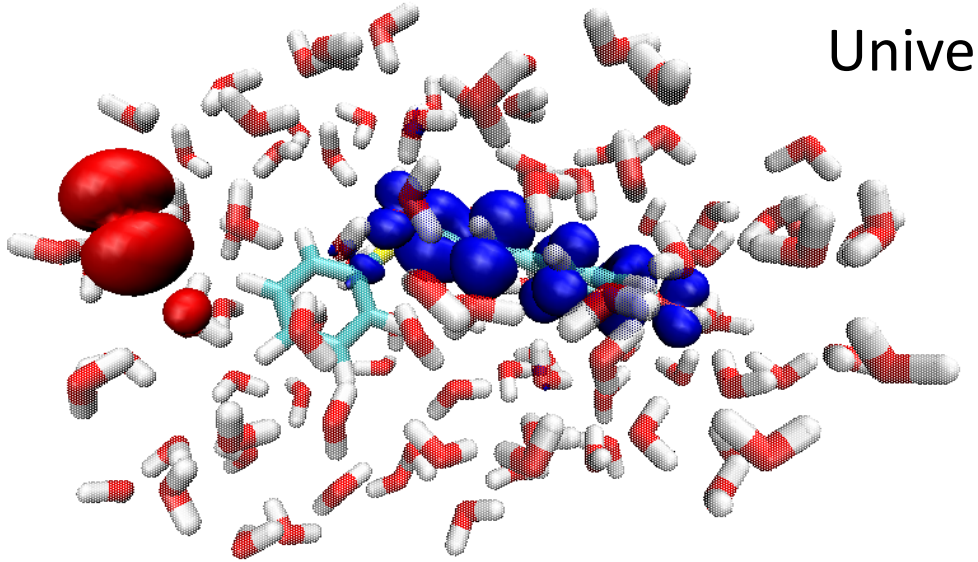
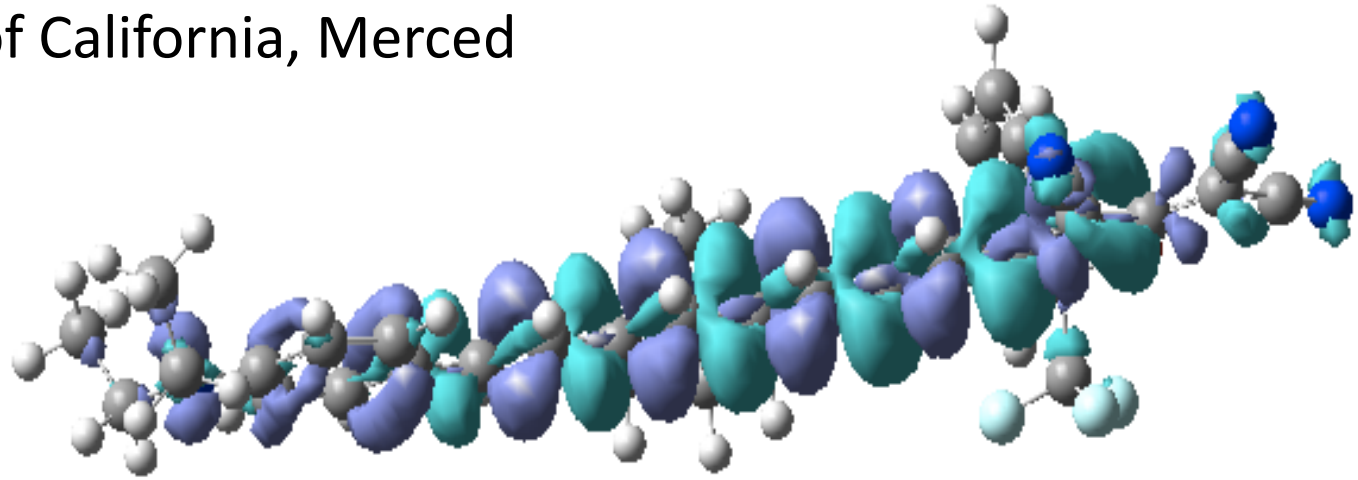
Accuracy concerns in TDDFT: Focus on exact exchange and charge-transfer error

Christine M. Isborn

University of California, Merced



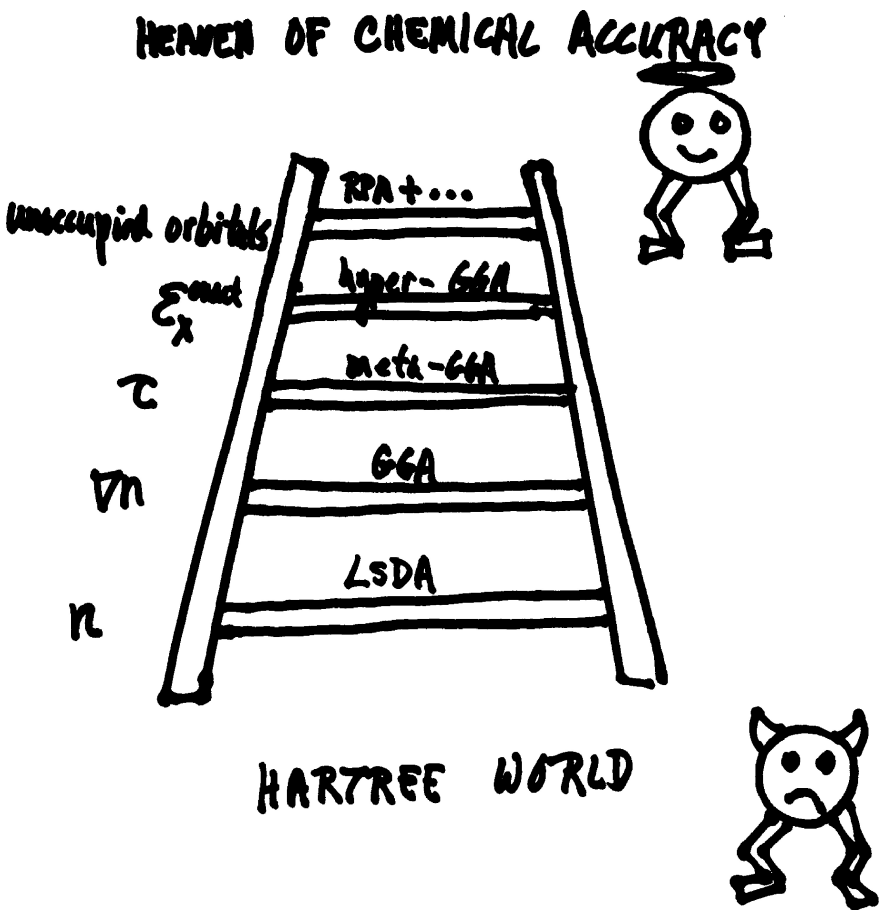


Outline

- Jacob's ladder of functionals – how do they do for TDDFT excitation energies? (**You want acronyms? I'll give you the acronyms!!**)
- 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
- Optimal tuning of long-range corrected hybrids

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.

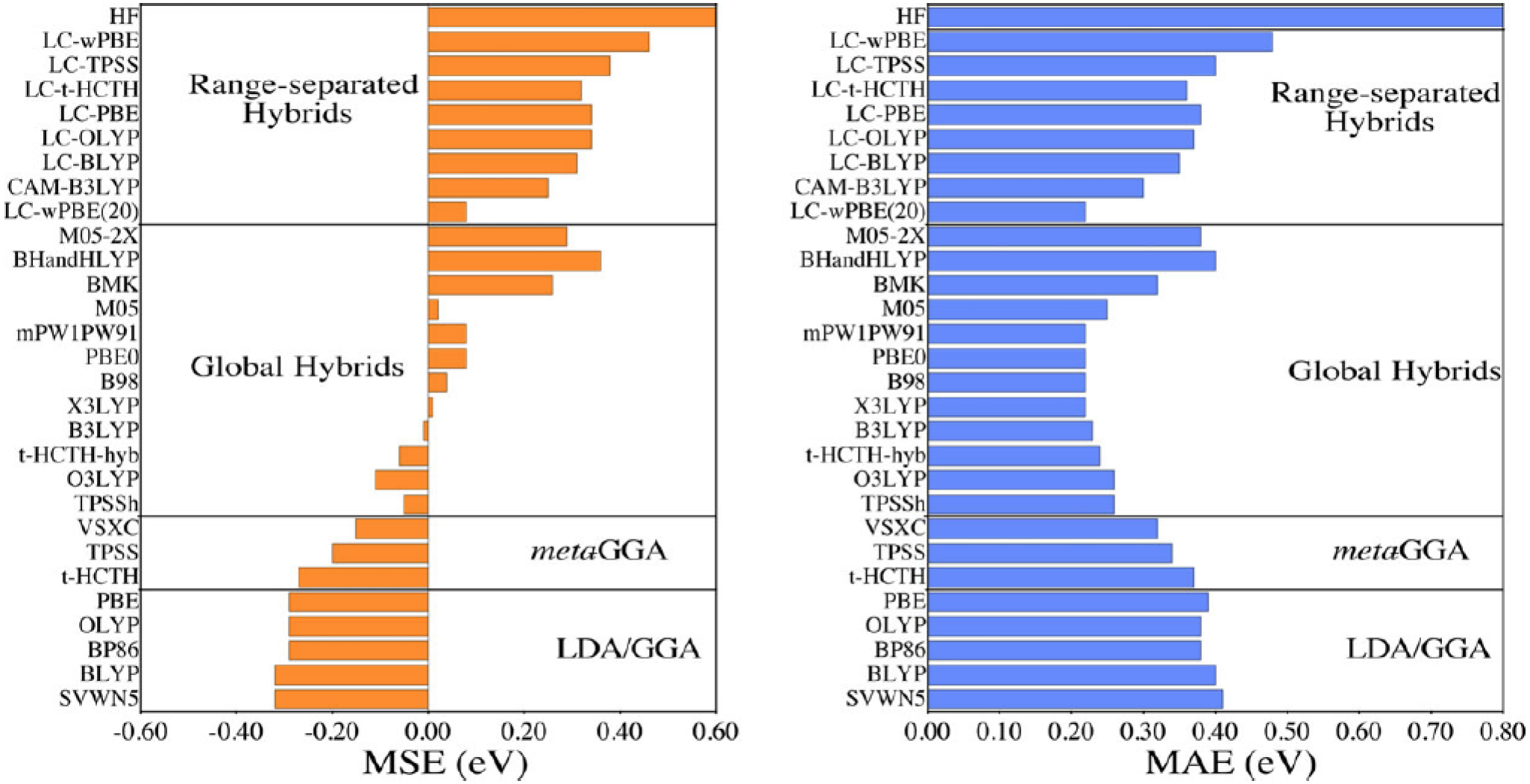
This is because (usually) increasing the amount of exact exchange in the functional will lead to higher excitation energies.

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

Perdew, Ruzsinszky, Constantin, Sun, Csonka
J. Chem. Theory Comp., 2009, 5, 902
DOI: 10.1021/ct800531s

How accurate is TDDFT for excitation energies?

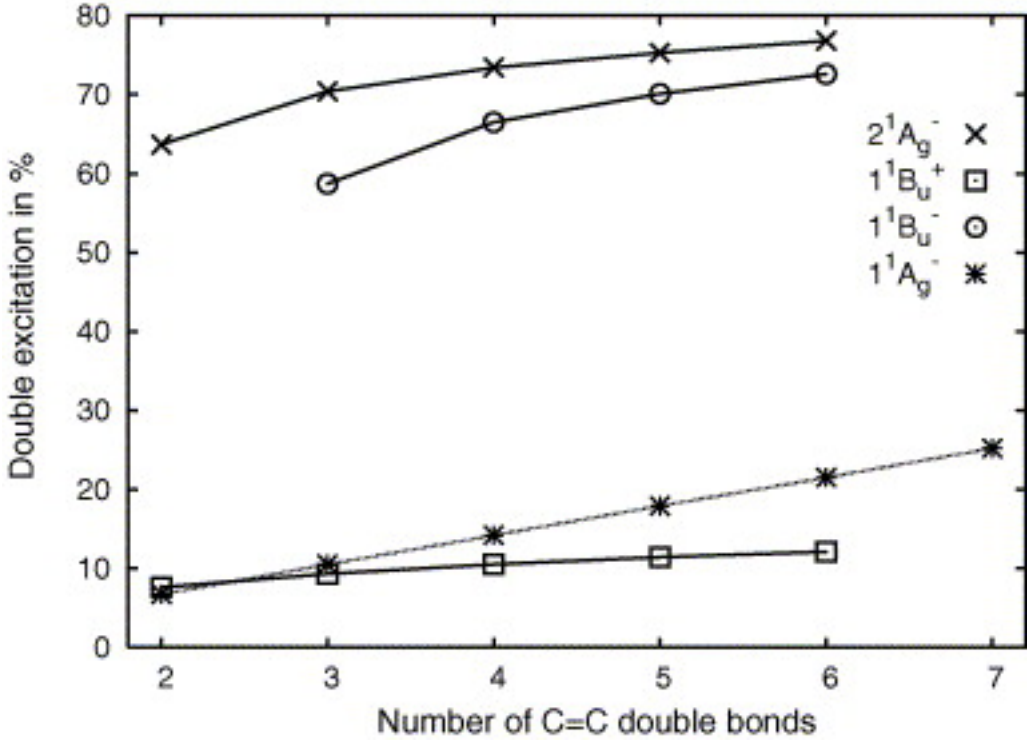


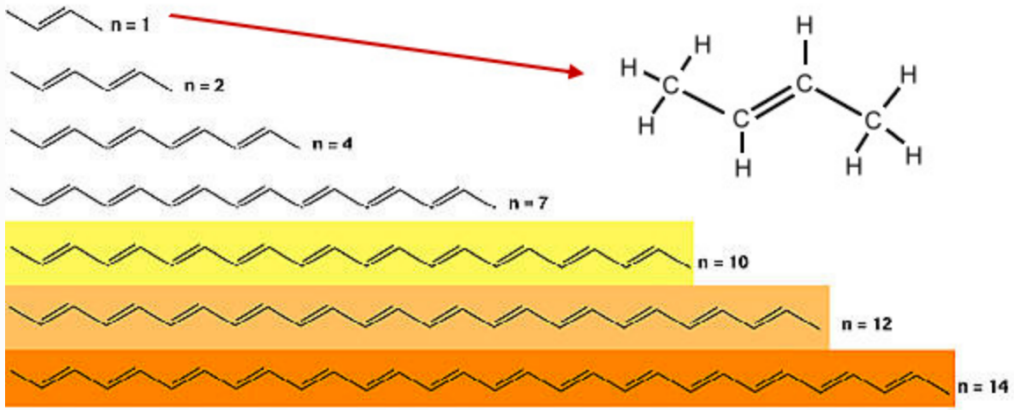
comparing 614 experimental λ_{max} to vertical transition energies

Laurent and Jacquemin
International Journal of Quantum Chemistry 2013, 113, 2019

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.



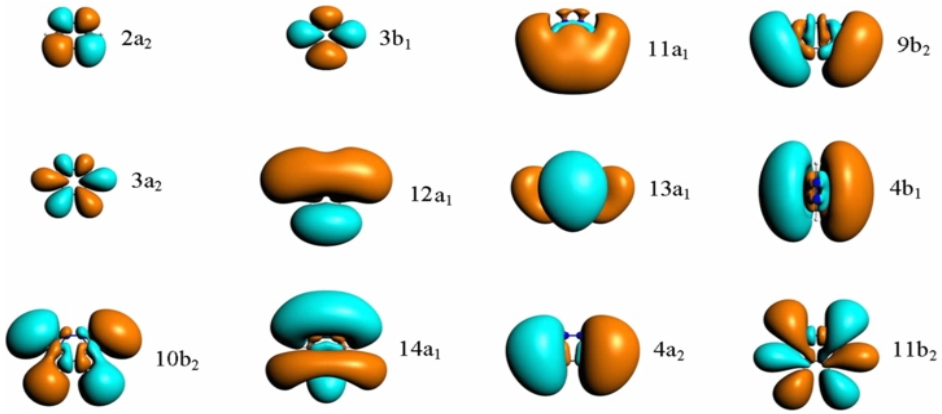


Starcke, Wormit, Schirmer, Dreuw
Chemical Physics, 329, 39, 2006
https://doi.org/10.1016/j.chemphys.2006.07.020,

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



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

- Rydberg transitions

- Charge-transfer transitions

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
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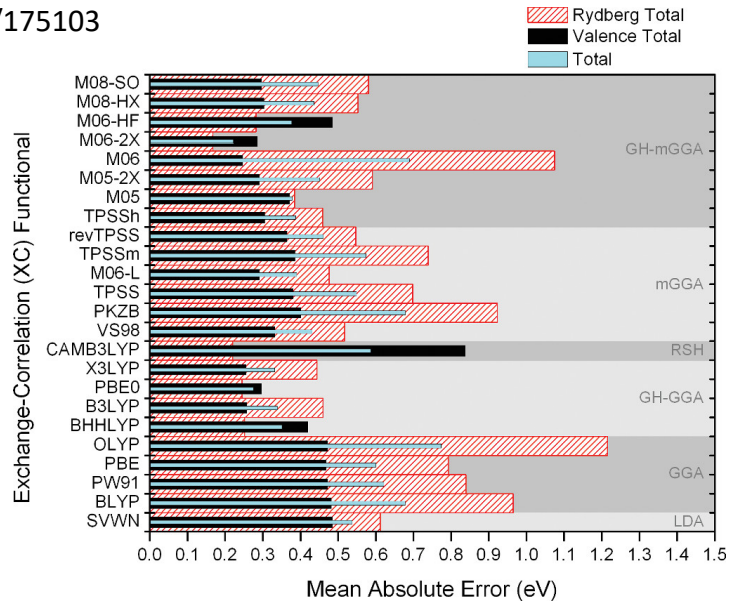
(Received 29 September 2003; accepted 23 October 2003)

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

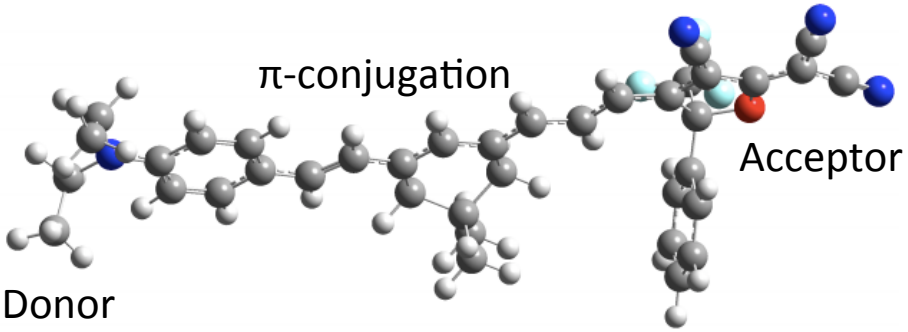
A **charge-transfer complex** (**CT complex**) or **electron-donor-acceptor complex** is an association of two or more molecules, or of different parts of one large molecule, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction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

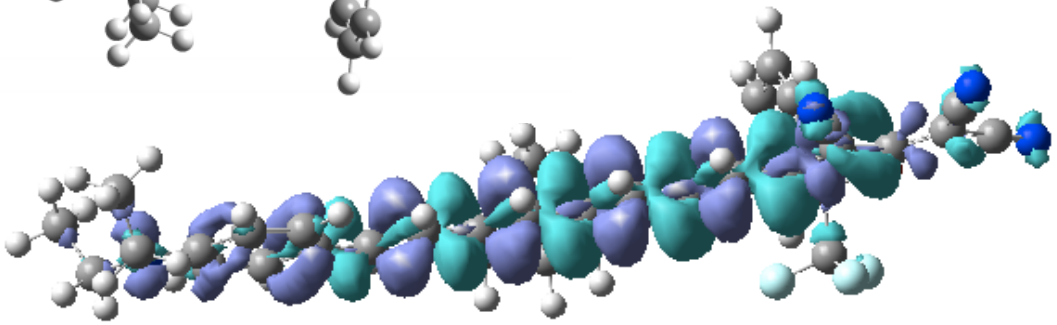
- May be on the same molecule (donor group and acceptor group) or between molecules
- Small overlap between donor and acceptor densities (movement of electron across space)
- Often associated with a large change in dipole moment
- The Coulombic attraction between the excited electron and hole should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

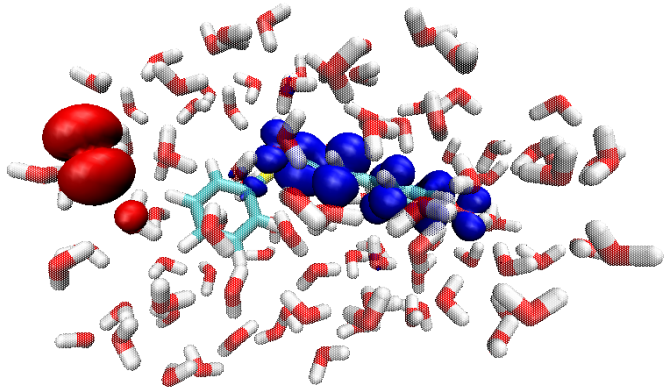
Examples of charge-transfer transitions

CT transitions important for:

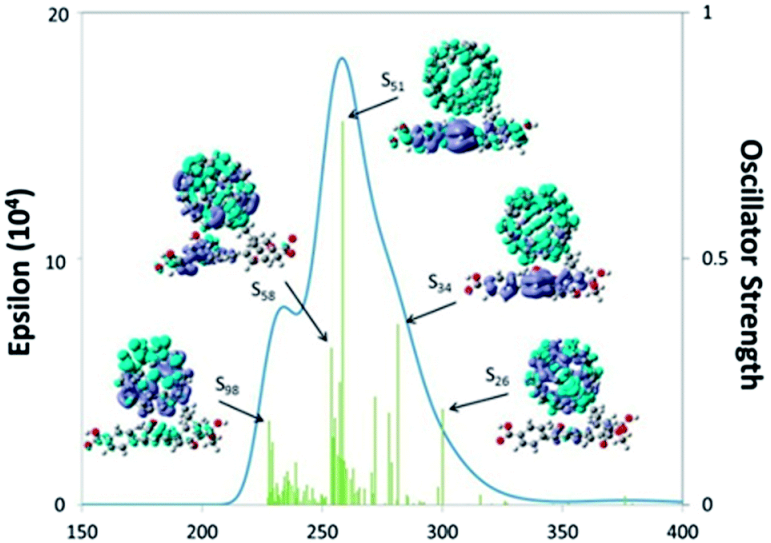
- organic electronics
- solar cell materials
- chromophores in solution



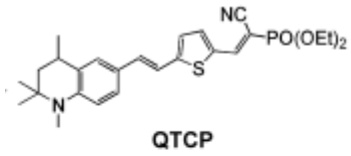


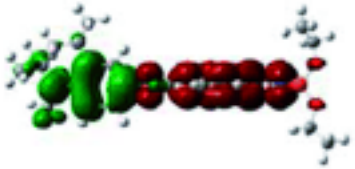


Isborn, Mar, Curchod, Tavernelli, Martinez
J. Phys. Chem. B 2013, 117, 12189
dx.doi.org/10.1021/jp4058274



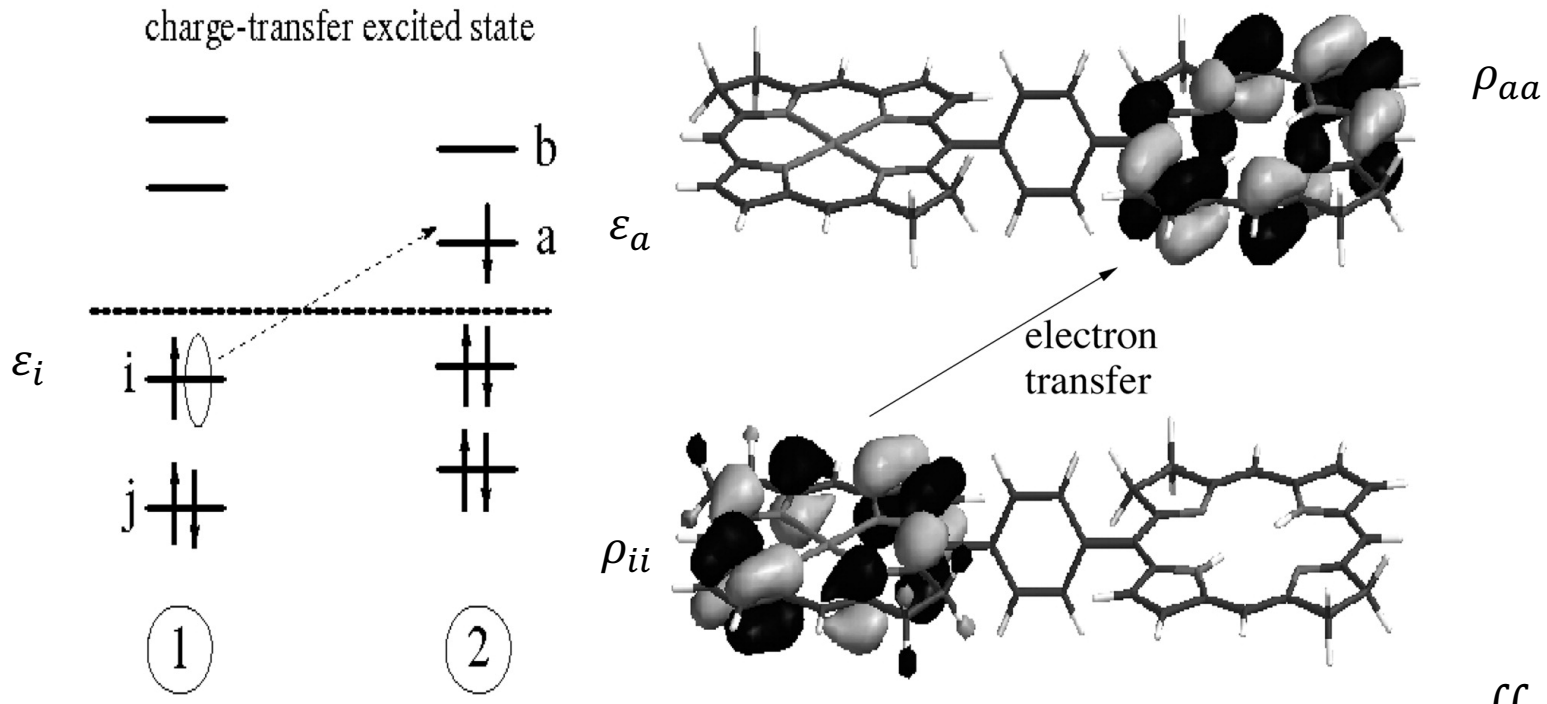
Leong , Foster, Wong, Spoerke, Van Gough, Deaton, Allendorf
J. Mater. Chem. A, 2014, **2**, 3389-3398
DOI: 10.1039/C3TA14328G





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

What should the excitation energy be?



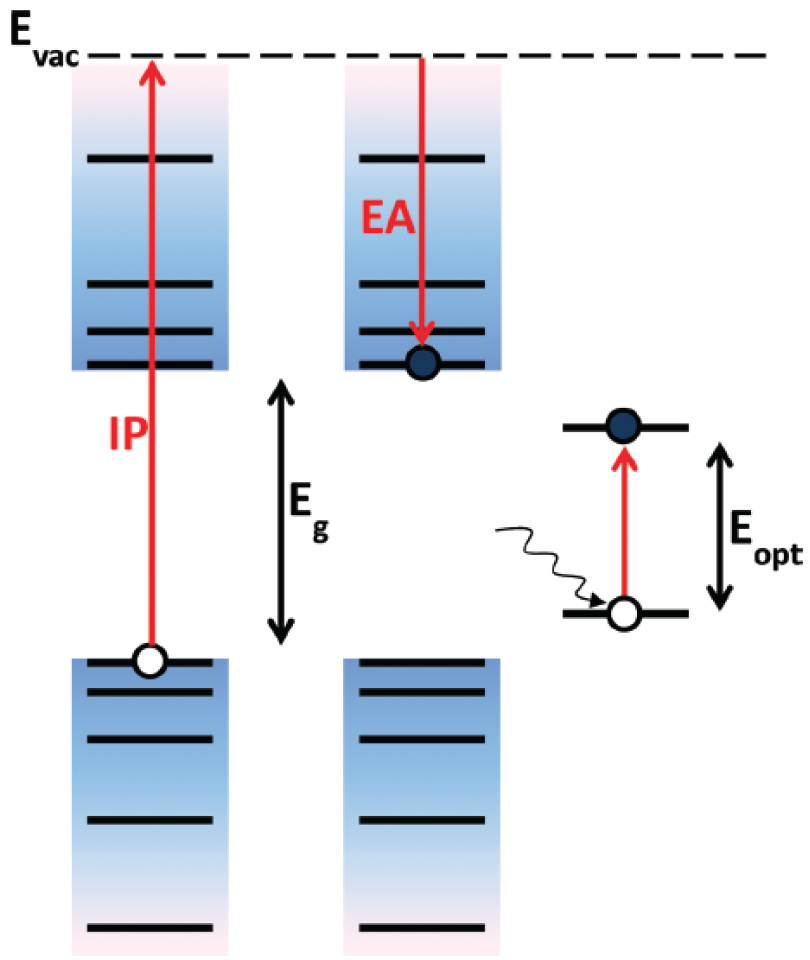
$$\varepsilon_i - \varepsilon_a - \frac{\rho_{ii}\rho_{aa}}{|r_i - r_a|}$$

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

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

Dreuw, Head-Gordon,
J. Am. Chem. Soc. **2004,** 126, 4007
DOI: 10.1021/ja039556n

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

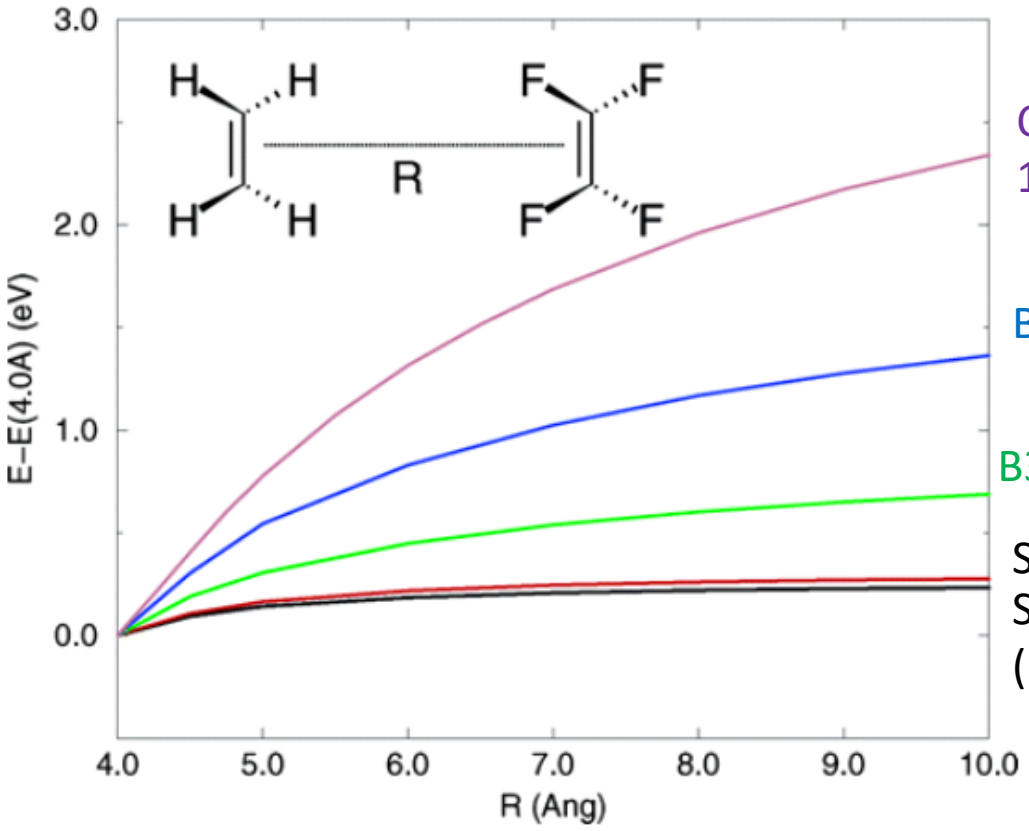


Electron-hole Coulombic electrostatic attraction (aka exciton binding energy) leads to a smaller optical gap.

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.

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

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)

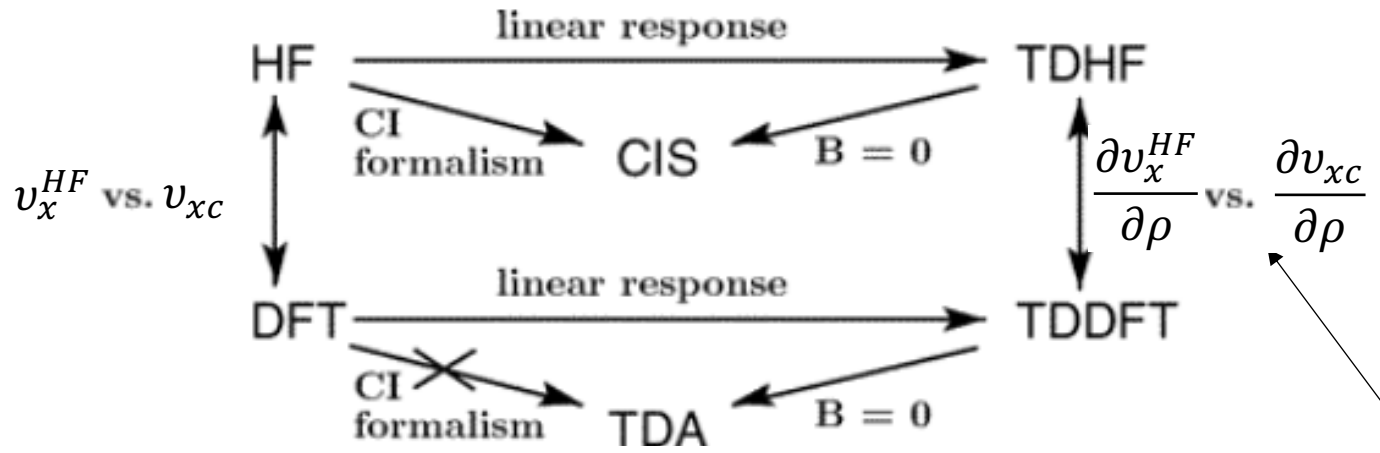
B3LYP (hybrid with 20% exact exchange)

SVWN / LB94
Similar behavior for LSDA, GGAs (BLYP, PBE), meta-GGAs

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

Dreuw, Weisman, Head-Gordon
J. Chem. Phys. 119, 2943, 2003
doi: http://dx.doi.org/10.1063/1.1590951

Why are charge-transfer states spuriously low in energy for TDDFT but not TDHF?



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

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

But 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

Exact exchange in the ground state leads to the correct Coulombic 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

$$F_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}[2(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)]$$

Coulomb (J) exchange (K)

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

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

$$\frac{\partial F_{ia}}{\partial P_{jb}}$$

Where i, j are occupied orbitals, and a,b are the virtual (unoccupied) orbitals

$$F_{ia} = \sum_{\lambda\sigma} P_{\lambda\sigma}[2(ia|\lambda\sigma) - (i\lambda|a\sigma)]$$

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

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

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

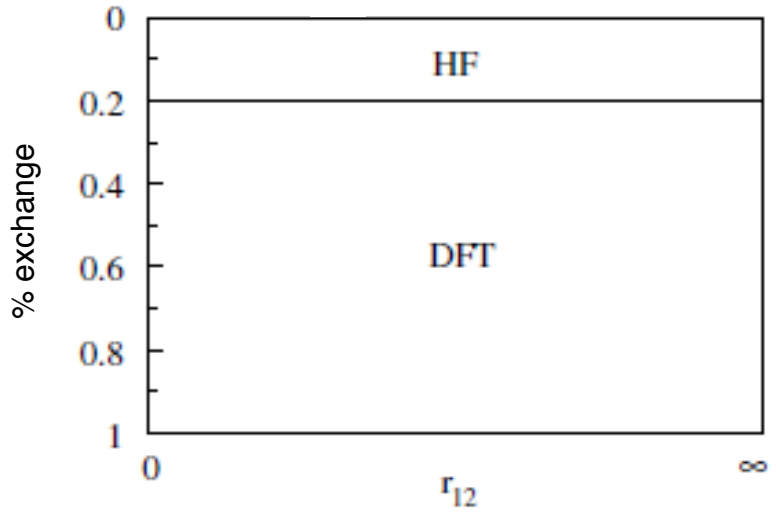
For the case where j=i and b=a, we get a Coulomb term from what was the exchange term: $[2(ia|ia) - (ii|aa)]$

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

Do hybrid functionals fix the TDDFT charge transfer error?

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

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:

$$\frac{1}{r_{12}} = \underbrace{\frac{1-\beta erf(\omega r_{12})}{r_{12}}}_{\text{Short-range}} + \underbrace{\frac{\beta erf(\omega r_{12})}{r_{12}}}_{\text{Long-range}}$$

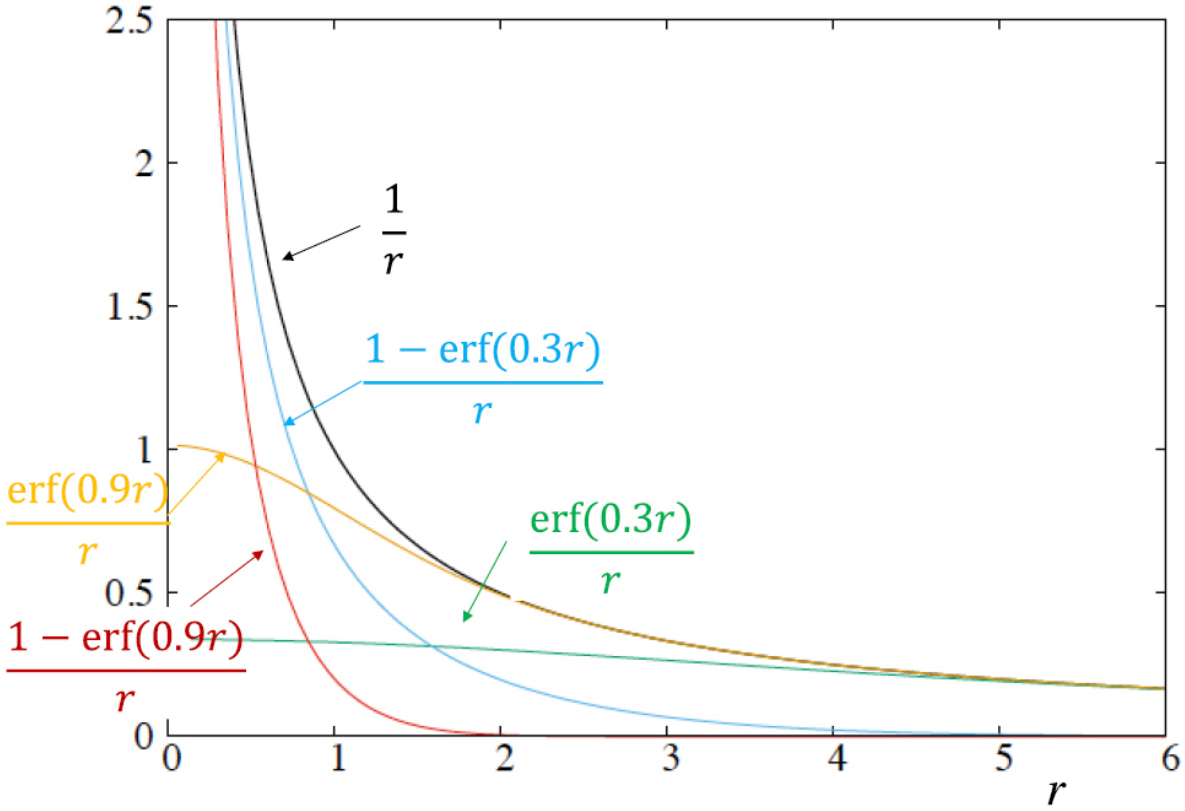
Leads to a range-separated hybrid (RSH) functional

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).



Maitra "Charge transfer in TDDFT" J. Phys.: Condens. Matter 2017 29, 423001

Long-range corrected functionals

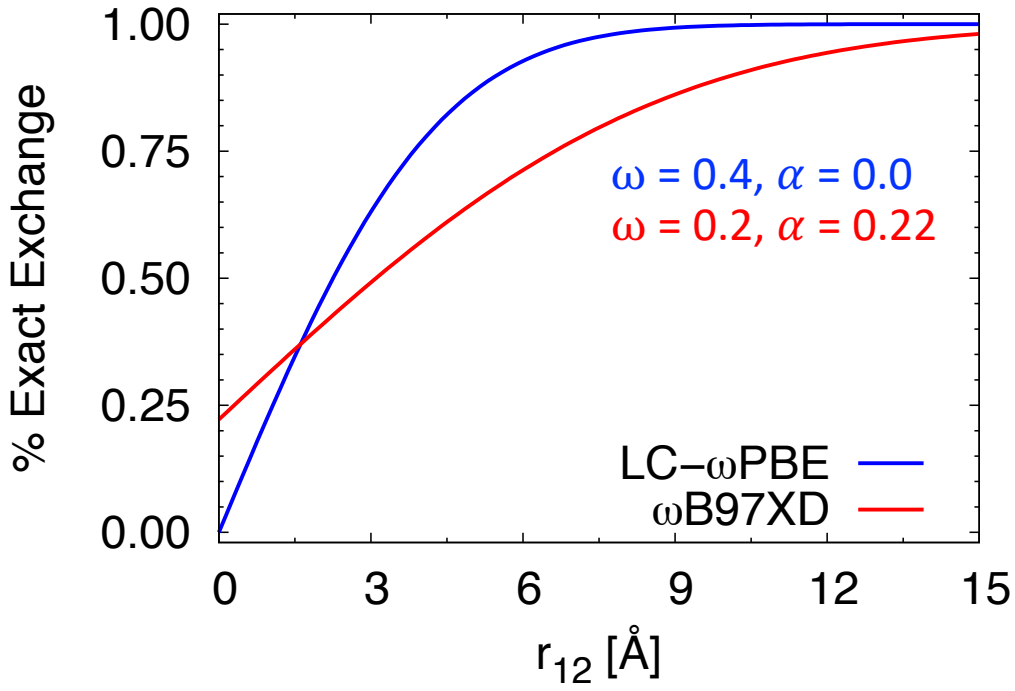
Using 100% exact exchange at long range yields a 'long-range corrected (LRC or LC) functional.

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

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

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

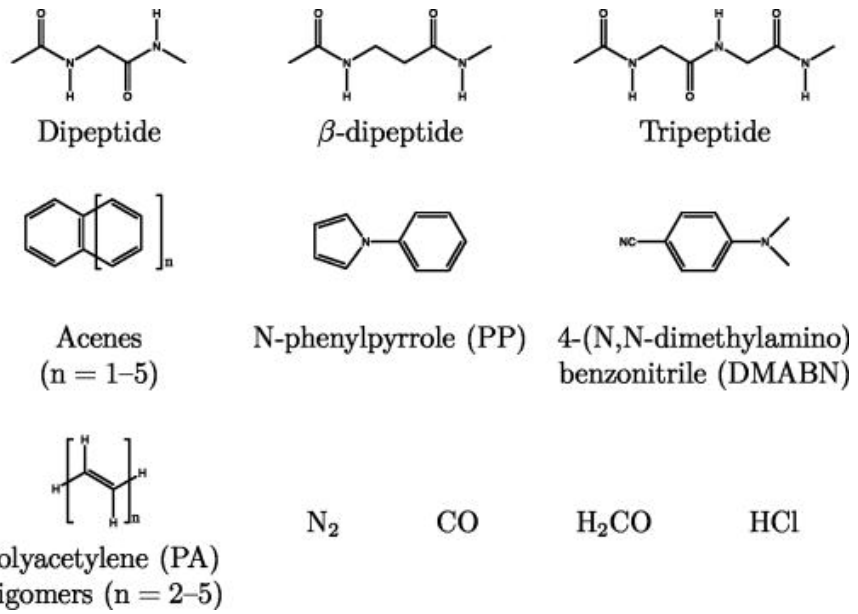


Examples of long-range corrected: LC-ωPBE, LC-BLYP, ωB97

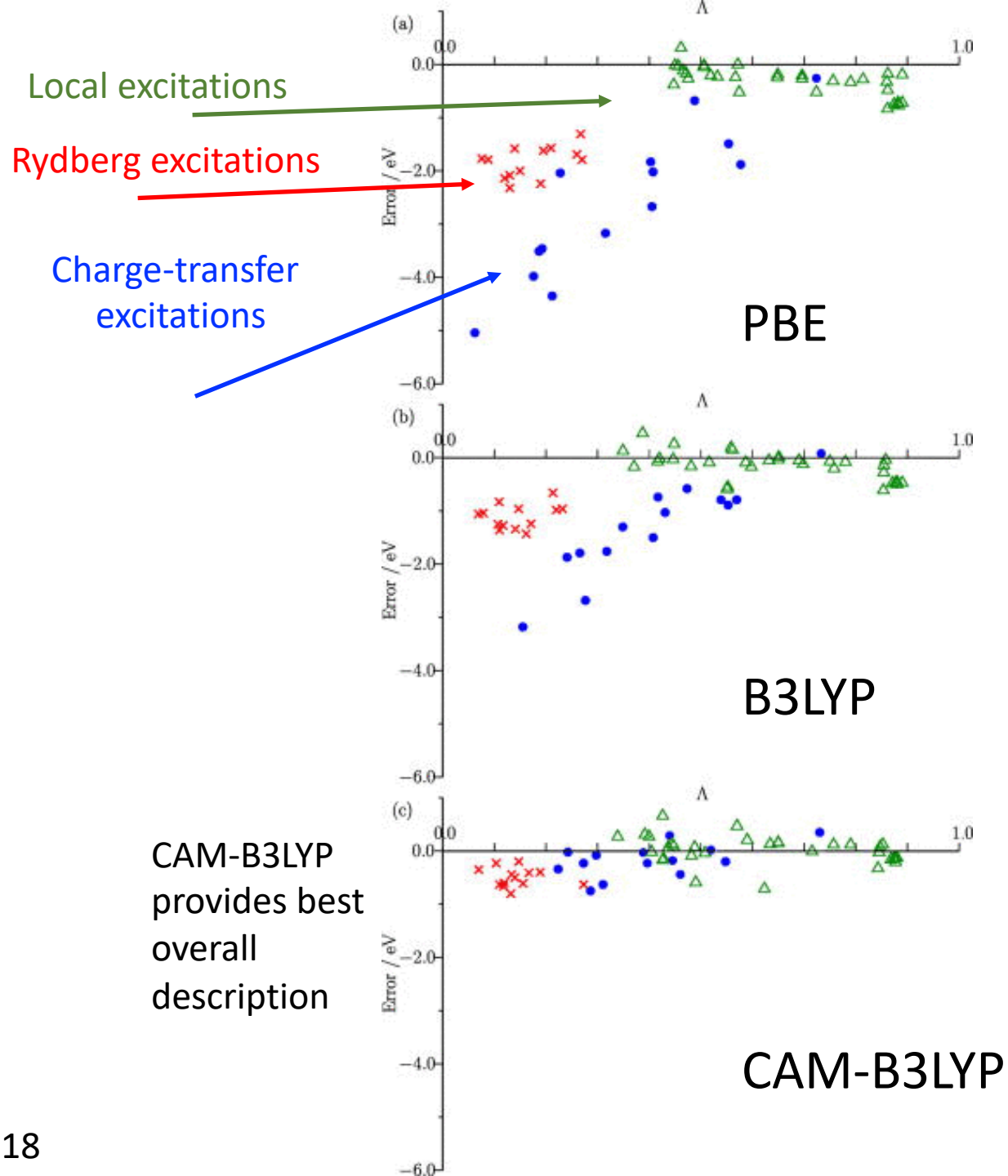
Examples of long-range corrected + short range exchange: LC-ωPBEh, ωB97x

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

Error comparisons for PBE, B3LYP, CAM-B3LYP



Λ = measure of overlap (quantifies CT character)

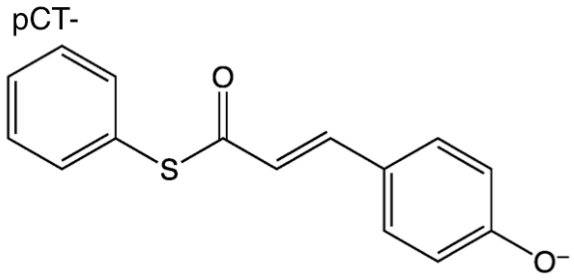


CAM-B3LYP provides best overall description

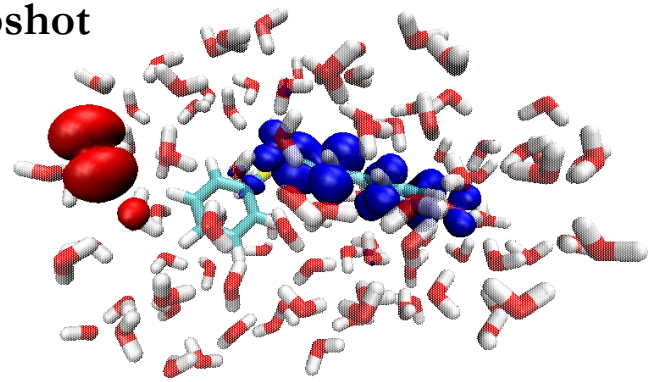
Peach, Benfield, Helgaker, Tozer, J. Chem. Phys. 2008, 128, 044118

An extreme CT problem: molecules in solution

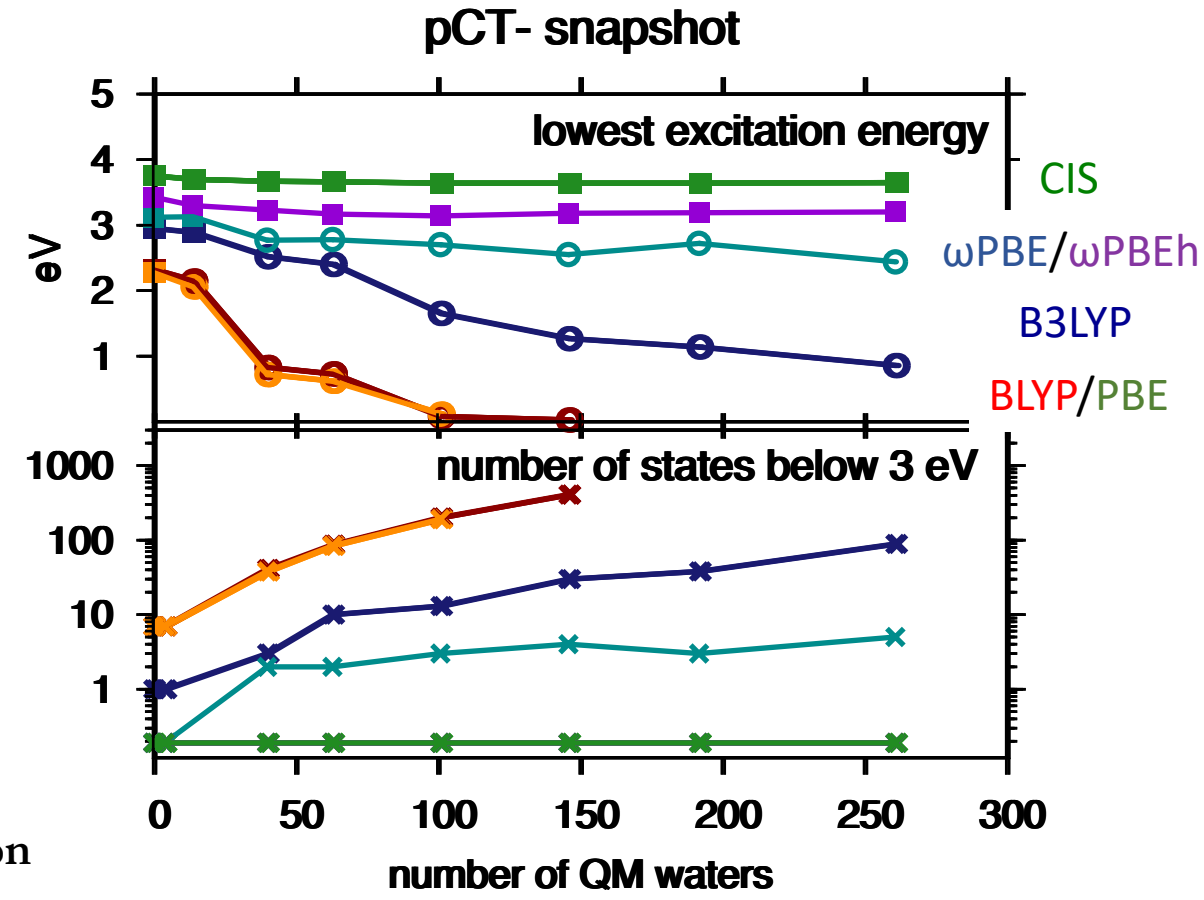
trans-thiophenyl-p-coumarate



Solvated snapshot



Need Coulombic stabilization of electron and hole



Isborn, Mar, Curchod, Tavernelli, Martinez
J. Phys. Chem. B 2013, 117, 12189
dx.doi.org/10.1021/jp4058274