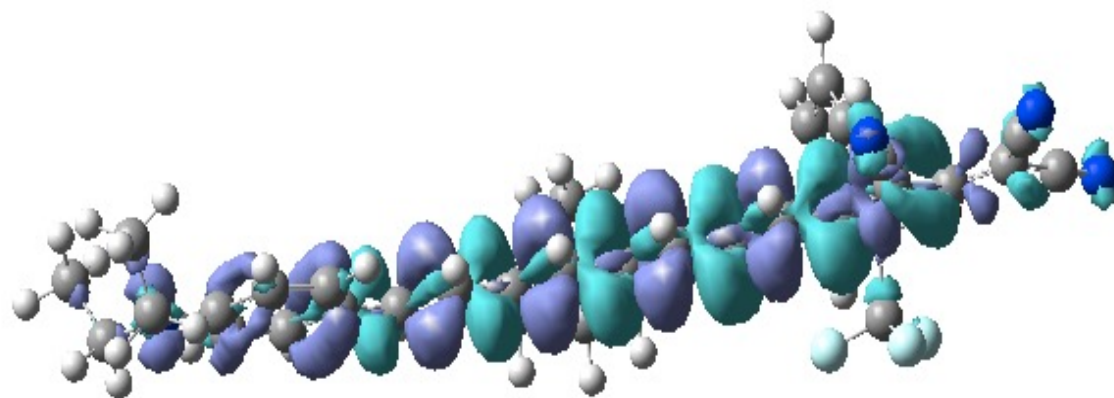
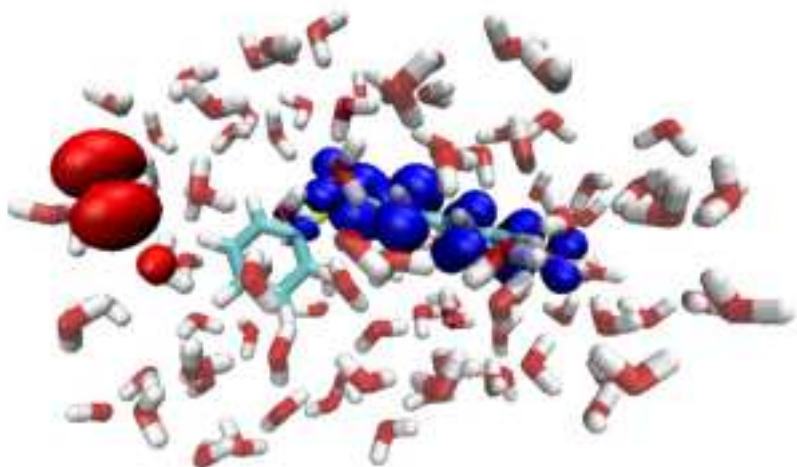


Charge transfer in TDDFT

Christine M. Isborn

University of California, Merced



Outline

- Charge-transfer dynamics
- Some basic TDDFT equations, Tamm-Dancoff approximation, and inclusion of exact exchange
- Jacob's ladder of functionals – how do they do for TDDFT excitation energies, including charge-transfer energies?
- Some challenges for TDDFT
- What is a charge-transfer transition?
- What is the TDDFT charge-transfer error and why does it exist?
- Hybrid and range-separated hybrid functionals to help fix charge-transfer error
- Optimal tuning of long-range corrected hybrids

Real-time TDDFT for modeling charge transfer dynamics

Matrix form of density evolution:

$$i \frac{\partial \mathbf{P}}{\partial t} = [\mathbf{H}(t), \mathbf{P}(t)]$$

Propagate the density matrix \mathbf{P} :

$$\mathbf{P}(t_{m+1}) = \mathbf{U}(t_m) \mathbf{P}(t_{m-1}) \mathbf{U}_m^\dagger(t_m)$$

$$\mathbf{U}(t_m) = \mathbf{c}(t_m) e^{i\varepsilon(t_m)2\Delta t} \mathbf{c}^\dagger(t_m)$$

Hamiltonian is the Kohn-Sham matrix (TDDFT) or Fock matrix (TDHF)

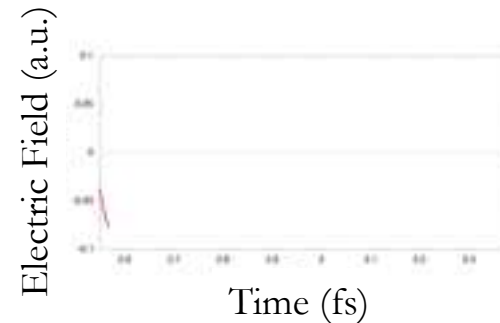
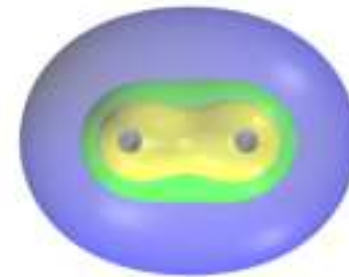
$$\hat{H}(t) = \hat{H}_0(t) + \hat{V}(t)$$

Field-free
Hamiltonian

Time-dependent
perturbation

$$\hat{H}_0(t) = \hat{h} + \hat{G}(\rho(t))$$

Time-dependent
potential



Real-time TDDFT: time-dependent dipole moment

Matrix form of density evolution:

$$i \frac{\partial \mathbf{P}}{\partial t} = [\mathbf{H}(t), \mathbf{P}(t)]$$

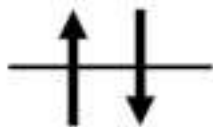
Apply a resonant field

$$\omega = \frac{E_{S1} - E_{S0}}{\hbar}$$

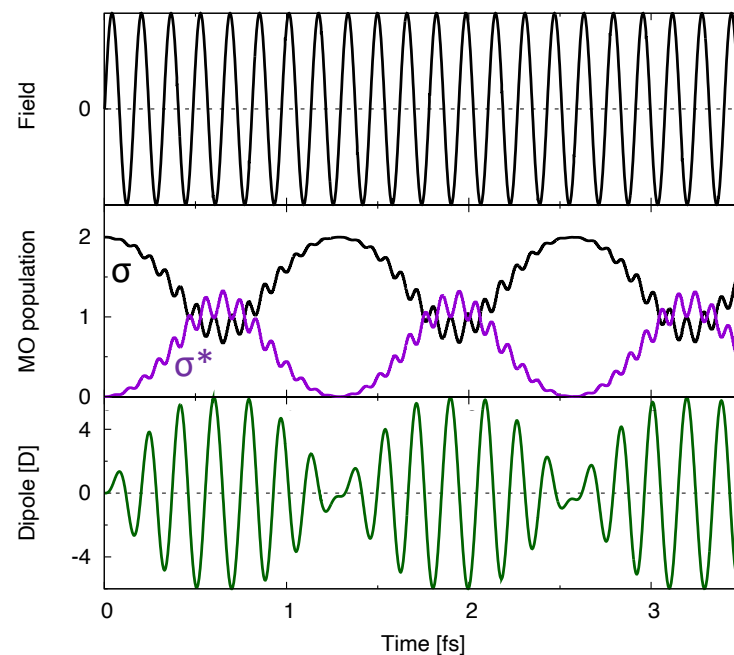
S_0



Project onto MOs,
get populations



Time-dependent dipole



Real-time TDDFT: time-dependent dipole moment

Matrix form of density evolution:

$$i \frac{\partial \mathbf{P}}{\partial t} = [\mathbf{H}(t), \mathbf{P}(t)]$$

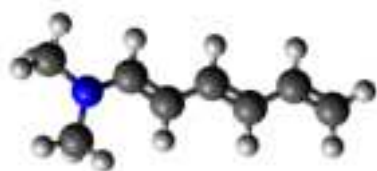
Can monitor charge transfer by looking at change in dipole moment



System 1, $(\text{CH}_3)_2\text{N}(\text{CH}=\text{CH})\text{H}$

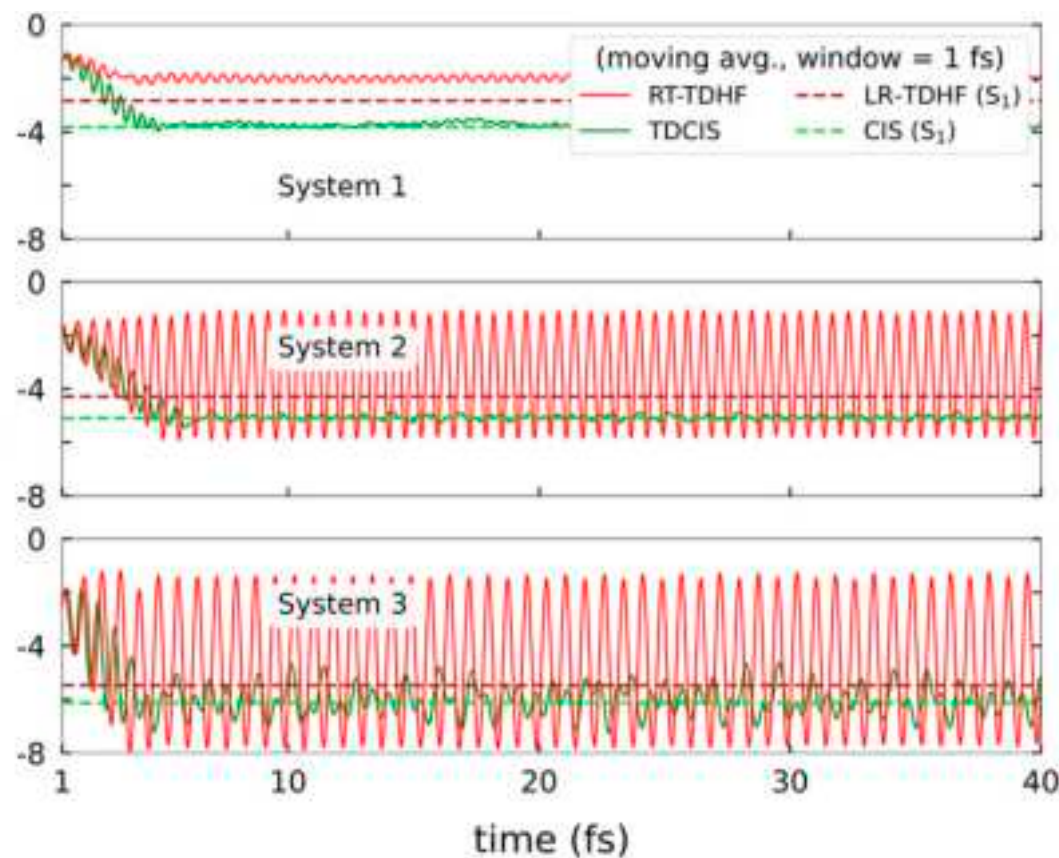


System 2, $(\text{CH}_3)_2\text{N}(\text{CH}=\text{CH})_2\text{H}$



System 3, $(\text{CH}_3)_2\text{N}(\text{CH}=\text{CH})_3\text{H}$

μ_x (D)



Problems with TDHF/TDDFT time-dependent charge transfer due to adiabatic approximation

From real time to LR matrix formulation

Matrix form of density evolution:

$$i \frac{\partial \mathbf{P}}{\partial t} = [\mathbf{H}(t), \mathbf{P}(t)]$$

linear response
approximation

Expand $\mathbf{H}(t)$, $\mathbf{P}(t)$ to
first order in field

Group terms and
divide out $e^{\pm i\omega t}$

Matrix formulation for LR-TDDFT

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

$$A_{ia,jb} = \delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i) + (ia|jb) + (ia|f_{xc}|jb)$$

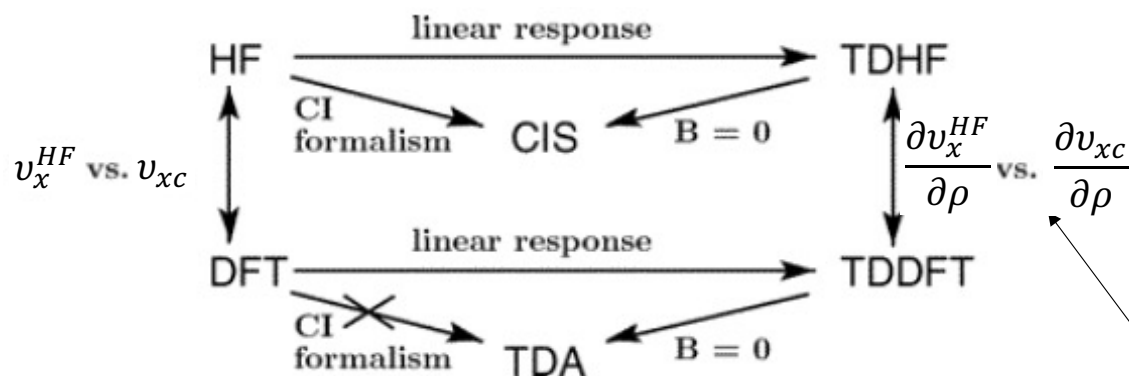
$$B_{ia,jb} = (ia|bj) + (ia|f_{xc}|bj)$$

$$(ia|f_{xc}|jb) = \int d^3r d^3r' \phi_i^*(r) \phi_a(r) \frac{\delta^2 E_{xc}}{\delta \rho(r) \delta \rho(r')} \phi_b^*(r') \phi_j(r')$$

Tamm-Dancoff
approximation
(ignore \mathbf{B} matrix)

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}$$

Relationship between TDHF and TDDFT



The orbital energies are quite different. The band gap is usually much larger with HF than DFT.

The key difference for charge-transfer states comes from this derivative term, which represents the change in the Fock/Kohn-Sham matrix due to the change in the density

Dreuw, Head-Gordon
 Chemical Reviews, 105, 4009, 2005
 DOI: 10.1021/cr0505627

Exact exchange in the ground state leads to the correct Coulombic $1/r$ interaction between electron and hole (excitonic interaction) in the TDDFT/TDHF equations

Note: CIS also has a charge-transfer error, getting these states too high in energy, see Subotnik, J. Chem. Phys. 2011, 135, 071104

Why is there a charge-transfer error for TDDFT but not TDHF?

The density dependent part of a general Fock matrix element $F_{\mu\nu}$ for a closed-shell system is

$$F_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} [2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)] \quad (\mu\nu|\lambda\sigma) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_\mu(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_\lambda(\mathbf{r}_2)\varphi_\sigma(\mathbf{r}_2)$$

Coulomb (J) exchange (K)

When deriving the linear response TDHF/TDDFT equations in particle-hole space (where we solve the matrix / Casida equations), the term we want is

$$\frac{\partial F_{ia}}{\partial P_{jb}} \quad \text{Where } i, j \text{ are occupied orbitals, and } a, b \text{ are the virtual (unoccupied) orbitals}$$

$$F_{ia} = \sum_{\lambda\sigma} P_{\lambda\sigma} [2(ia|\lambda\sigma) - (i\lambda|a\sigma)] \quad \frac{\partial}{\partial P_{jb}} F_{ia} = \sum_{jb} P_{jb} [2(ia|jb) - (ij|ab)]$$

This is how exact exchange gives the correct Coulombic interaction between the electron and hole.

For the case where $j=i$ and $b=a$, we get a Coulomb term from what was the exchange term:

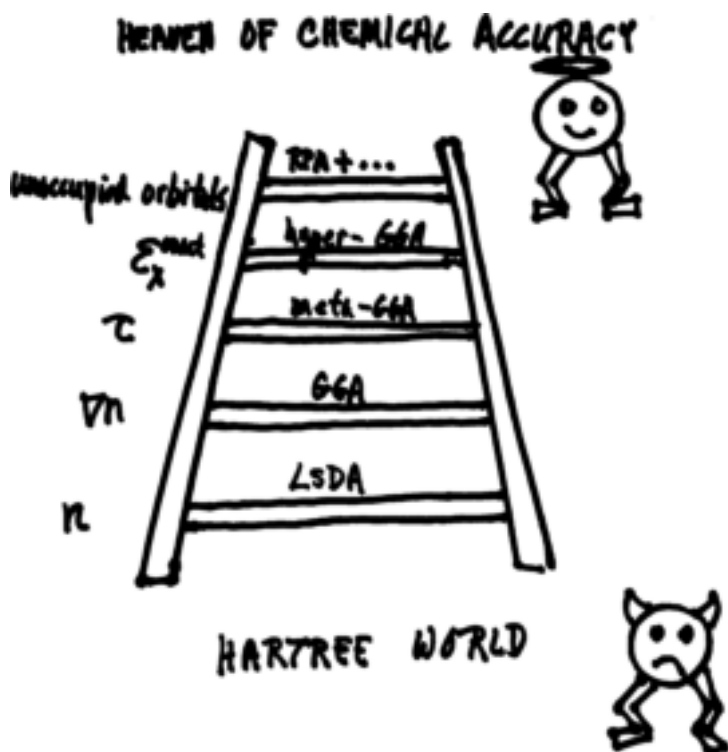
$$[2(ia|ia) - (ii|aa)]$$

This is what we have in the A matrix for TDHF: $A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 2(ia|jb) - (ij|ab)$

This last term is the stabilizing $1/r$ interaction for the electron and hole, which is missing from TDDFT

What kinds of transitions does TDDFT get correct?

The answer depends on the functional....



Some people think that you can get any excitation energy you want, by simply choosing the appropriate functional.

This is because (usually) increasing the amount of exact exchange in the functional will lead to higher excitation energies.

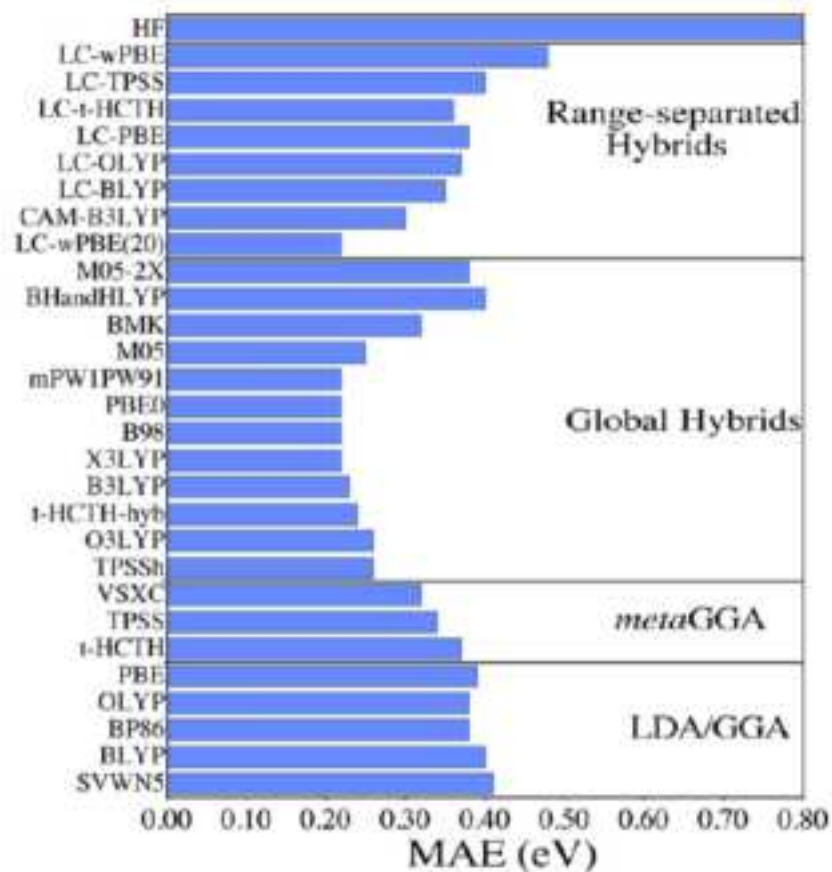
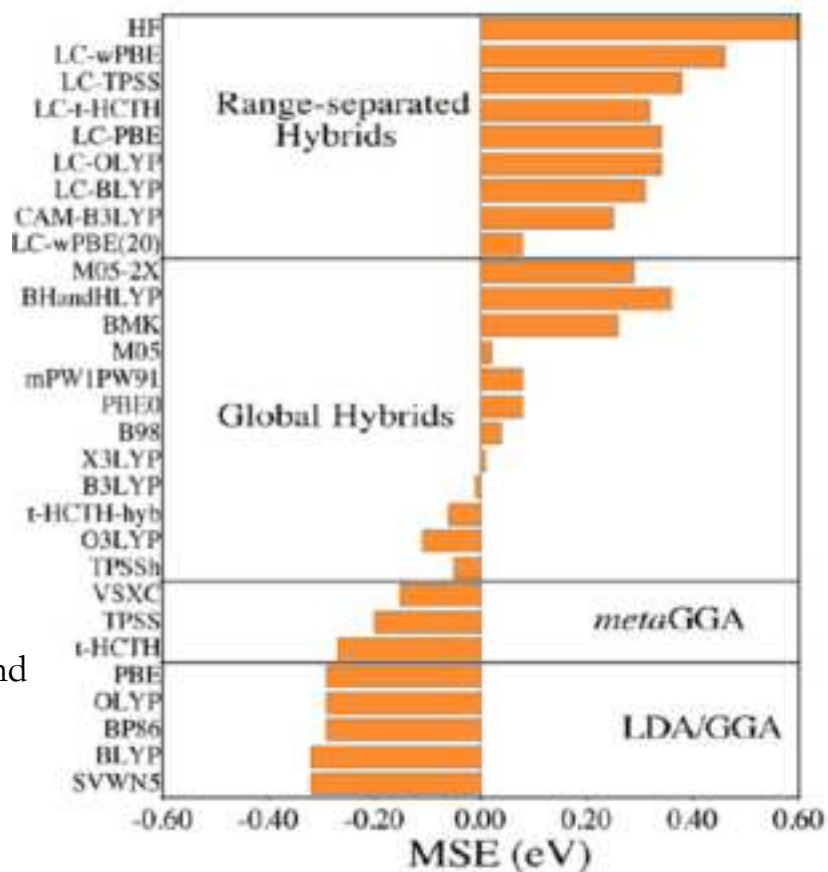
Although we ideally want a functional that will be accurate for all excitations, we might settle for one that has errors, but treats various kinds of excitations equally well / equally poorly. Then, we might still be able to:

- Get the correct ordering of states
- Compare various kinds of chromophores
- Accurately take into account environmental effects

How accurate is TDDFT for excitation energies?

More exact exchange,
tend to overestimate
excitation energies

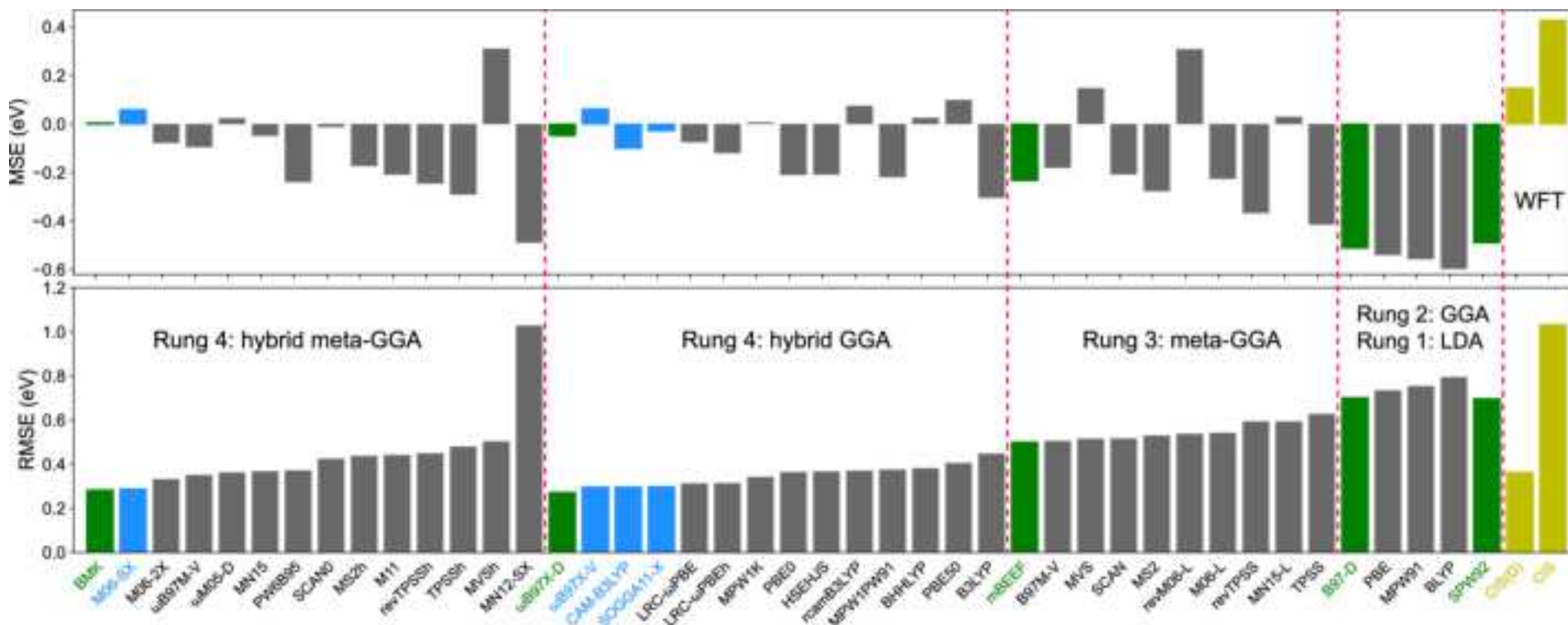
No exact exchange, tend
to underestimate
excitation energies



comparing 614 experimental λ_{\max} to vertical transition energies

How accurate is TDDFT for excitation energies?

comparing 463 theoretical best estimates in QUEST database

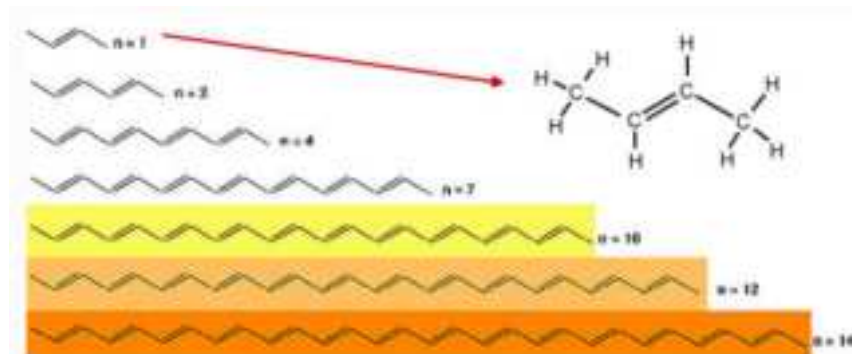
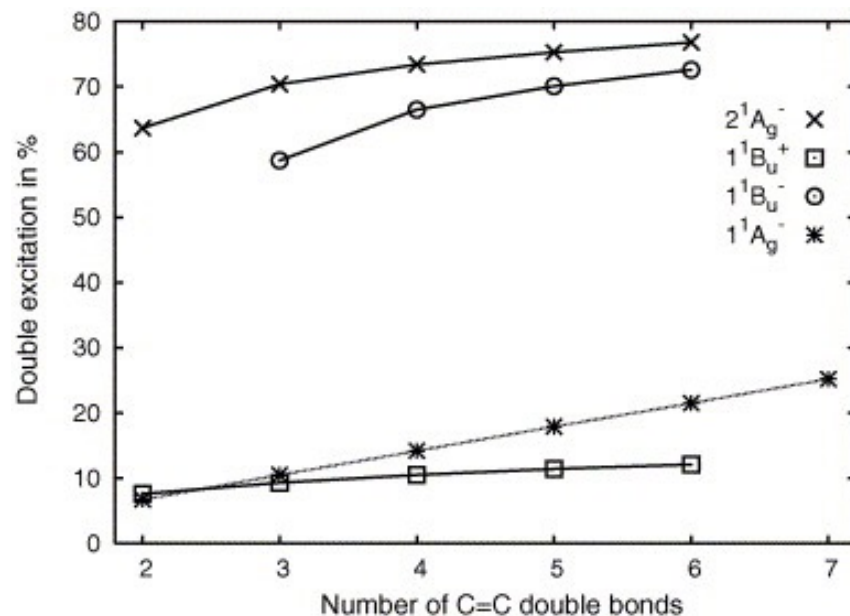


- Tamm-Dancoff approximation is preferred over full TDDFT for excitations because of its improved accuracy (esp. for triplet excitations) versus cost trade-off
- TDDFT/TDA with the best functionals yields RMSEs of 0.25–0.3 eV for excitation energies, which is a little better than the CIS(D) wave function method at a significantly lower computational cost.

Liang, Feng, Hait,
Head-Gordon
J. Chem. Theory
Comput. 2022, 18,
3460

What kinds of transitions does TDDFT have problems modeling?

Those with double excitation character (e.g. polyenes). This could be fixed using a frequency dependent functional, i.e. going beyond the adiabatic approximation. Also leads to incorrect topology of potential energy surfaces.



Starcke, Wormit, Schirmer, Dreuw

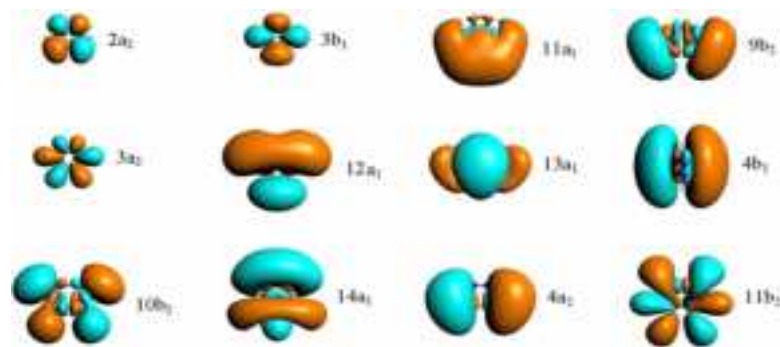
Chemical Physics, 329, 39, 2006

<https://doi.org/10.1016/j.chemphys.2006.07.020>,

<https://chemiezauber.de/index.php/inhalt/q2/farbmittel-und-textilien/struktur-von-farbstoffmolekuelen/lichtabsorption-von-organischen-verbindungen/410-chromophore>

What kinds of transitions does TDDFT have problems modeling?

- Those with double excitation character
- Rydberg transitions
- Charge-transfer transitions



Holland, Shaw, Coriani, Stener, Decleva
 J. Phys. B: At. Mol. Opt. Phys. 46 175103, 2013
 doi:10.1088/0953-4075/46/17/175103

JOURNAL OF CHEMICAL PHYSICS VOLUME 119, NUMBER 24 22 DECEMBER 2003

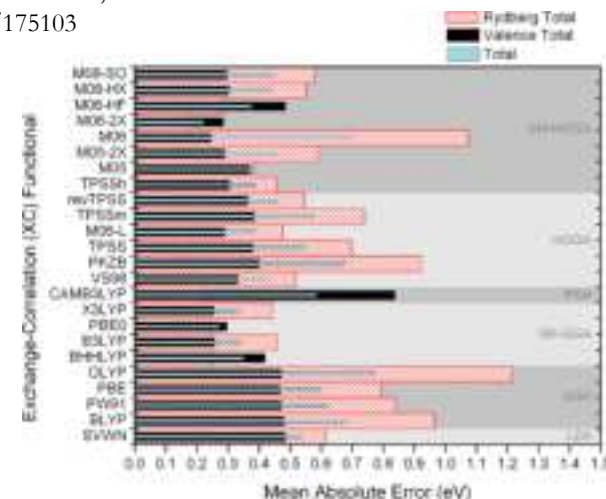
COMMUNICATIONS

Relationship between long-range charge-transfer excitation energy error and integer discontinuity in Kohn–Sham theory

David J. Tozer
 Department of Chemistry, University of Durham, South Road, Durham, DH1 1LE UK

(Received 29 September 2003; accepted 23 October 2003)

Charge-transfer (CT) electronic excitation energies are known to be very poorly predicted by time-dependent density functional theory (TDDFT) using local exchange–correlation functionals. Insight into this observation is provided by a simple analysis of intermolecular CT excitations at infinite separation. It is argued that the first TDDFT CT excitation energy approximately underestimates the experimental excitation by the average of the integer discontinuities of the donor and acceptor molecules; errors are of the order of several electron volts. © 2003 American Institute of Physics. [DOI: 10.1063/1.1633756]



Leang; Zahariev; Gordon;
 The Journal of Chemical Physics 2012, 136, 104101
 DOI: 10.1063/1.3689445

What is a charge-transfer transition?

Charge-transfer complex

From Wikipedia, the free encyclopedia

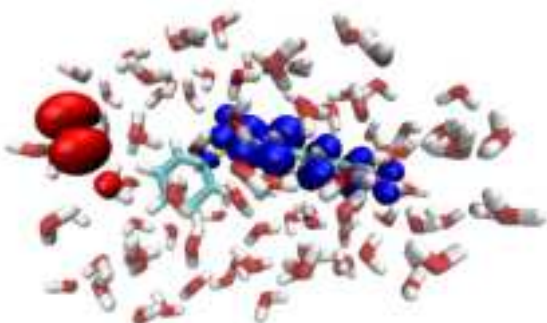
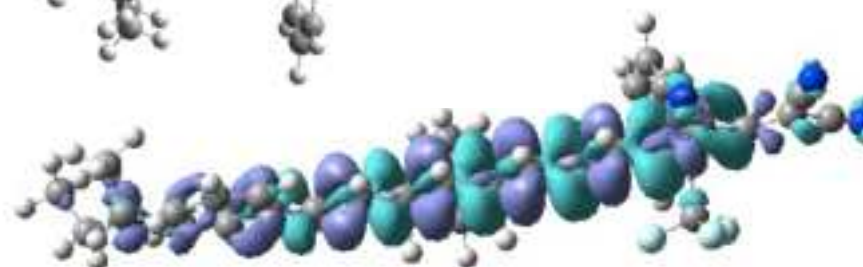
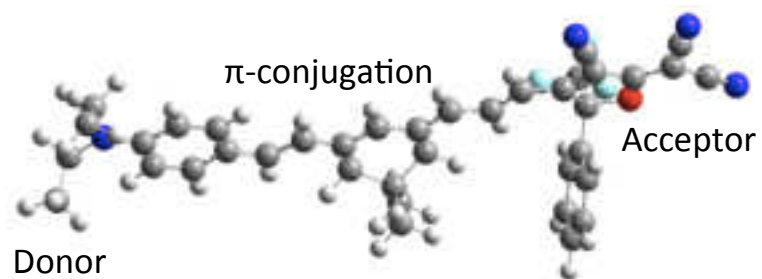
A **charge-transfer complex (CT complex)** or **electron-donor-acceptor complex** is an association of two or more **molecules**, or of different parts of one large molecule, in which a fraction of electronic charge is transferred between the molecular entities. The resulting **electrostatic** attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the **electron donor** and the receiving species is called the **electron acceptor**.

- May be on the same molecule (donor group and acceptor group) or between molecules
- Small overlap between donor and acceptor densities (movement of electron across space)
- Often associated with a large change in dipole moment
- The Coulombic attraction between the excited electron and hole should be smaller than for a valence transition

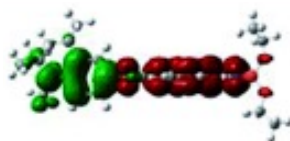
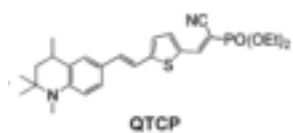
Examples of charge-transfer transitions

CT transitions important for:

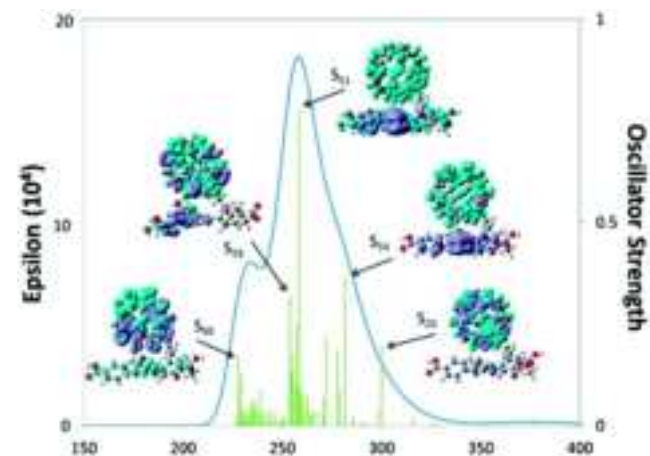
- organic electronics
- solar cell materials
- chromophores in solution



Isborn, Mar, Curchod, Tavernelli, Martinez
 J. Phys. Chem. B 2013, 117, 12189
[dx.doi.org/10.1021/jp4058274](https://doi.org/10.1021/jp4058274)

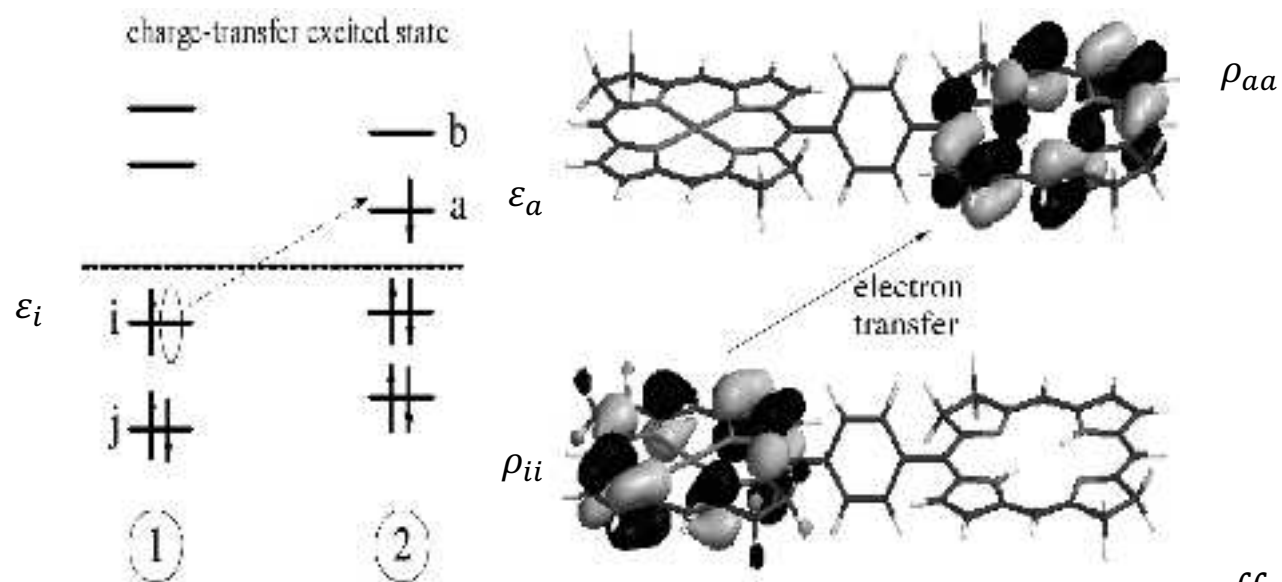


Zhao, Chen, Sun, Liu, Li, Gao, Han, Yang, Sun
 Chem. Eur. J., 14, 6935, 2008
 DOI: 10.1002/chem.200701868



Leong, Foster, Wong, Spoerke, Van Gough, Deaton, Allendorf
 J. Mater. Chem. A, 2014, 2, 3389-3398
 DOI: [10.1039/C3TA14328G](https://doi.org/10.1039/C3TA14328G)

What should the excitation energy be?

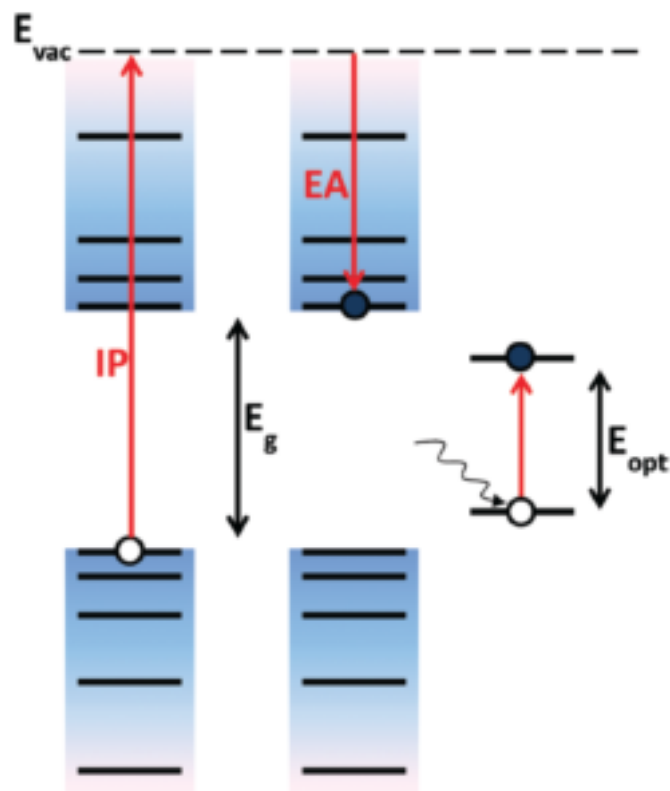


$$\varepsilon_i - \varepsilon_a - \frac{\rho_{ii}\rho_{aa}}{|r_i - r_a|}$$

$$\varepsilon_i - \varepsilon_a - (ii|aa)$$

$$(\mu\nu|\lambda\sigma) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_\mu(\mathbf{r}_1)\varphi_\nu(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_\lambda(\mathbf{r}_2)\varphi_\sigma(\mathbf{r}_2)$$

Which is smaller: the optical gap (the excitation energy) or the band gap?



Electron-hole Coulombic electrostatic attraction (aka exciton binding energy) leads to a smaller optical gap.

Important for organic molecules, which have a small dielectric constant, leading to **excitonic states**.

Not as important for conductors, which generally screen the excited electron from the hole.

Do hybrid functionals fix the TDDFT charge transfer error?

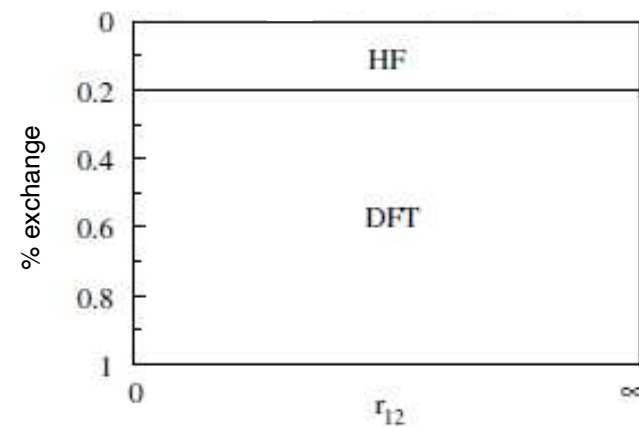
Note that these hybrid functionals use

GENERALIZED KOHN-SHAM THEORY, in which we

consider the exact exchange contribution as taking into account electrons that are partially interacting via the exact, nonlocal exchange interaction.

Examples: B3LYP, PBE0, BH&HLYP, M06-2X, M06-HF

$$E_X = \alpha E_X^{DFT} + (1 - \alpha) E_X^{HF}$$



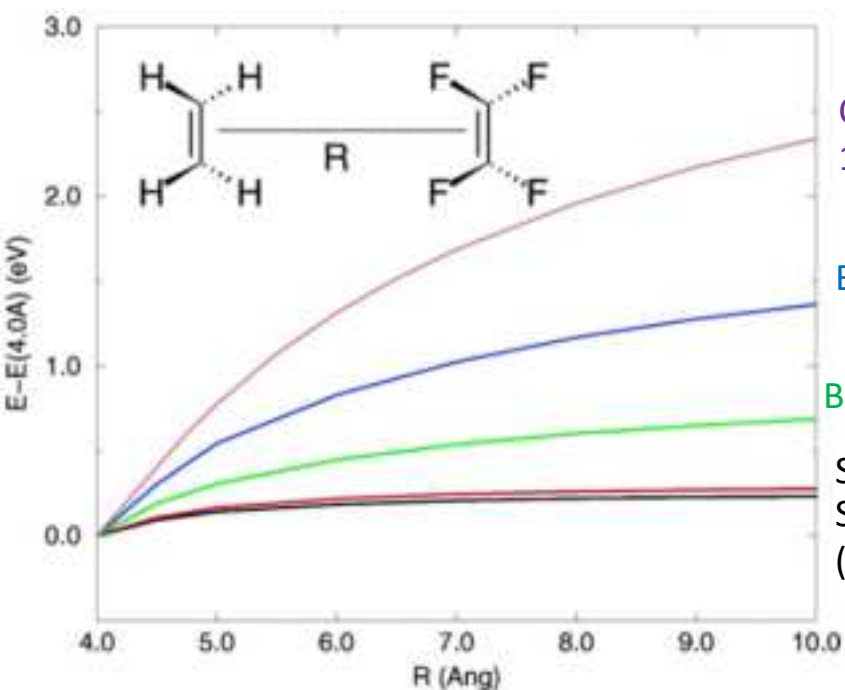
T. Yanai et al. / Chemical Physics Letters 393 (2004) 51–57

It will depend on the % of exact exchange.

Question: Why not use 100% exact exchange?

Answer: The local DFT exchange balances the local DFT correlation

What is the charge-transfer (CT) error in TDDFT?



Configuration interaction singles (CIS) has 100% exact exchange

→ gives the correct distance dependence

BH&HLYP (hybrid with 50% exact exchange)

B3LYP (hybrid with 20% exact exchange)

SVWN / LB94

Similar behavior for LSDA, GGAs (BLYP, PBE), meta-GGAs

- The TDDFT CT excitation energy does not vary as $1/r$ as would be expected for a Coulombic interaction
- The CT states are too low in energy.

How do we get both short-range DFT local exchange and correct long-range exact exchange?

The Coulomb operator can be separated into short-range and long-range components:

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - \beta \operatorname{erf}(\omega r_{12})}{r_{12}}}_{\text{Short-range}} + \underbrace{\frac{\beta \operatorname{erf}(\omega r_{12})}{r_{12}}}_{\text{Long-range}} \quad \text{Leads to a range-separated hybrid (RSH) functional}$$

ω is the range-separation parameter

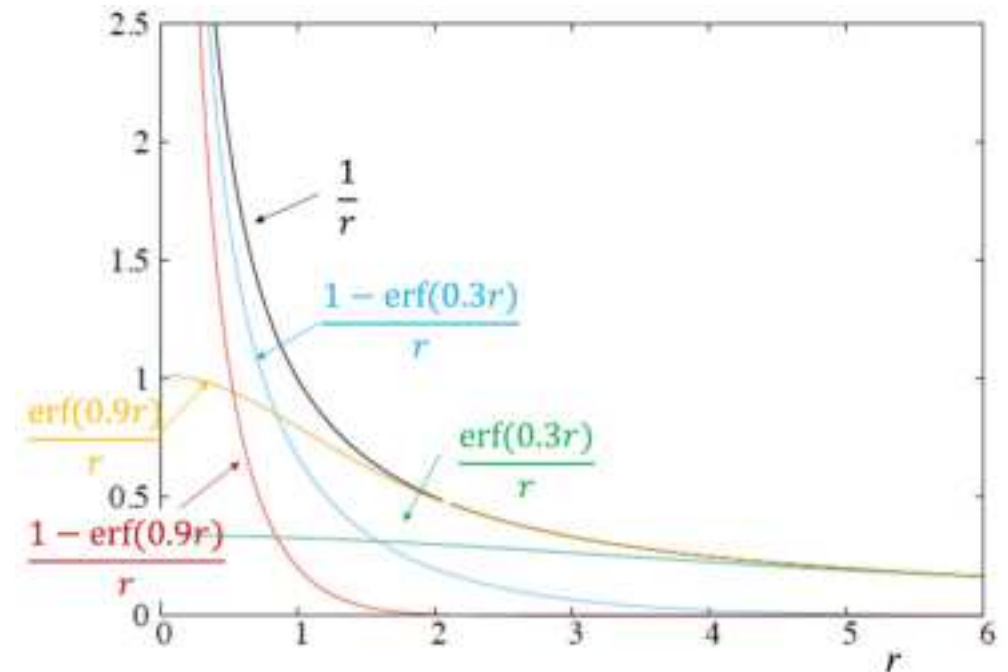
(sometimes also denoted with the symbol μ or γ),

β determines if the long-range value should be scaled.

Exact exchange can be used at short range or long range.

Short range exact exchange is useful for correcting the band gap of periodic systems.

Long range exact exchange is useful for correcting the excitation energies that occur over large distances (Rydberg and charge-transfer).



Long-range corrected functionals

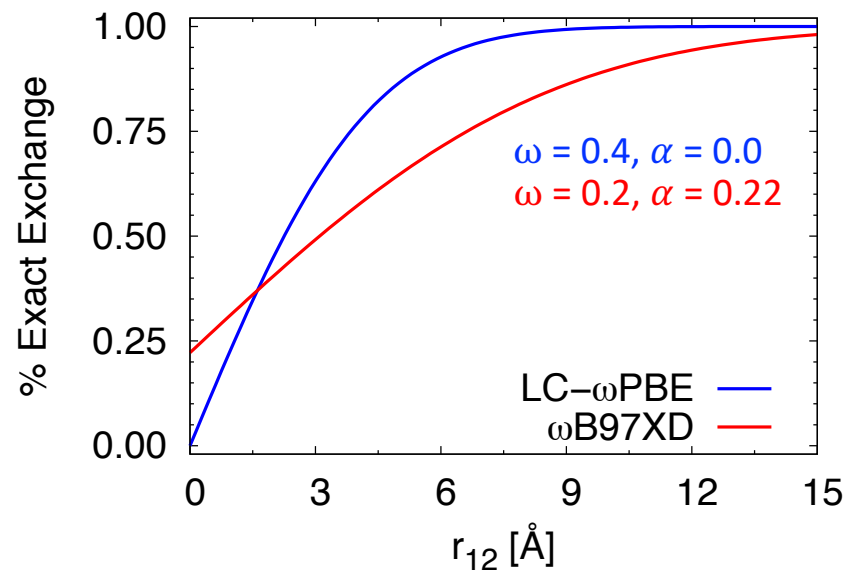
Using 100% exact exchange at long range yields a ‘long-range corrected (LRC or LC) functional.

These functionals have the correct distance dependence for the energies of charge-transfer transitions and are very useful for modeling charge-transfer transitions.

The long-range correction can also be combined with some percentage of short-range exact exchange

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \operatorname{erf}(\omega r_{12})]}{r_{12}} + \frac{\alpha + \beta \operatorname{erf}(\omega r_{12})}{r_{12}}$$

Some short-range exact exchange is important for accurate ground state properties (ex. Reaction barrier heights)

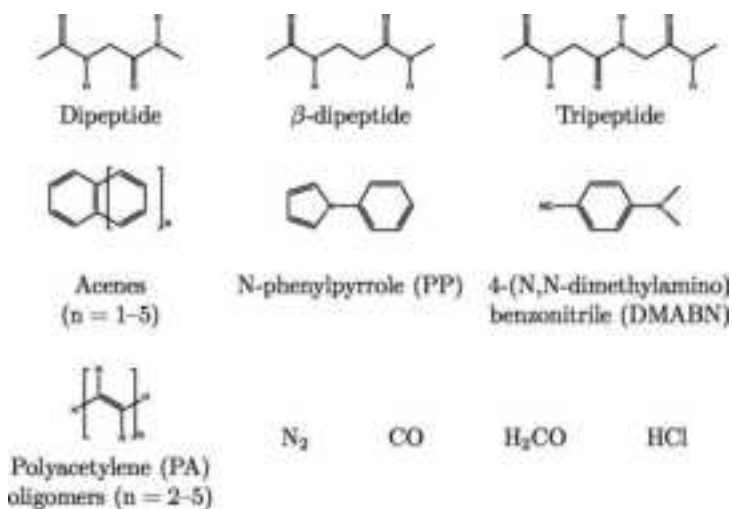


Examples of long-range corrected: LC- ω PBE, LC-BLYP, ω B97

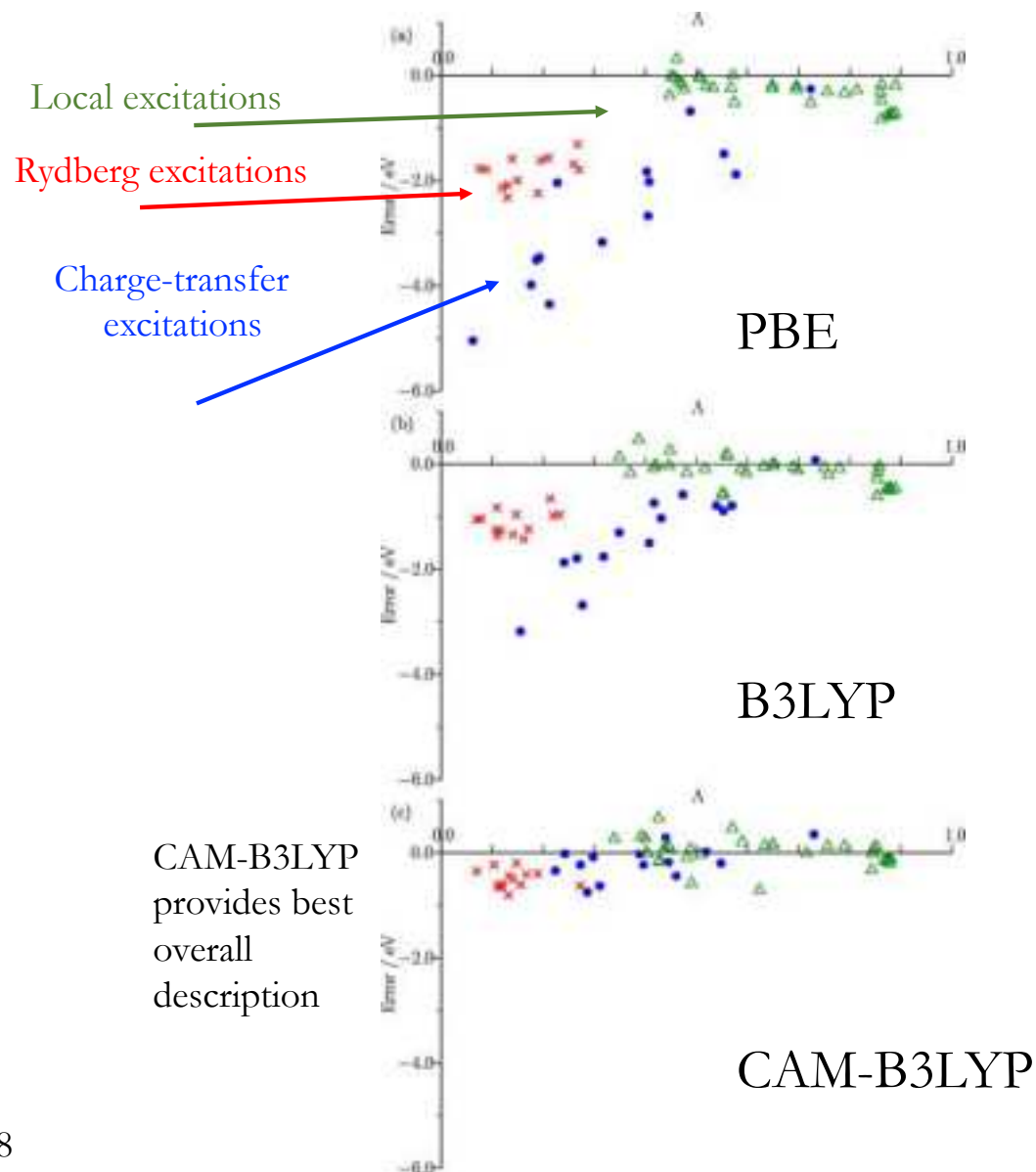
Examples of long-range corrected + short range exchange: LC- ω PBEh, ω B97x

Also: CAM-B3LYP
(not 100% at long-range)

Error comparisons for PBE, B3LYP, CAM-B3LYP

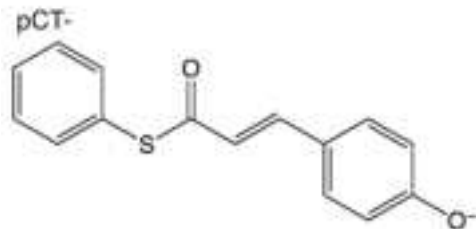


Λ = measure of overlap (quantifies CT character)

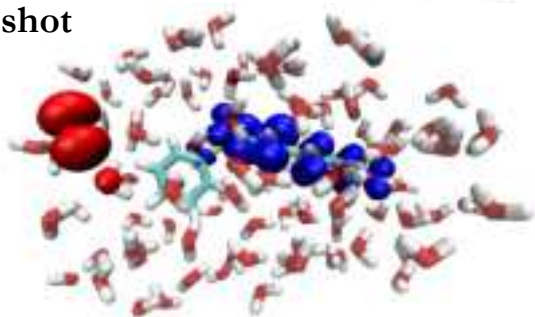


An extreme CT problem: molecules in solution

trans-thiophenyl-p-coumarate

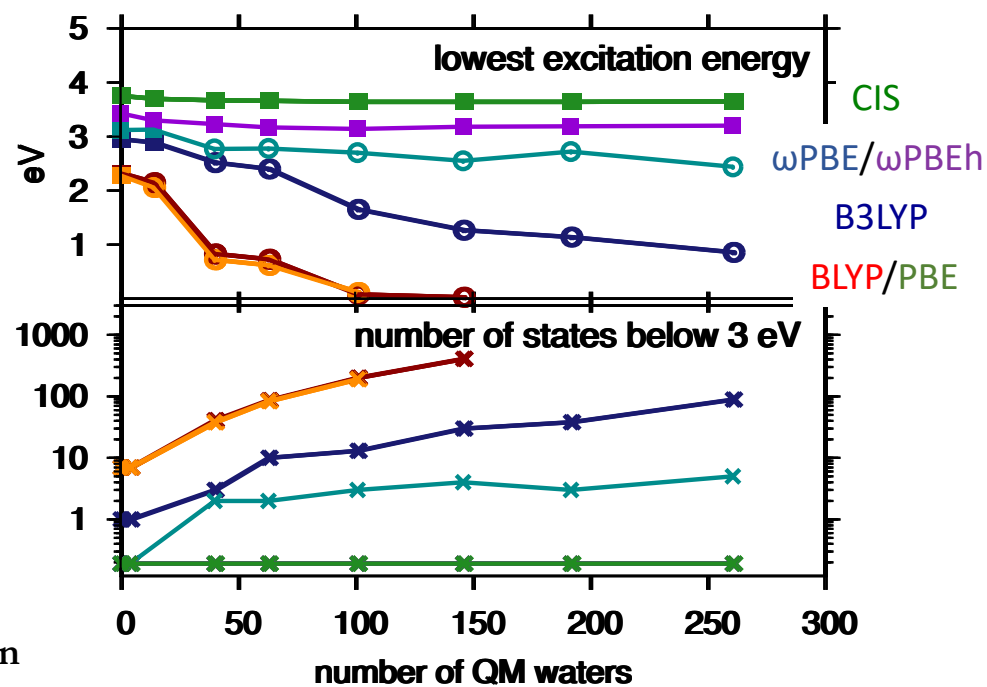


Solvated snapshot



Need Coulombic stabilization
of electron and hole

pCT- snapshot



Isborn, Mar, Curchod, Tavernelli, Martinez
J. Phys. Chem. B 2013, 117, 12189
[dx.doi.org/10.1021/jp4058274](https://doi.org/10.1021/jp4058274)

C. M. Isborn

Is there an 'optimal' range-separation parameter?

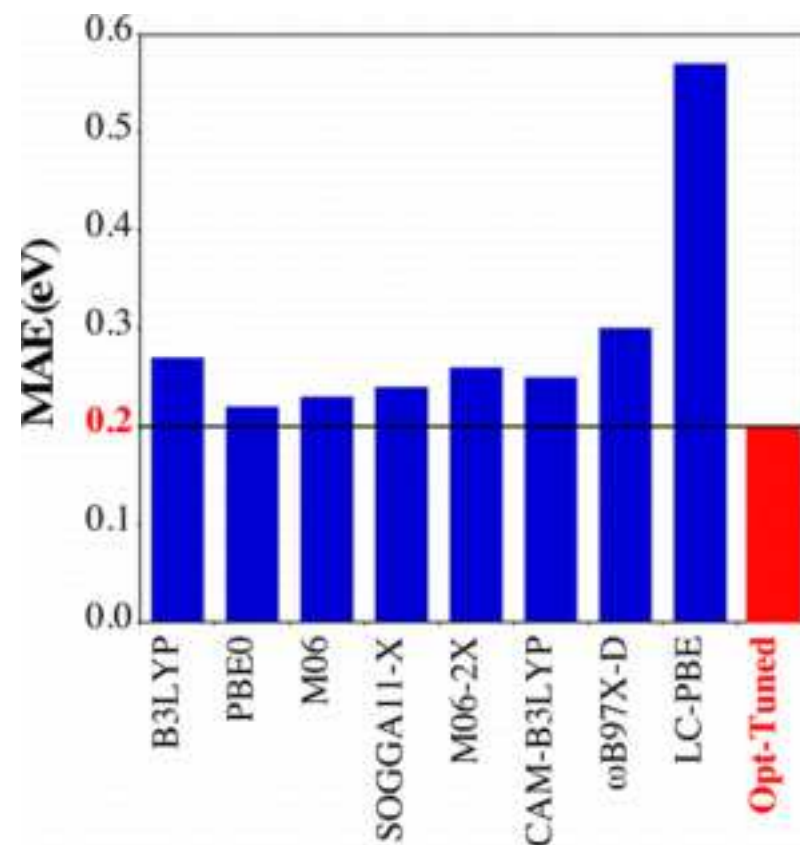
Charge Transfer Excitation Energies, in eV, for Four Donor-Tetracyanoethylene Complexes compared to gas phase experiment

donor	TDDFT				experiment
	PBE	B3LYP	BNL ($\gamma = 0.5$)	BNL (tuned γ)	
benzene	1.6	2.1	4.4	3.8	3.59
toluene	1.4	1.8	4.0	3.4	3.36
o-xylene	1.0	1.5	3.7	3.0	3.15
naphthalene	0.4	0.9	3.3	2.7	2.60
MAE	2.1	1.7	0.8	0.1	

Kronik, Stein, Refaely-Abramson, Baer
[dx.doi.org/10.1021/ct2009363](https://doi.org/10.1021/ct2009363)
J. Chem. Theory Comput., 8, 1515, 2012

A review:
Delocalization Error and "Functional Tuning" in Kohn–Sham
Calculations of Molecular Properties
Jochen Autschbach and Monika Srebro
Acc. Chem. Res. 2014, 47, 2592–2602

Excitation energies for 40 conjugated molecules



Jacquemin, Moore, Planchat, Adamo, Autschbach
J. Chem. Theory Comput., 10, 1677, 2014

Tuning the range-separation parameter

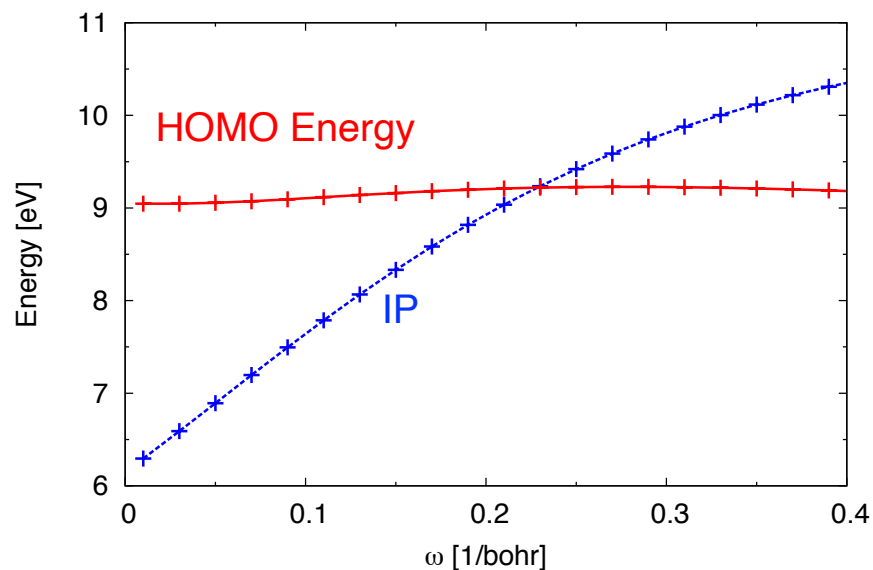
In an exact theory, the energy of the HOMO is equal to the ionization potential

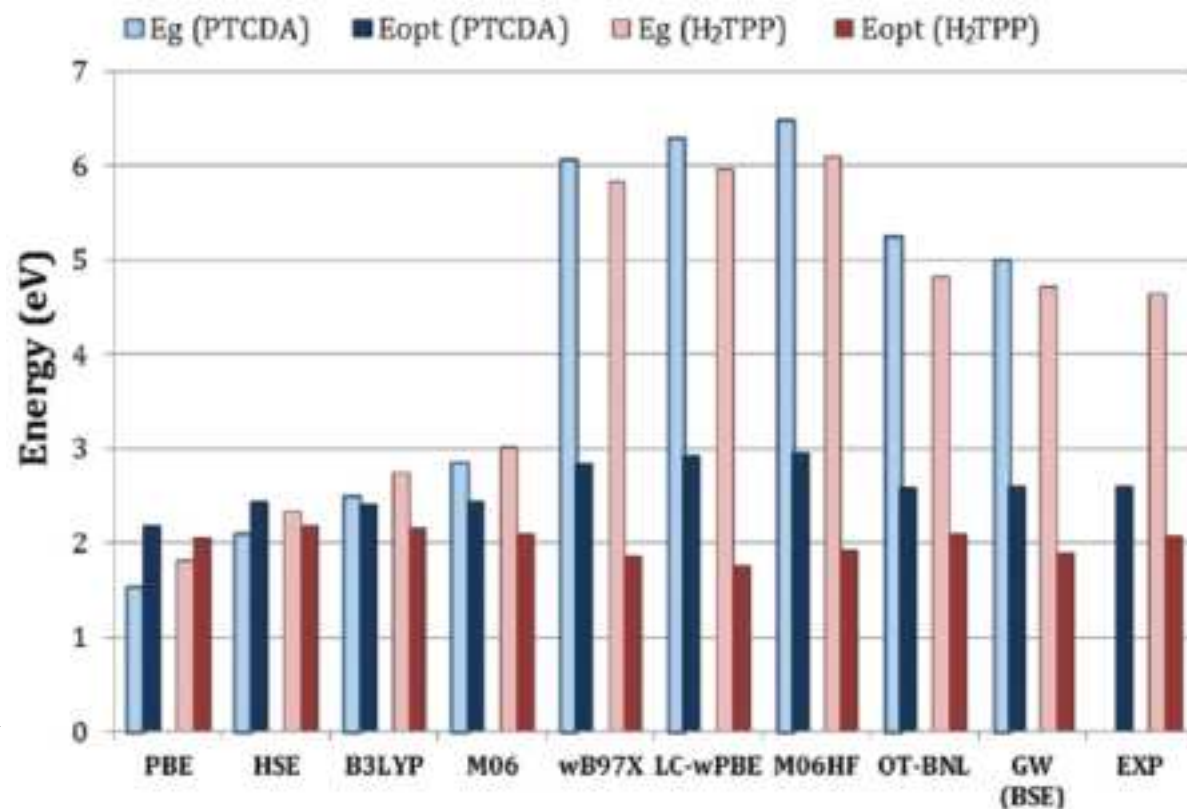
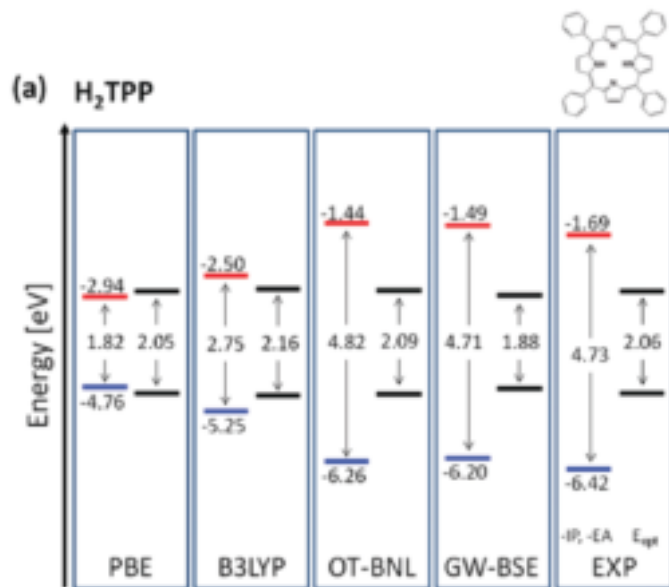
Koopmans' theorem:

$$\varepsilon_{HOMO} = -IP$$

Choose the ω that enforces
Koopmans' theorem (no empirical
parameters!).

Requires additional computational
effort: compute energies for neutral
and cation for various ω values.





Kronik, Stein, Refaely-Abramson, and Baer
 dx.doi.org/10.1021/ct2009363 | J. Chem. Theory Comput. 2012, 8, 1515–1531

See also: **Curvature and Frontier Orbital Energies in Density Functional Theory**
 Tamar Stein, Jochen Autschbach, Niranjan Govind, Leeor Kronik, and Roi Baer
<http://pubs.acs.org/doi/abs/10.1021/jz3015937>

Andreas Karolewski, Leeor Kronik, and Stephan Kümmel
 The Journal of Chemical Physics **138**, 204115 (2013); doi: <http://dx.doi.org/10.1063/1.4807325>

Fundamental and optical gaps for PTCDA and H₂TPP, compared to many-body perturbation theory and experimental values

Charge-Transfer Excitations: A Challenge for Time-Dependent Density Functional Theory That Has Been Met

Stephan Kümmel

Correctly predicting charge-transfer states in complex molecules and molecular materials has been a major challenge for first-principles theory. With the computational cost of accurate ab initio wave-function methods often being too high for exploring systems of technological relevance, one has to resort

to time-dependent density functional theory (TDDFT). However, for a long time the incorrect description of charge-transfer excitations has been considered one of the hallmark failures of TDDFT. As charge-transfer states play an important role in organic solar cells, and generally in many new materials that are aimed at converting sunlight into other forms of energy, the contribution of first principles theory to the field of energy relevant materials was seriously limited. However, in the past years this limitation has been overcome.

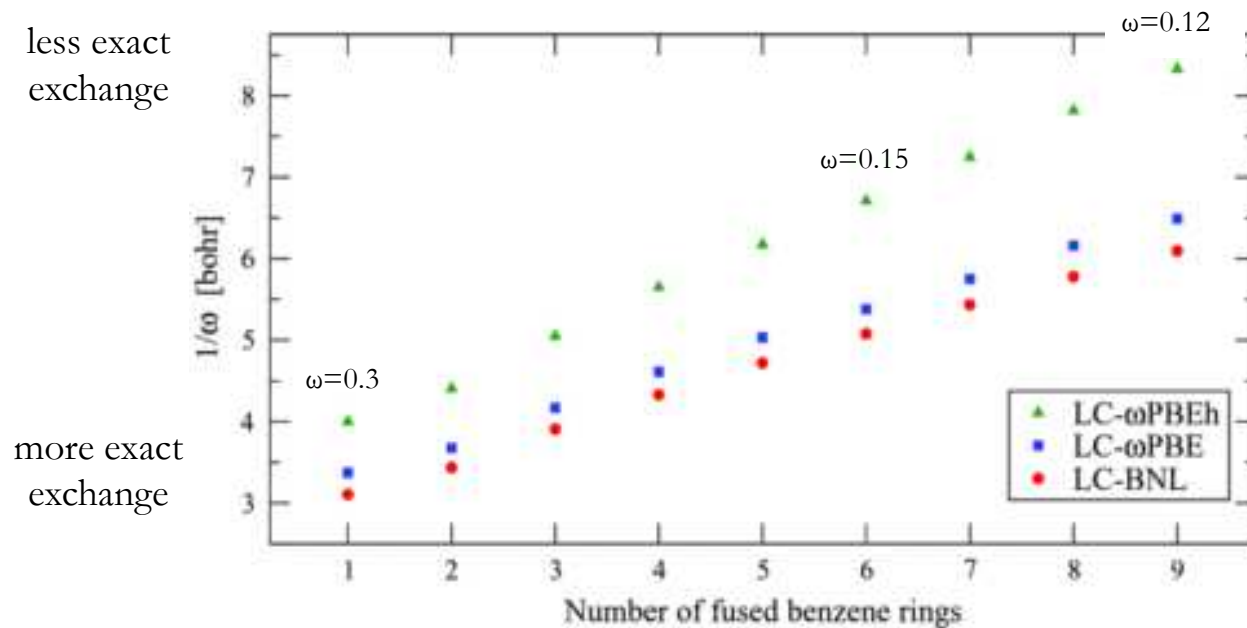
A new class of nonempirical density functionals can predict charge transfer excitations in molecules reliably. The approach by now has been extended to describe molecular solids and solvated systems. The predictive power of TDDFT has thus greatly increased, and computational studies can be expected to give true guidance in material design.

So far, this article painted the picture of tuned range-separated hybrid functionals employed in the generalized Kohn–Sham framework in bright colors. Rightfully so, because for the CT problem in TDDFT, they provide a viable solution. However, the picture of tuned functionals would not be complete without a few shades of gray.

Adv. Energy Mat.
2017, 7, 1700440.

Size-Dependent Exchange Tuning

Create system dependent exchange by tuning the range-separation parameter

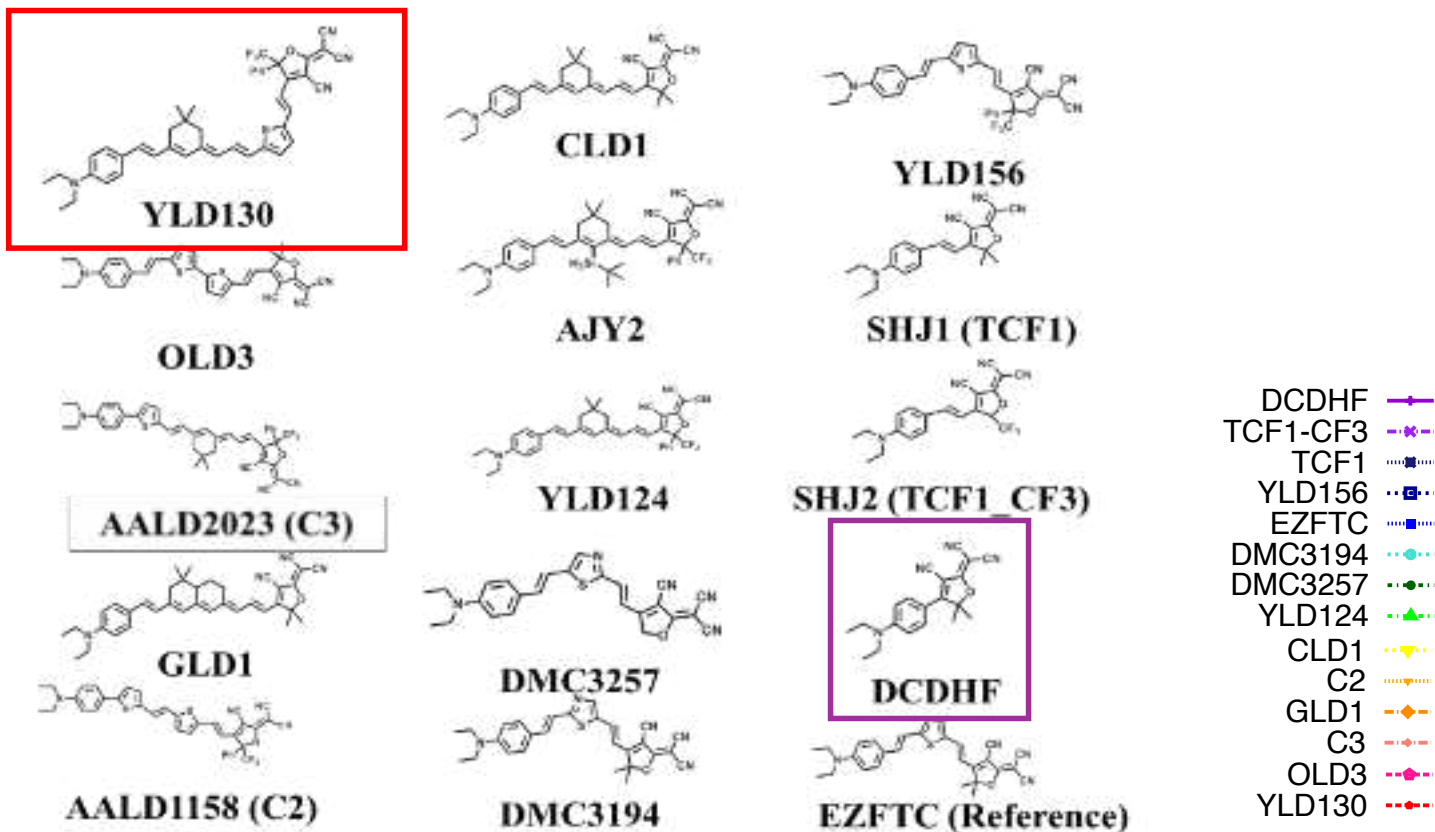


Körzdörfer, Sears, Sutton, and Brédas
J. Chem. Phys., 135, 204107, 2011

Optimal tuning predicts less exact exchange for larger systems

Size-Dependent Exchange Tuning

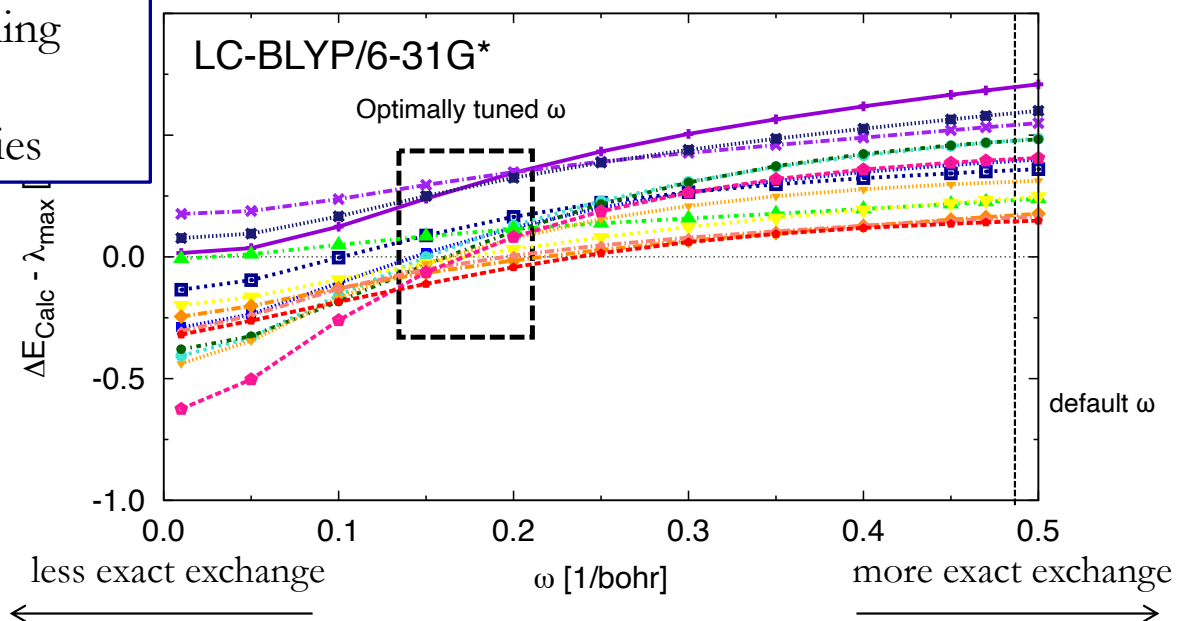
We wanted good excitation energies for this set of charge transfer chromophores



Size-Dependent Excitation Energy Accuracy

Does optimal tuning of exchange improve the excitation energies?

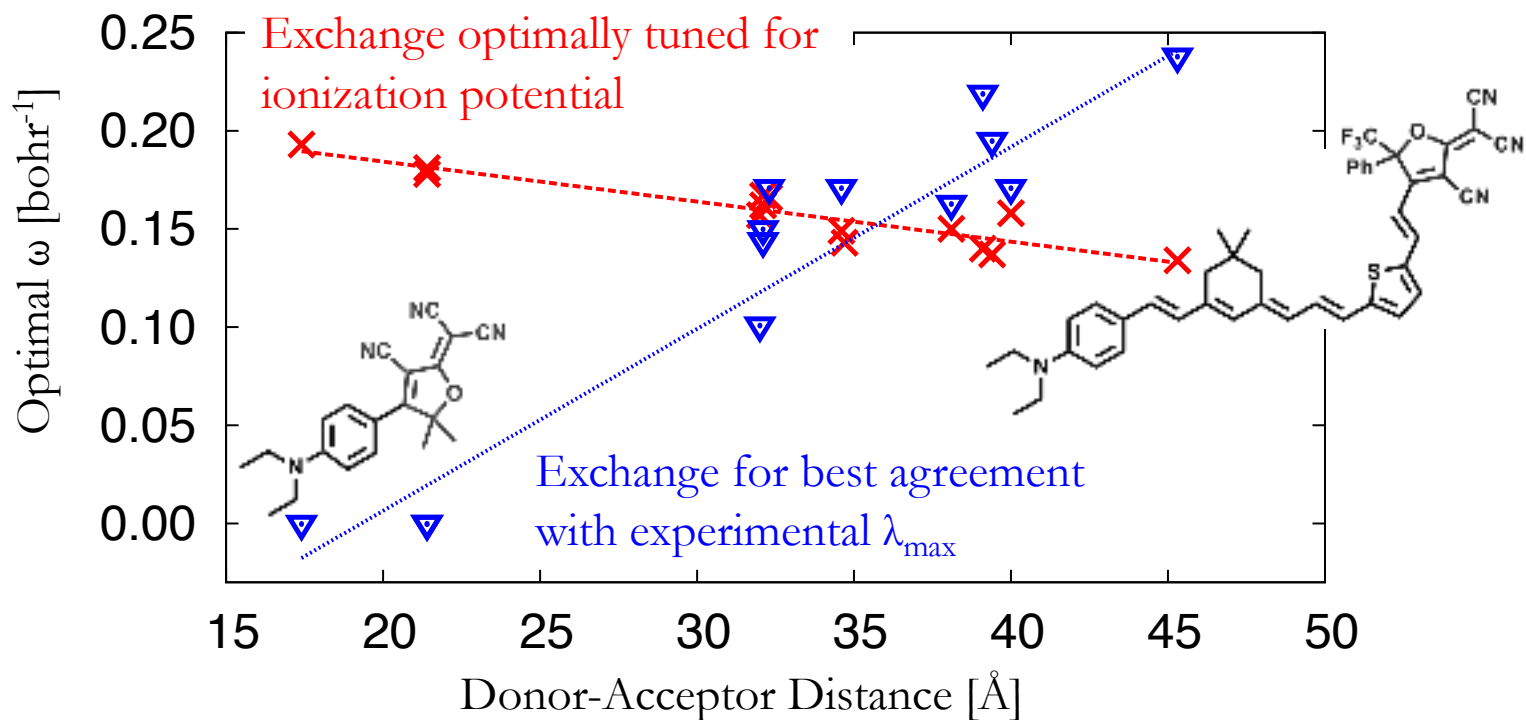
Yes, optimal tuning improves the excitation energies



Garrett, Sosa Vazquez, Egri, Wilmer, Johnson, Robinson, Isborn
J. Chem. Theory Comp., 10, 3821, 2014

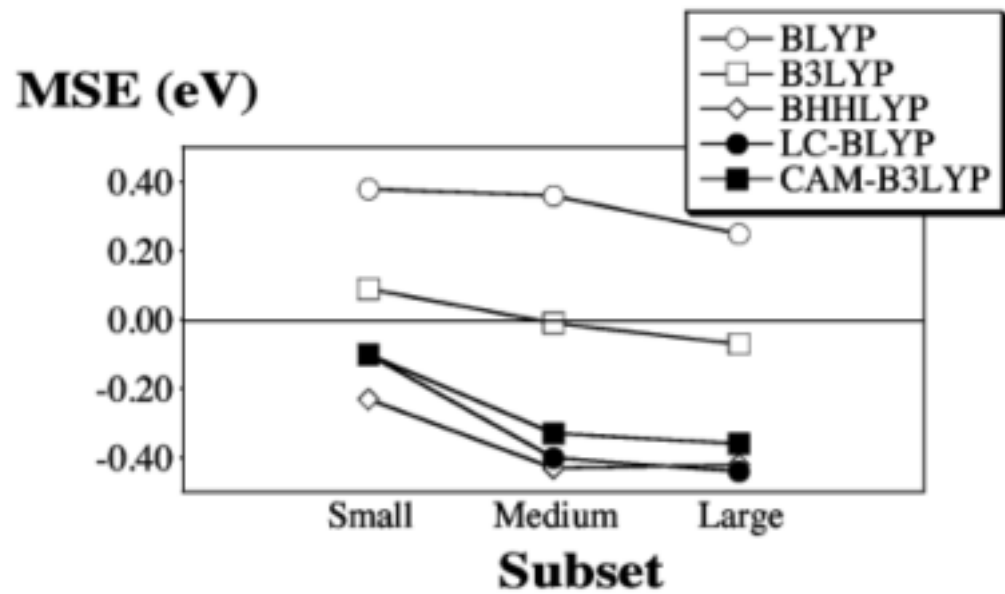
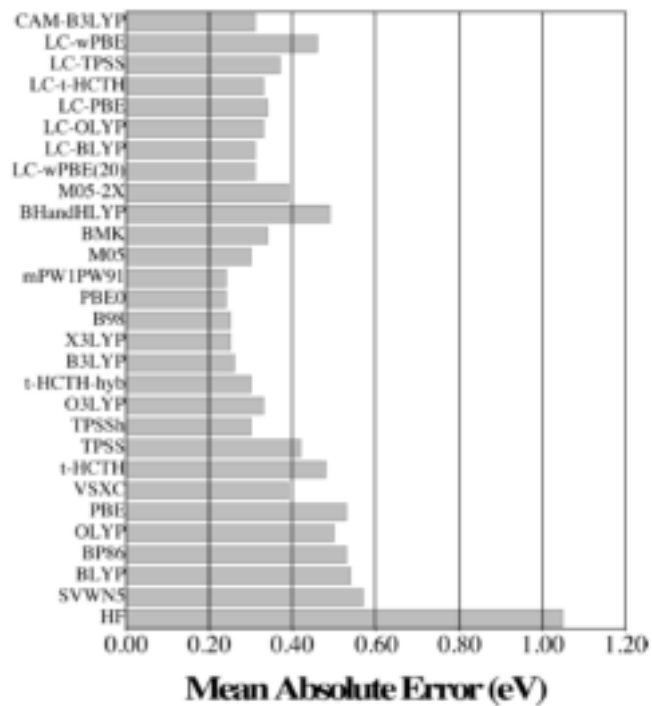
But, the best agreement with λ_{max} predicts more exact exchange for larger systems

Size-Dependent Exchange: Tuning vs Accuracy



Garrett, Sosa Vazquez, Egri, Wilmer, Johnson, Robinson, Isborn
J. Chem. Theory Comp., 10, 3821, 2014

Size-Dependent TDDFT Errors



the VT set contains 28 molecules and 103 excited states (not a significant number of CT states)

Jacquemin, Wathelet, Perpète, Adamo
 J. Chem. Theory Comput. 2009, 5, 2420–2435

Summary

Three big developments have helped to solve the charge-transfer problem in TDDFT:

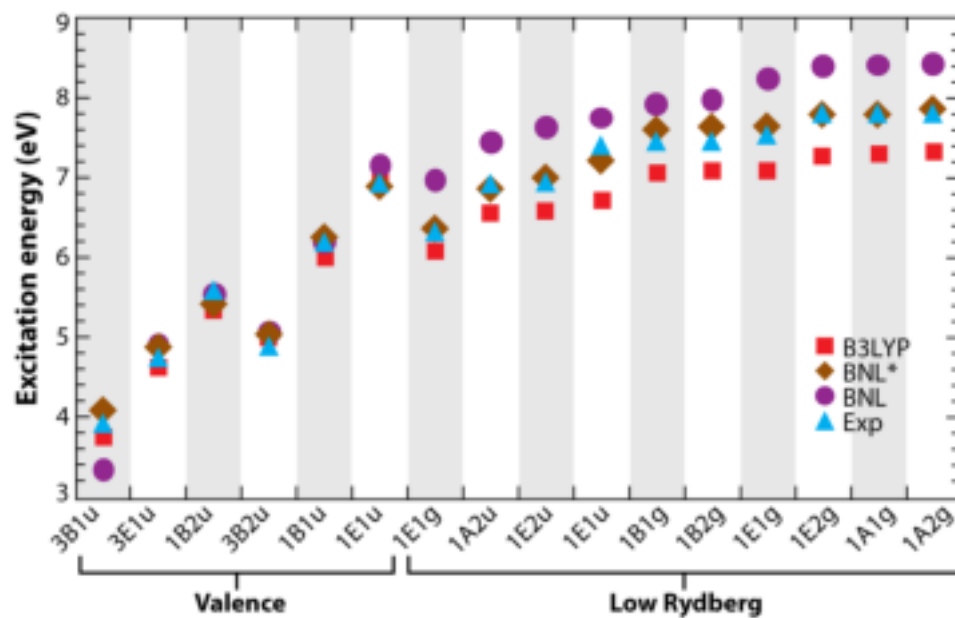
1. Generalized Kohn-Sham theory allows for orbital dependence and hybrid functionals
2. Range-separation of the Coulomb operator enables long-range correction
3. Optimal tuning of the range-separation parameter leads to accurate energies, with some drawbacks


Concerns with optimal tuning

- * Not size-consistent
- * Has incorrect exact exchange trend with system size compared to experiment!

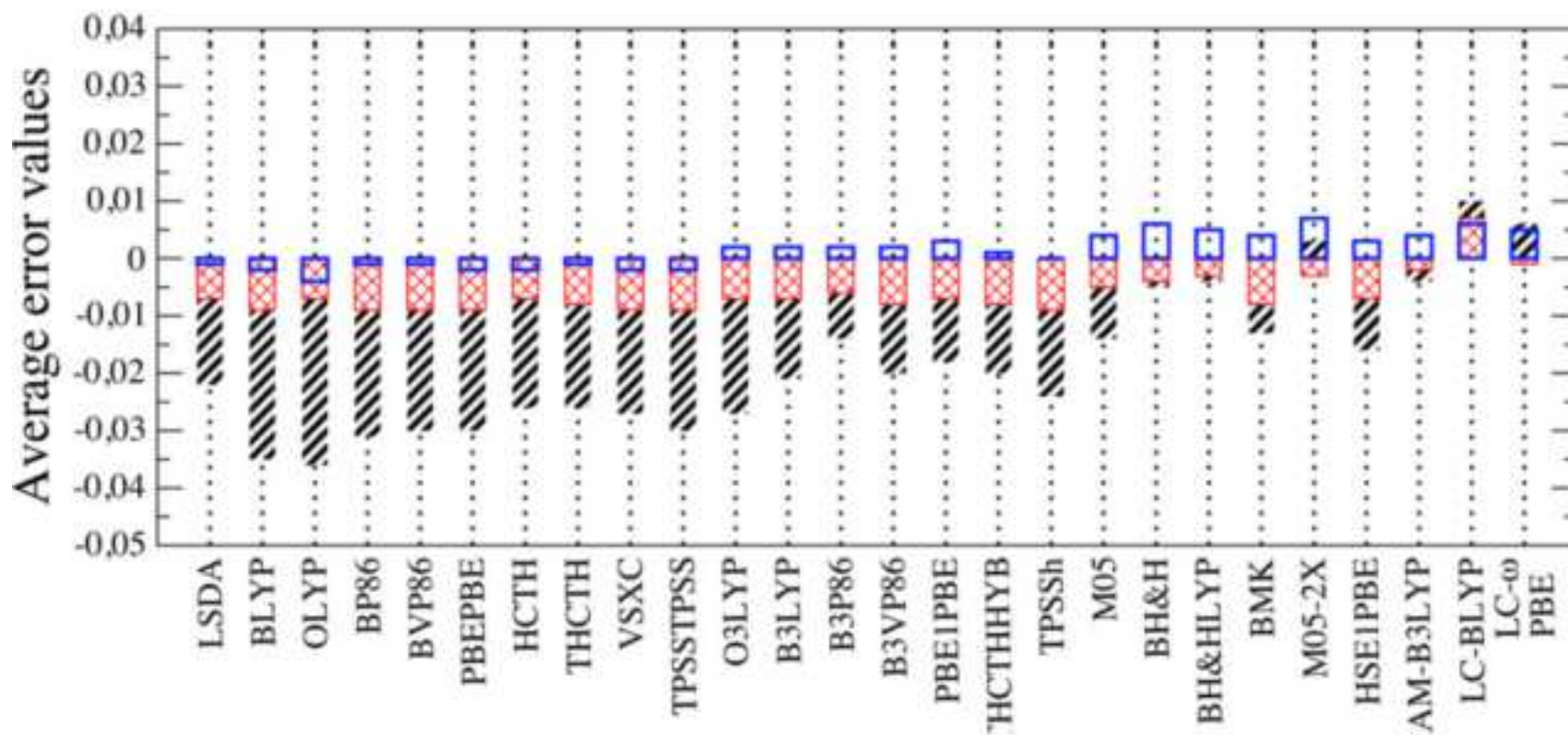
TDDFT seems to have different errors with systems of different size?

Does tuning improve Rydberg transitions?



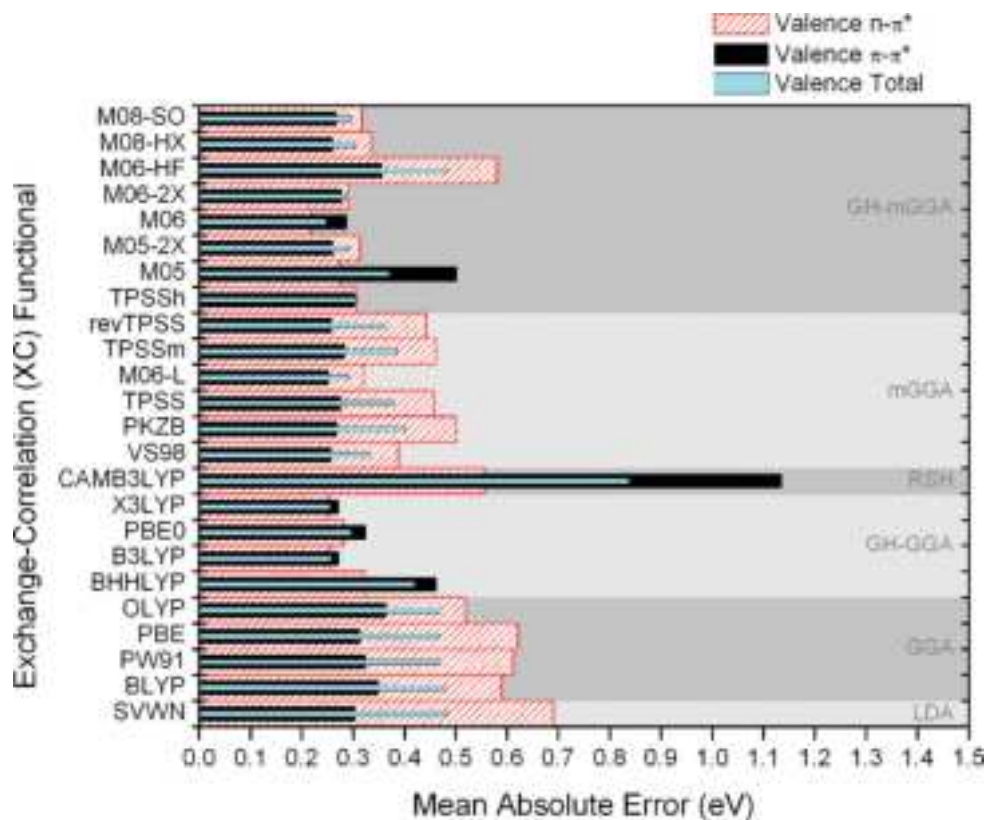
 Baer R, et al. 2010.
Annu. Rev. Phys. Chem. 61:85–109

TDDFT oscillator strengths



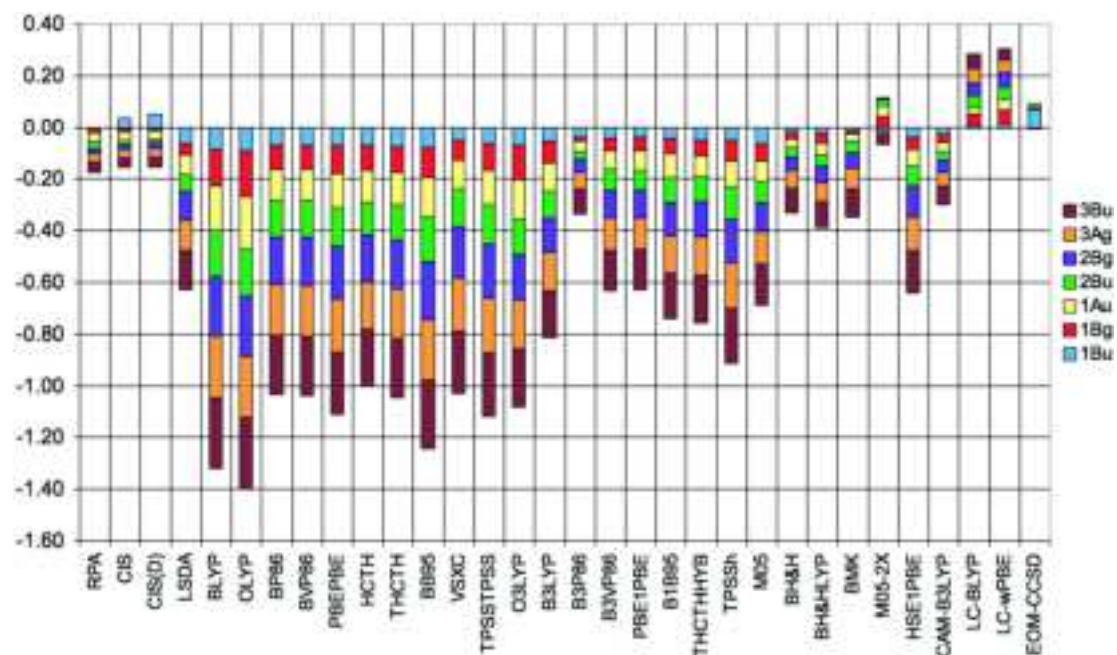
M. Caricato, G. Trucks, M. Frisch, K. Wiberg,
J. Chem. Theory Comput.
2010, 7, 456.

What kinds of transitions does TDDFT get correct?

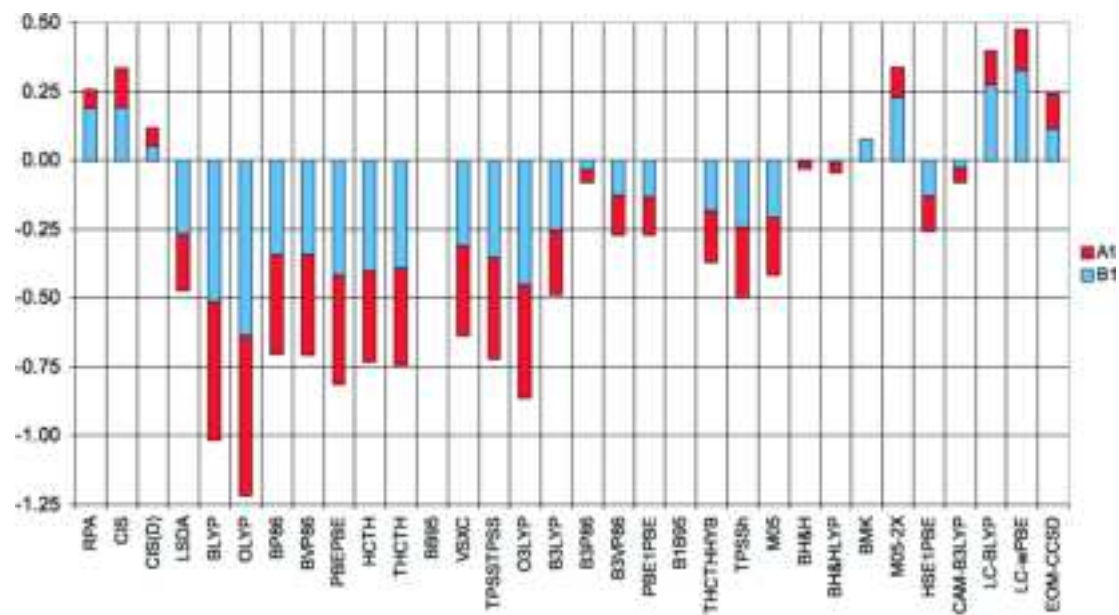


14 small- to medium-sized compounds with 60 valence experimental excited state energies

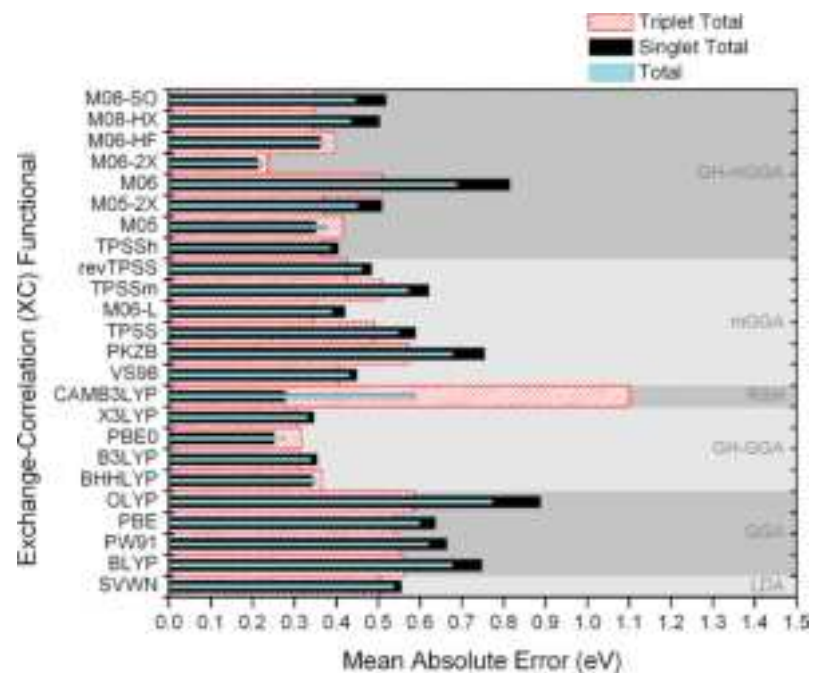
Valence transitions are often predicted within 0.2-0.5 eV of the correct value



Errors (eV) for trans-1,3-butadiene. The 1Bu transition is $\pi \rightarrow \pi^*$, the rest are Rydberg.



Errors (eV) for isobutene. The SCF of BB95 and B1B95 did not converge. The transitions are Rydberg.



vertical excitation energies against an experimental benchmark set comprising 14 small- to medium-sized compounds with 101 total excited states. The experimental benchmark set consists of singlet, triplet, valence, and Rydberg excited states

FIG. 1. Comparison of density functional mean absolute errors for singlet and triplet excited states.