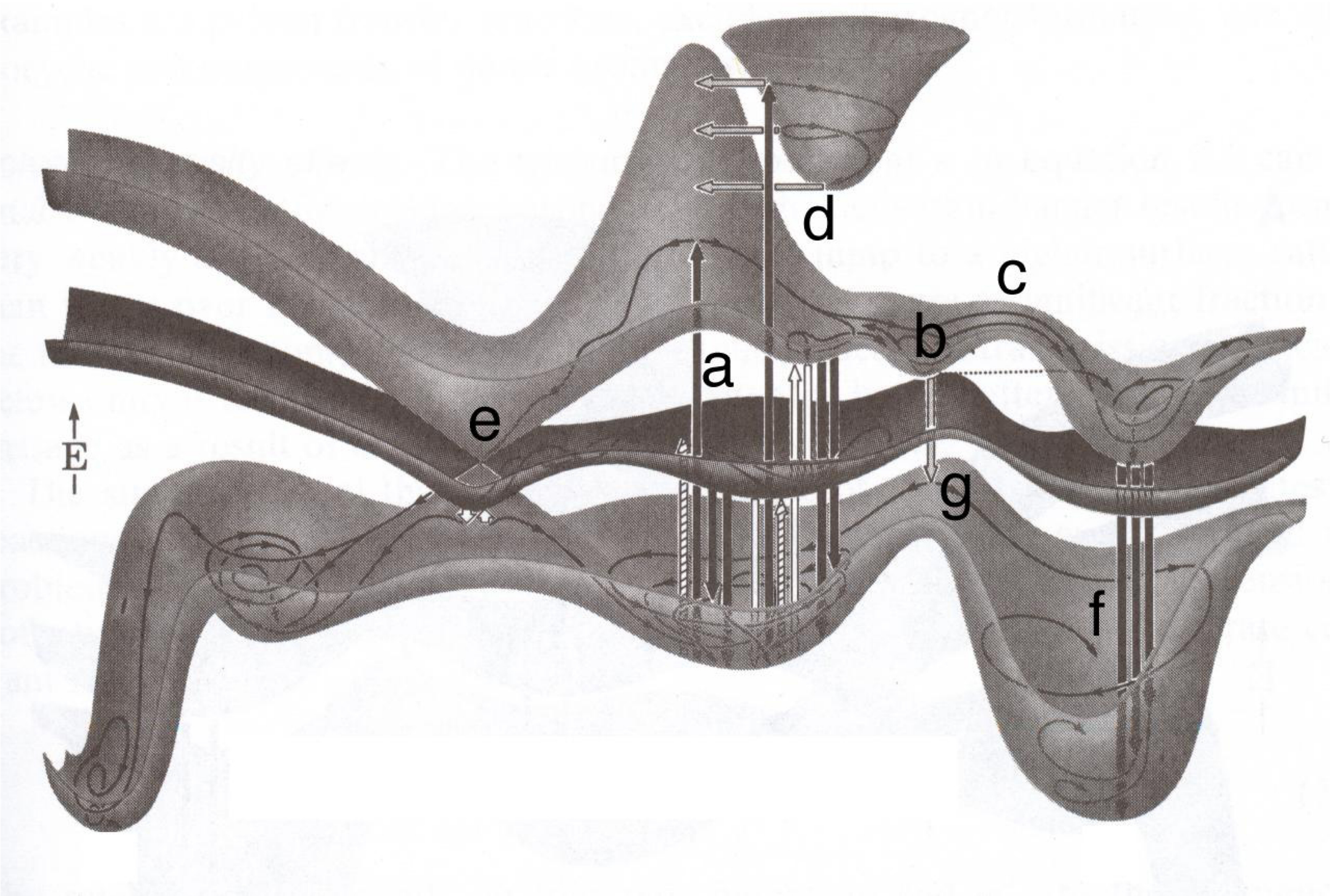


How can we get the required electronic structure quantities?

$$\Psi(\mathbf{r},\mathbf{R},t)=\sum_{J}^{\infty}\Phi_J(\mathbf{r};\mathbf{R})\chi_J(\mathbf{R},t)$$

Credit: J. Michl and V. Bonacic-Koutecký, “Electronic Aspects of Organic Photochemistry”. John Wiley and Sons, Inc., New York, 1990.

Crash course on potential energy surfaces



Credit: Electronic Aspects of Organic Photochemistry, J. Michl and V. Bonačić-Koutecký

Challenge for electronic structure theory

Excited-state dynamics is a real challenge for electronic structure theory.

Electronic structure method should, ideally...

1. ... describe equally well the different electronic states of interest
2. ... be able to describe accurately the couplings between electronic states
3. ... be efficient if used in combination with on-the-fly (direct) dynamics
4. ... not require an extremely large basis set to be converged
5. ... be robust when visiting different regions of the configuration space
6. ... provide all the quantities we need for the nuclear dynamics

As of today, no method can satisfy all of the different points listed above.

We will always be looking for a compromise between efficiency and accuracy.

Challenge for electronic structure theory

Electronic structure methods that could be used for excited-state dynamics:

- CIS (configuration interaction singles)
- LR-TDDFT (linear-response time-dependent density functional theory)
- ADC(2) (algebraic diagrammatic construction of second order)
- CC2 (approximate coupled-cluster method of second order)
- (SA-)CASSCF
- (MS-)CASPT2
- MR-CI
- FOMO-CASCI (floating occupation molecular orbital CASCI)
- SI-SA-REKS (state-interaction state-average spin-restricted ensemble-referenced Kohn Sham)
- MRCI-OM2 (MRCI based on the orthogonalization method 2)

(Important to keep in mind that the method should not only provide $E_I^{el}(\mathbf{R})$, but also $\mathbf{F}_{I,\gamma} = -\nabla_{\mathbf{R}_\gamma} E_I^{el}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}^\alpha}$ and $\mathbf{d}_{IJ}(\mathbf{R}) = \langle \Phi_I(\mathbf{R}) | \nabla_{\mathbf{R}} | \Phi_J(\mathbf{R}) \rangle_{\mathbf{r}}$ if we want on-the-fly dynamics in the adiabatic representation.)

Methods commonly employed for excited-state dynamics

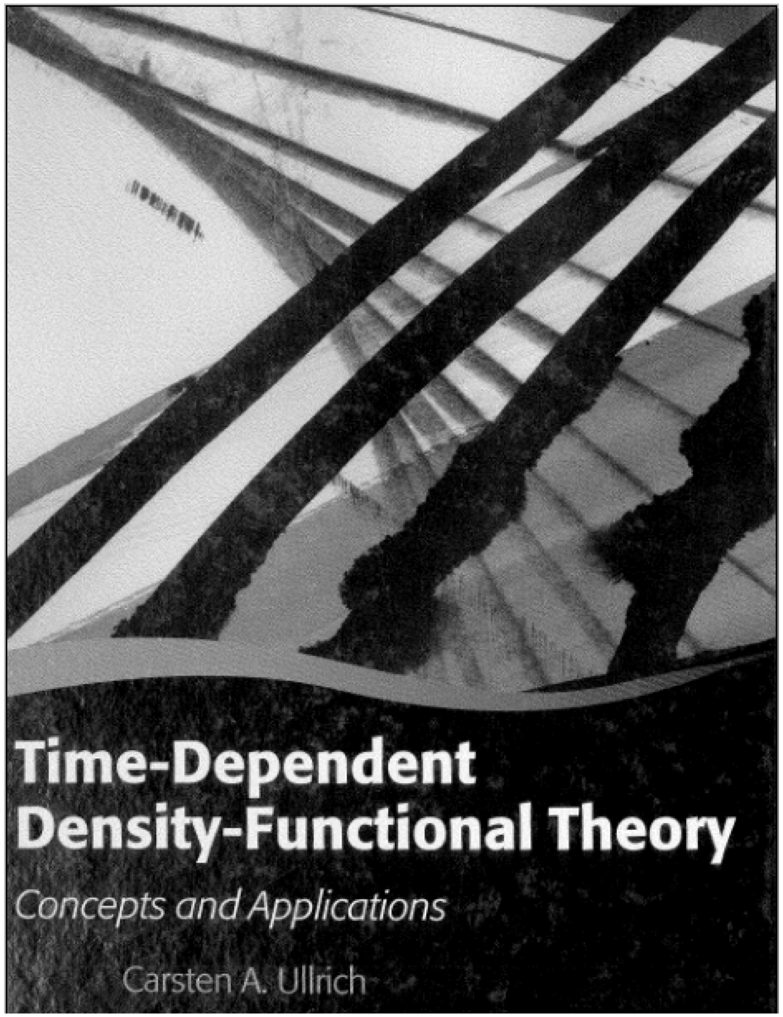
In practice, most commonly employed methods for excited-state dynamics:

- LR-TDDFT (within the adiabatic approximation and approximate exchange/correlation potential+kernel): failure with CT states, S_0/S_1 CIs, double excitations, can formally describe only ground-to-excited-state quantities (quadratic response theory needed beyond that but unstable within the adiabatic approximation[1,2]; but LR is a good approximation[3]).
- ADC(2): failure with S_0/S_1 CIs, might need a large basis set, approximate way of calculating $\mathbf{d}_{IJ}$[4].
- CC2: instabilities in regions where electronic states are degenerate[2,4].
- (SA-)CASSCF: neglect of dynamic correlation, imbalance description of electronic states[5].
- (MS-)CASPT2: intruder states, cost, instabilities (XMS-CASPT2 better)[5,6].

[1] JCP, **145**, 134105 (2016); [2] JCP, **141**, 244105 (2014); [3] JCP, **133**, 194104 (2010); [4] JCTC, **10**, 1395 (2014); [5] CPC, **13**, 28 (2011); [6] PCCP, **15**, 262 (2013).

(Important to keep in mind that the method should not only provide $E_I^{el}(\mathbf{R})$, but also $\mathbf{F}_{I,\gamma} = -\nabla_{\mathbf{R}_\gamma} E_I^{el}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}^\alpha}$ and $\mathbf{d}_{IJ}(\mathbf{R}) = \langle \Phi_I(\mathbf{R}) | \nabla_{\mathbf{R}} | \Phi_J(\mathbf{R}) \rangle_{\mathbf{r}}$ if we want on-the-fly dynamics in the adiabatic representation.)

Reference for TDDFT

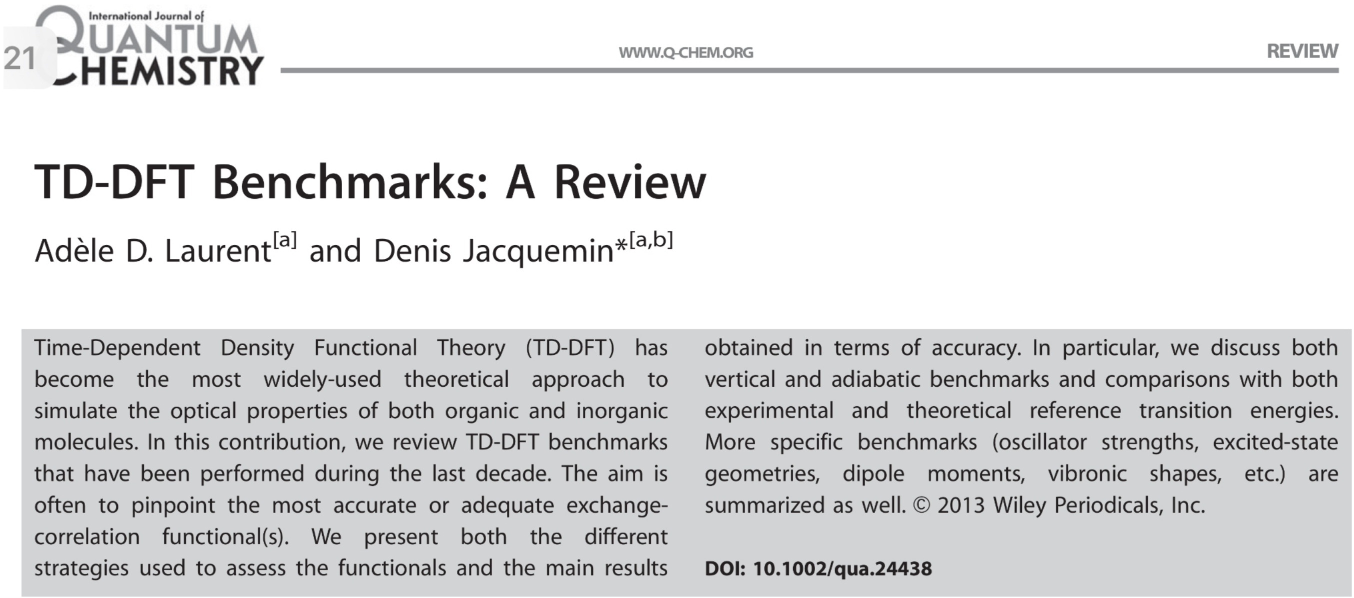

Time-Dependent Density-Functional Theory

Concepts and Applications

Carsten A. Ullrich

Benchmarks for TDDFT

A large number of benchmarks for LR-TDDFT based on excitation energies and geometries are available in the literature.
We can find reviews of benchmarks [IJQC, **113**, 2019 (2013)].



21 International Journal of QUANTUM CHEMISTRY WWW.Q-CHEM.ORG REVIEW

TD-DFT Benchmarks: A Review

Adèle D. Laurent[a] and Denis Jacquemin*[a,b]

Time-Dependent Density Functional Theory (TD-DFT) has become the most widely-used theoretical approach to simulate the optical properties of both organic and inorganic molecules. In this contribution, we review TD-DFT benchmarks that have been performed during the last decade. The aim is often to pinpoint the most accurate or adequate exchange-correlation functional(s). We present both the different strategies used to assess the functionals and the main results obtained in terms of accuracy. In particular, we discuss both vertical and adiabatic benchmarks and comparisons with both experimental and theoretical reference transition energies. More specific benchmarks (oscillator strengths, excited-state geometries, dipole moments, vibronic shapes, etc.) are summarized as well. © 2013 Wiley Periodicals, Inc.

DOI: 10.1002/qua.24438

Maybe more interesting are benchmarks of different functionals for oscillator strengths [*JCTC*, **7**, 456 (2011)], singlet/triplet splitting [*JCTC*, **6**, 1532 (2010)], spin-orbit couplings [*JCTC*, **13**, 515 (2017)], nonadiabatic dynamics [*JCTC*, **10**, 1395 (2014)]...

Nonadiabatic coupling vectors within LR-TDDFT? Yes! Not straightforward but they can be calculated! See for example *ChemPhysChem*, **14**, 1314 (2013).

An important failure: charge transfer (CT) problem

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

An important failure: charge transfer (CT) problem

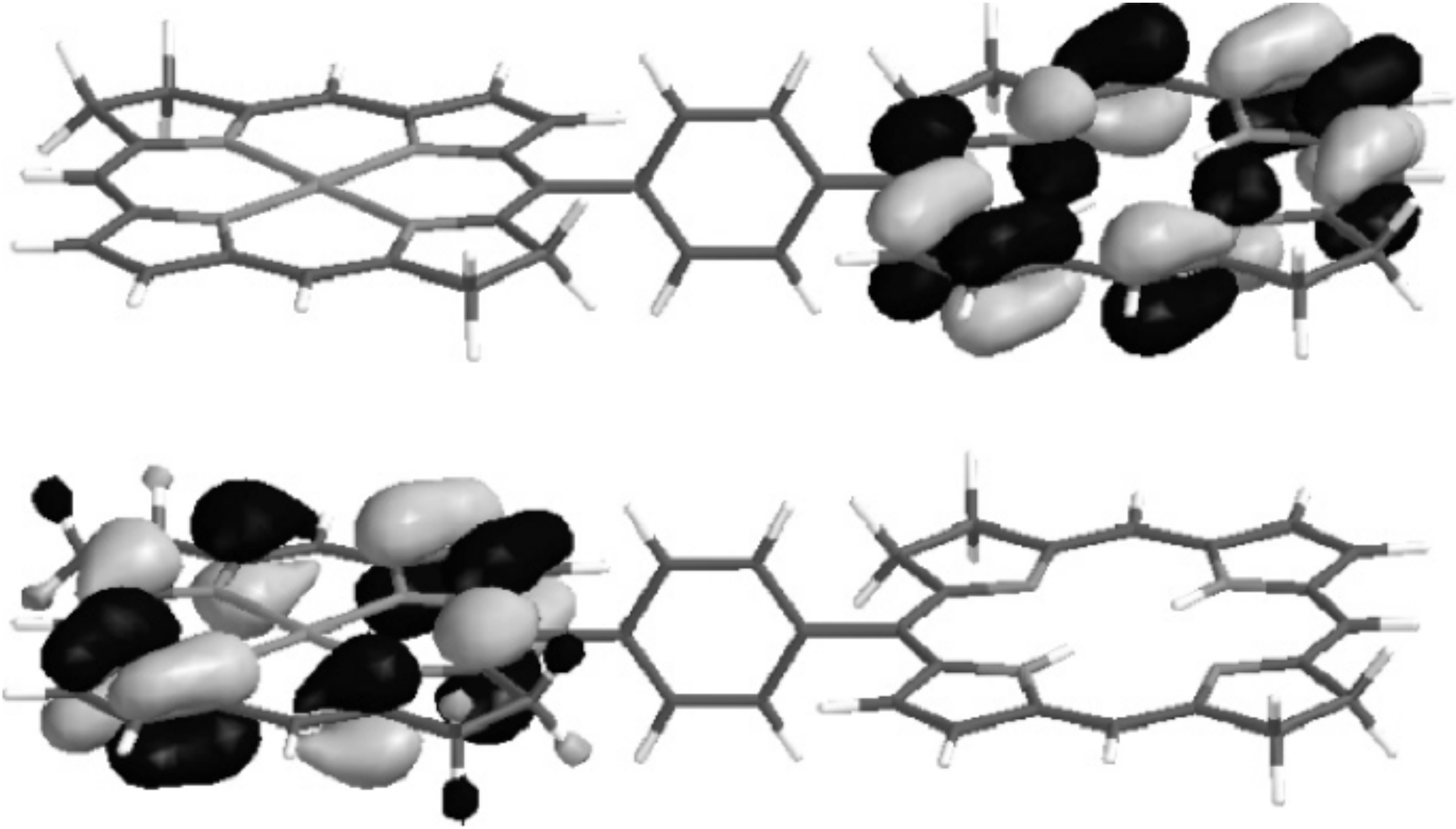
Current *xc*-functionals usually underestimate dramatically charge-transfer excitation energies.

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).

An important failure: charge transfer (CT) problem

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



An important failure: charge transfer (CT) problem

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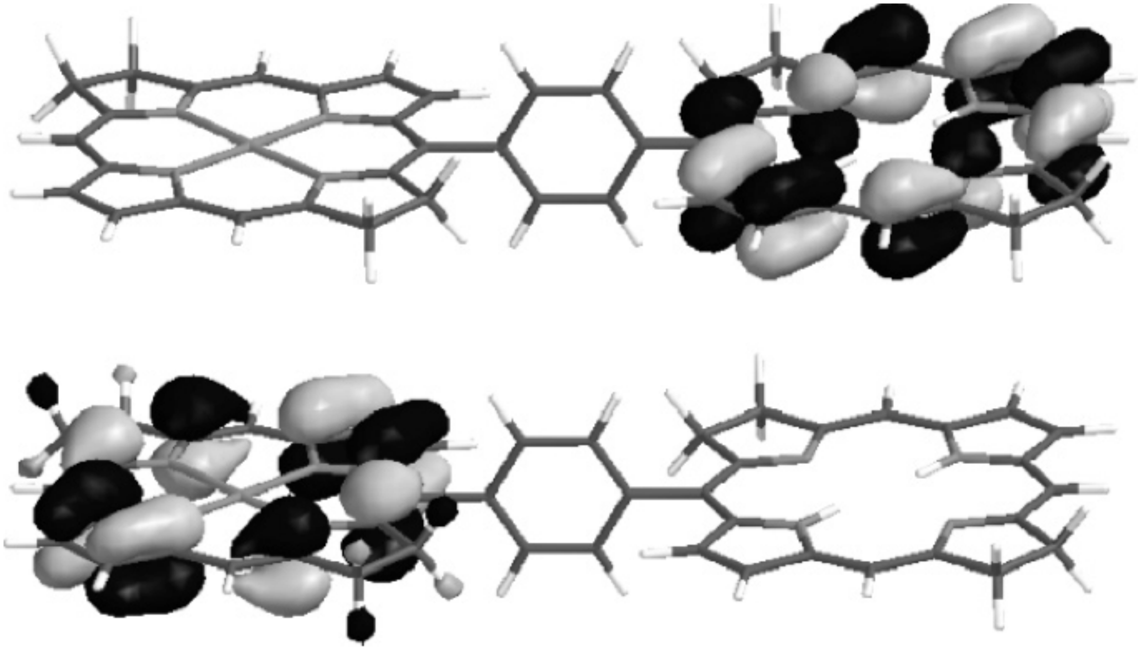


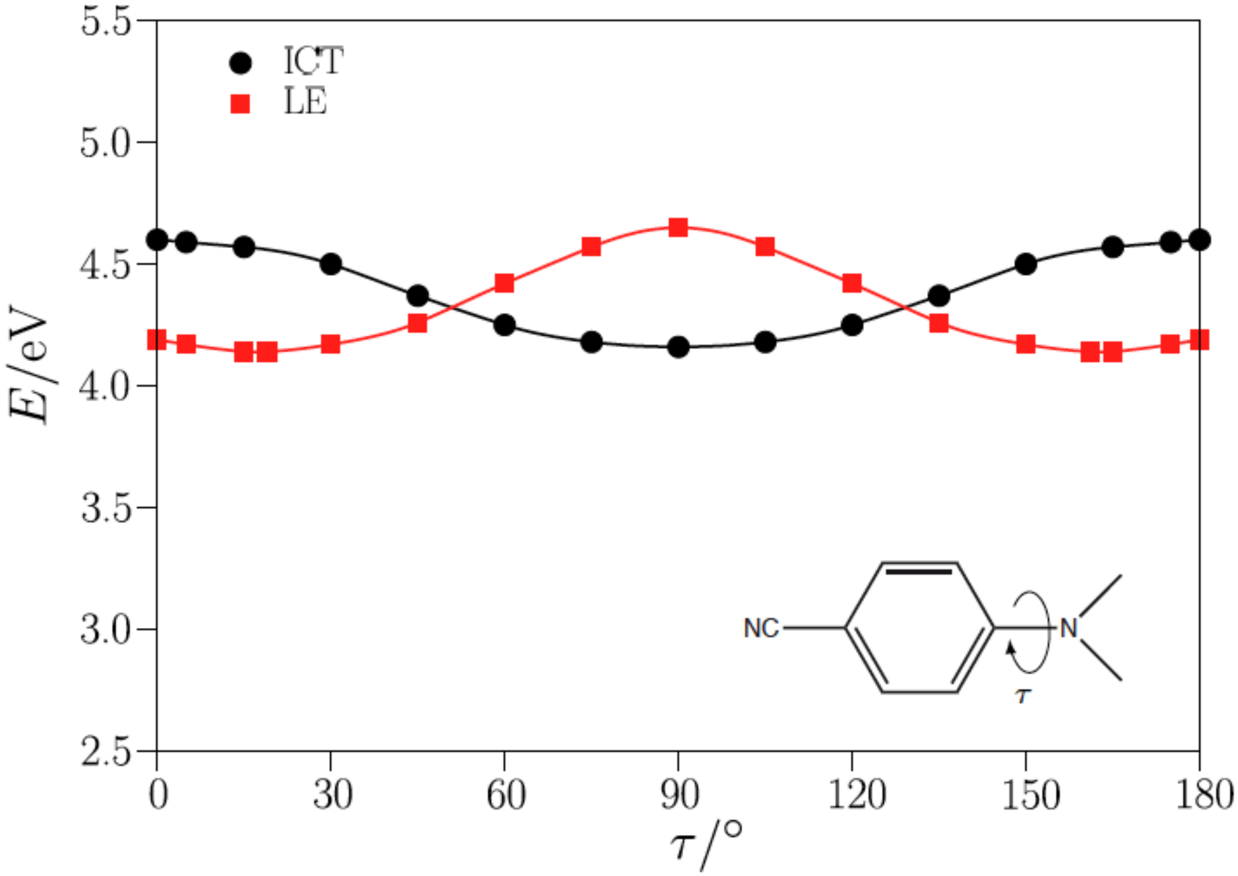
Figure: JACS, **126**, 4007 (2004)

More on this issue during Christine's lecture. Just keep in mind that the CT problem mostly emanates from the adiabatic approximation inherent to a practical use of LR-TDDFT.

Example of CT problem

N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
[*JCP*, **131**, 091101 (2009)]

CC2 (wavefunction-based method)



Example of CT problem

N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
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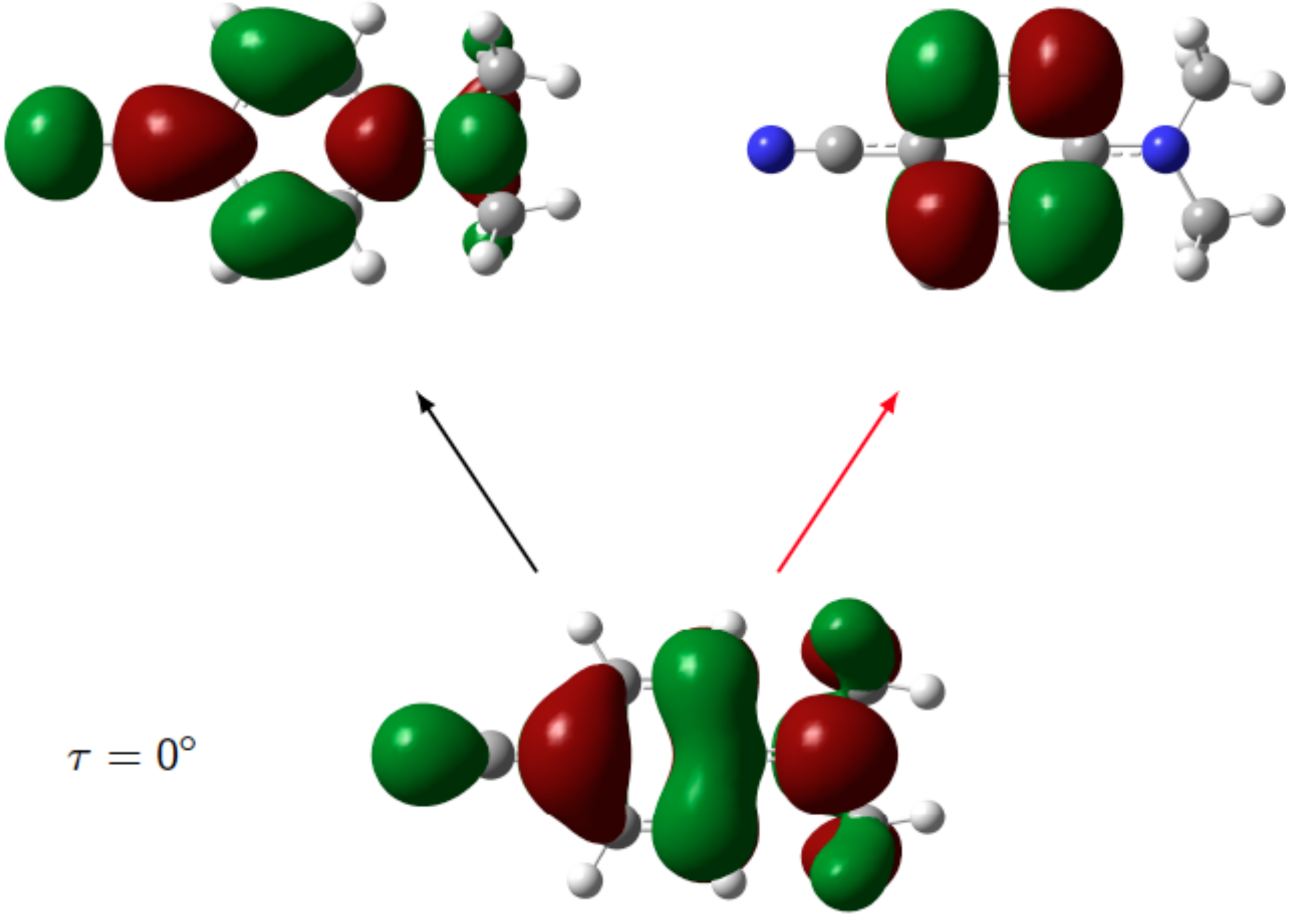

$\tau = 0^\circ$

Example of CT problem

N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
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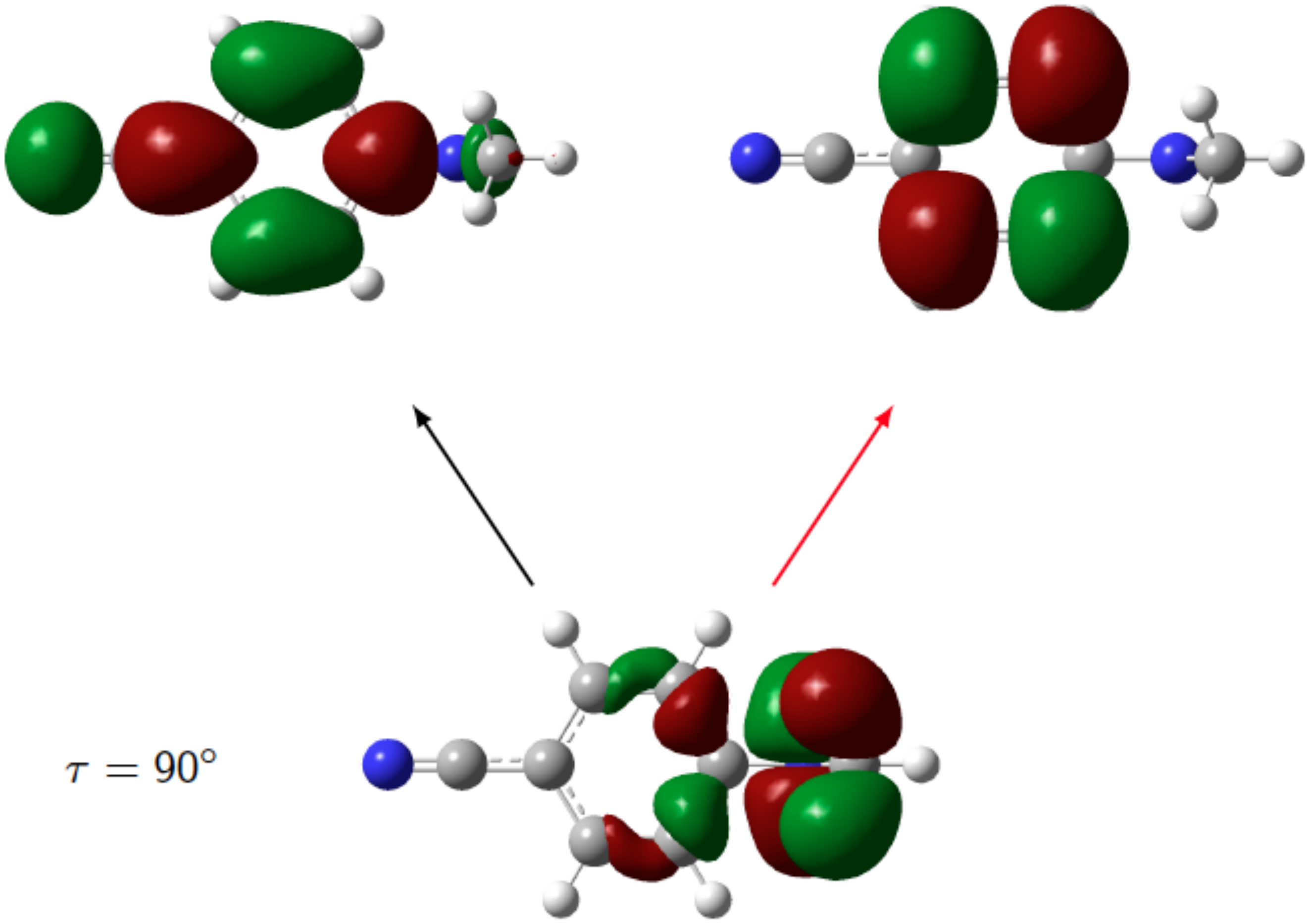
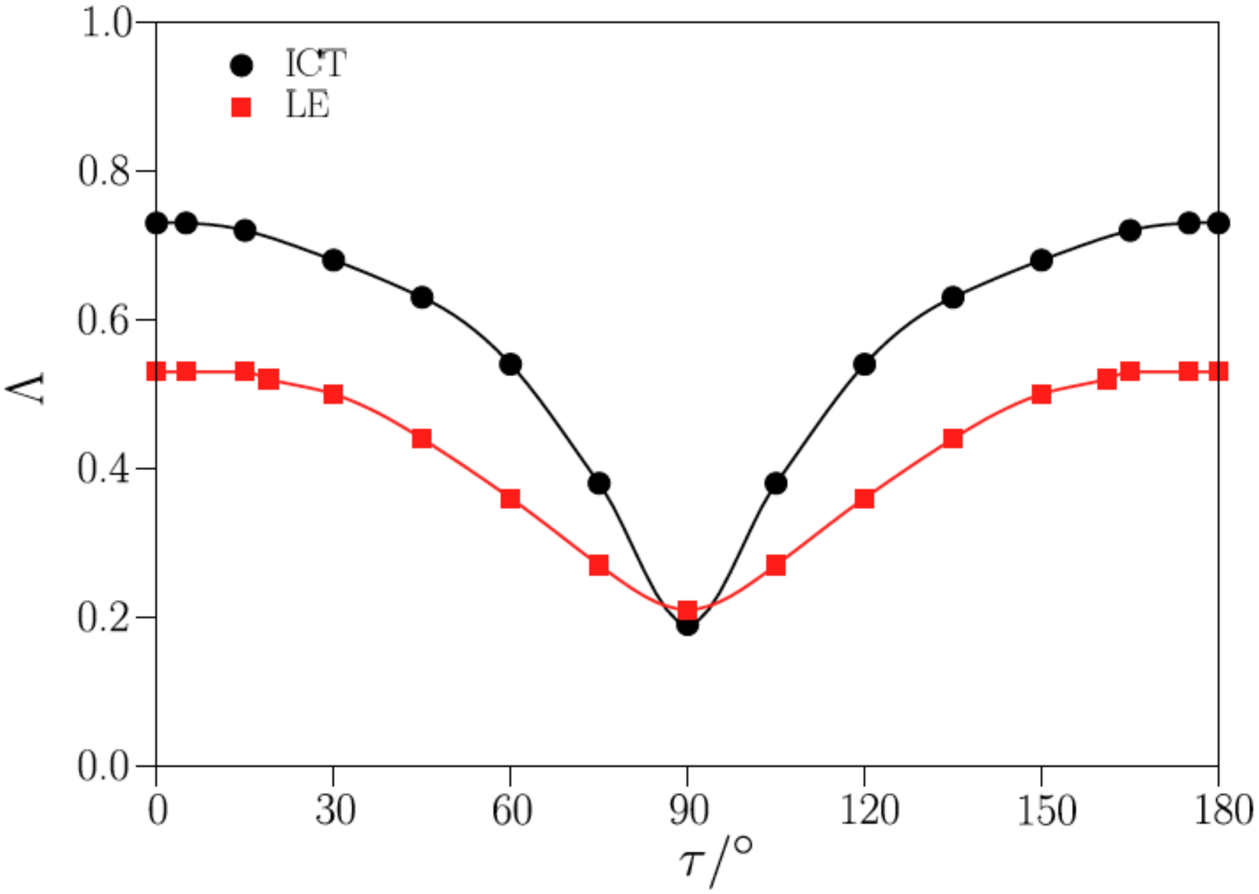


Example of CT problem

N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
[*JCP*, **131**, 091101 (2009)]

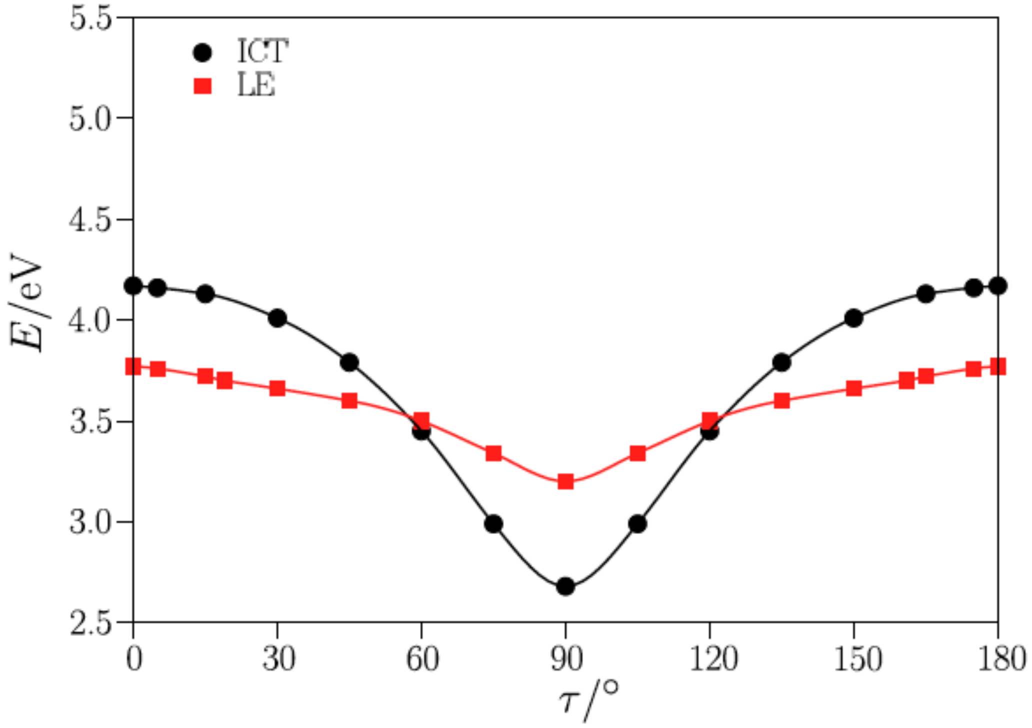
Overlap of the orbitals

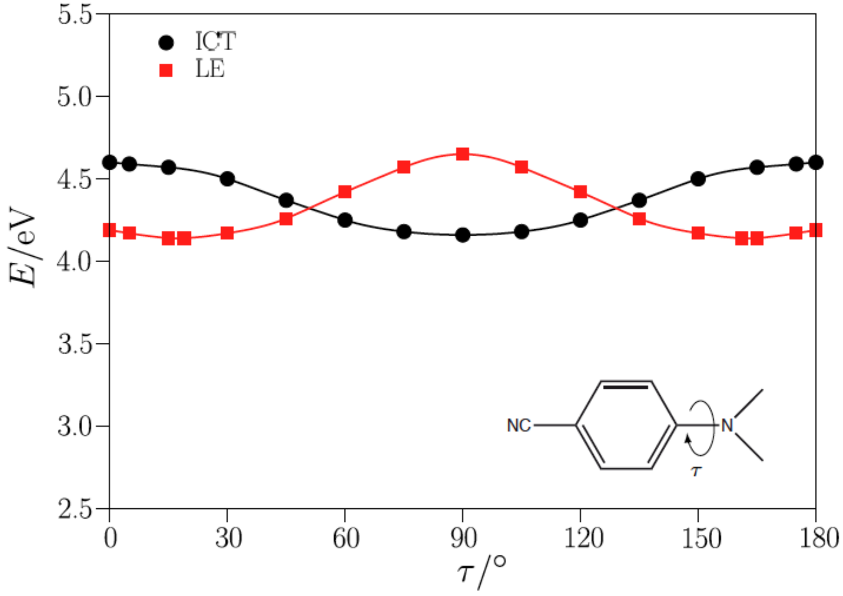


Example of CT problem

N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
[*JCP*, **131**, 091101 (2009)]

PBE

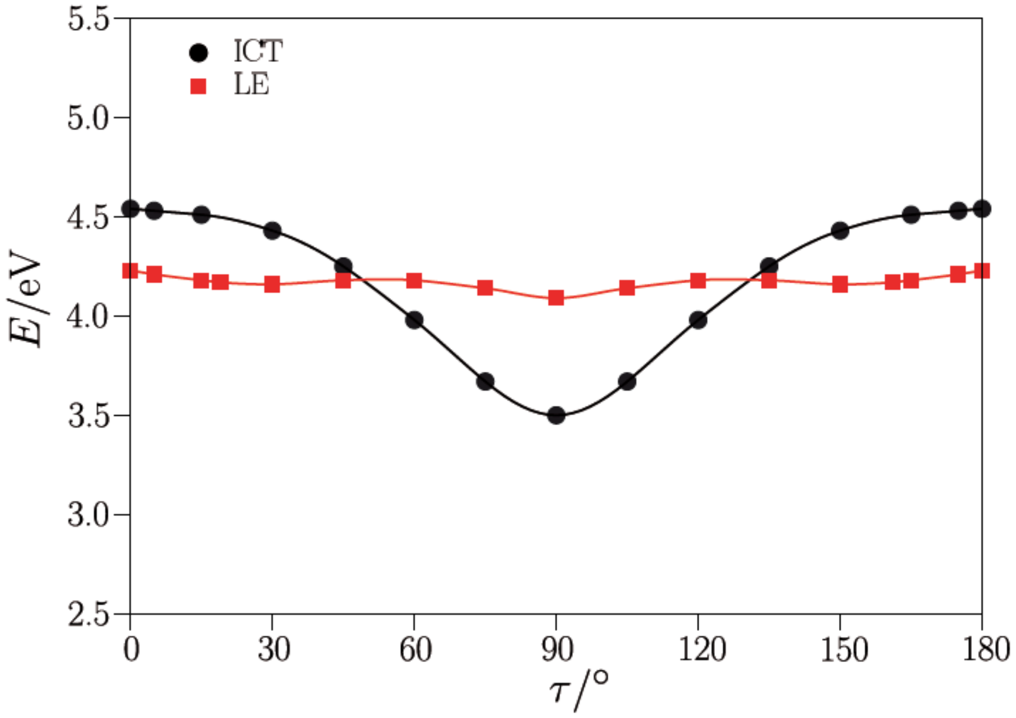


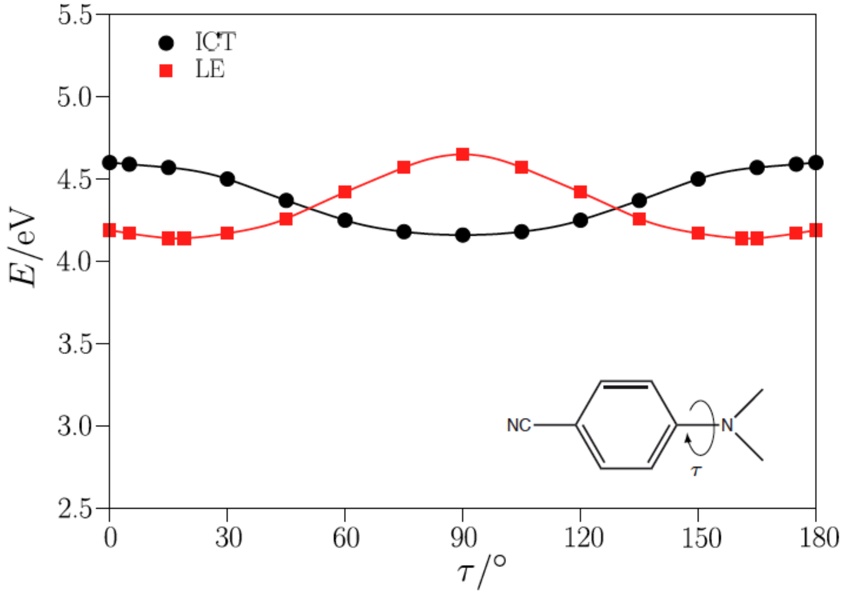


Example of CT problem

N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
[*JCP*, **131**, 091101 (2009)]

B3LYP

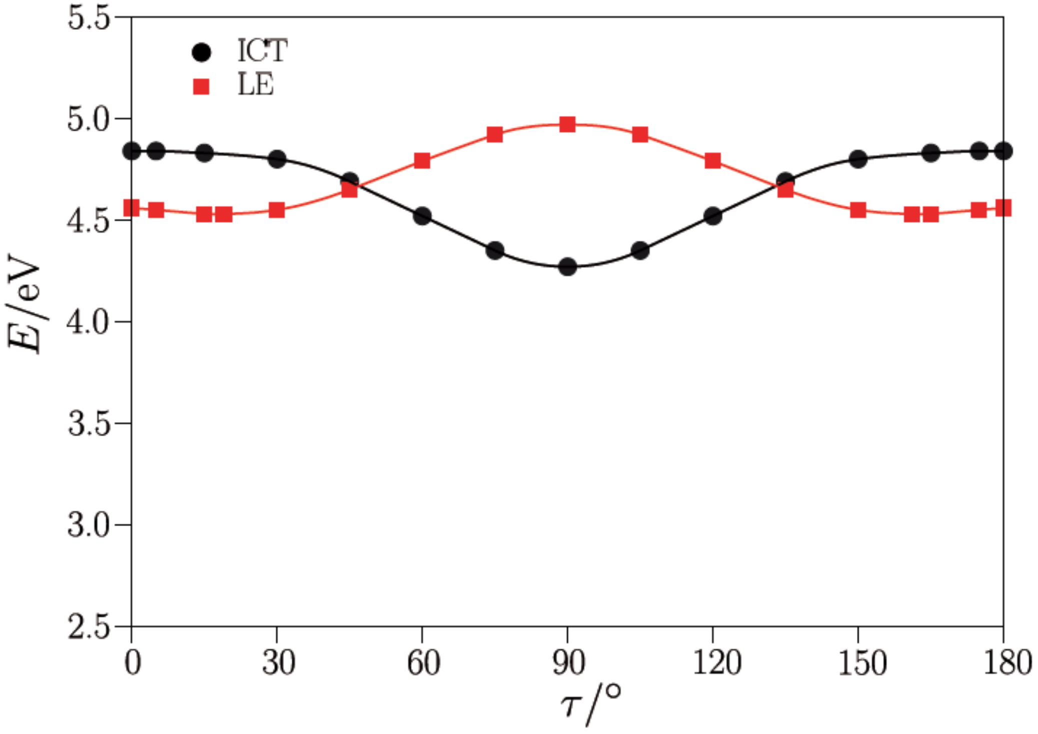


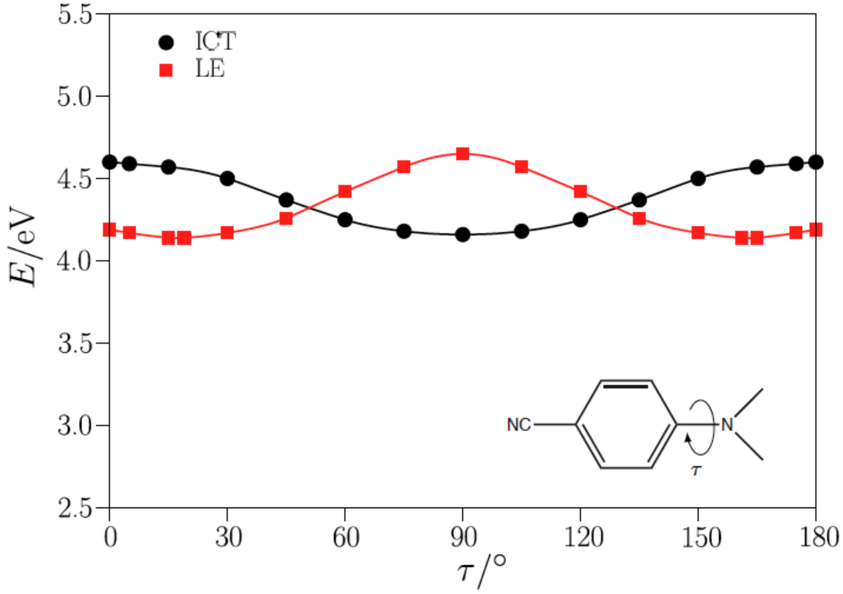


Example of CT problem

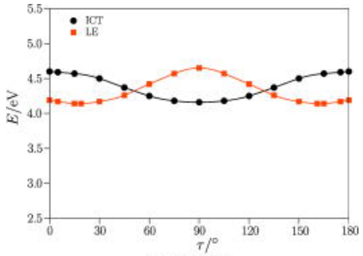
N,N-dimethylaminobenzonitrile (DMABN) - Complete analysis by Tozer *et al.*
[*JCP*, **131**, 091101 (2009)]

CAM-B3LYP

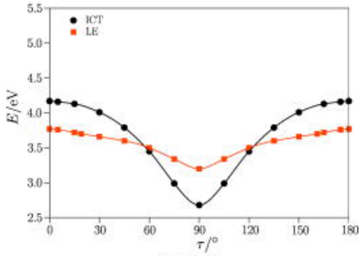




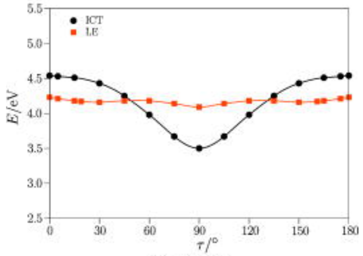
Failures of *xc*-functionals for charge-transfer states



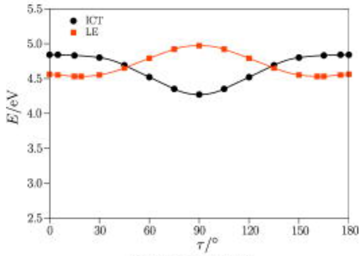
(a) RI-CC2



(b) PBE



(c) B3LYP



(d) CAM-B3LYP

- CT failures may affect dramatically the shape of the potential energy surfaces.
- CT failures may affect the ordering of the electronic states.
- Quality of the PESs is not uniform.
- Dramatic for dynamics on excited states!
- Long-range corrected functionals can help alleviate the CT problem, but often at the cost of blue-shifted valence excitation energies.

LR-TDDFT for nonadiabatic dynamics – summary

LR-TDDFT is an efficient methods to obtain electronic energies, nonadiabatic couplings, and nuclear forces, but...

- The quality of the potential energy surfaces might not always be good.
- Sometimes, problems to describe all electronic state character with the same accuracy (CT, “double excitations”, Rydberg excited states, large π systems).
- Coupling between the ground and the first excited state is not always described properly.
- Important: the listed issues are not a problem with LR-TDDFT *per se* but of its practical approximations.

CAUTION

- Always carefully test PESs obtained with a specific *xc*-functional. GGA vs Hybrids vs long-range corrected...
- Possible test methods : CC2, ADC(2), MS-CASPT2, MR-CISD...