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
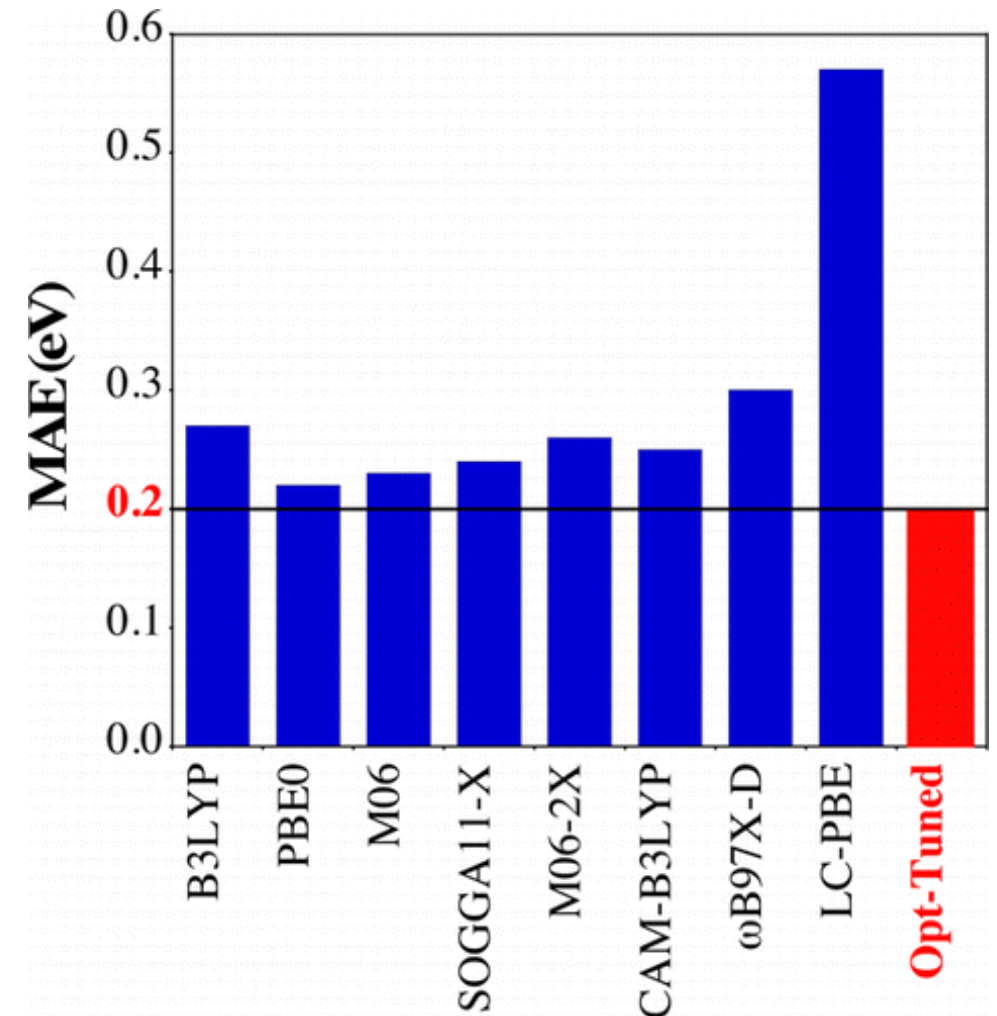dx.doi.org/10.1021/ct2009363
J. Chem. Theory Comput., 8, 1515, 2012

A review:
Delocalization Error and "Functional Tuning" in Kohn–Sham Calculations of Molecular Properties
Jochen Autschbach*,† and Monika Srebro‡
dx.doi.org/10.1021/ar500171t | 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
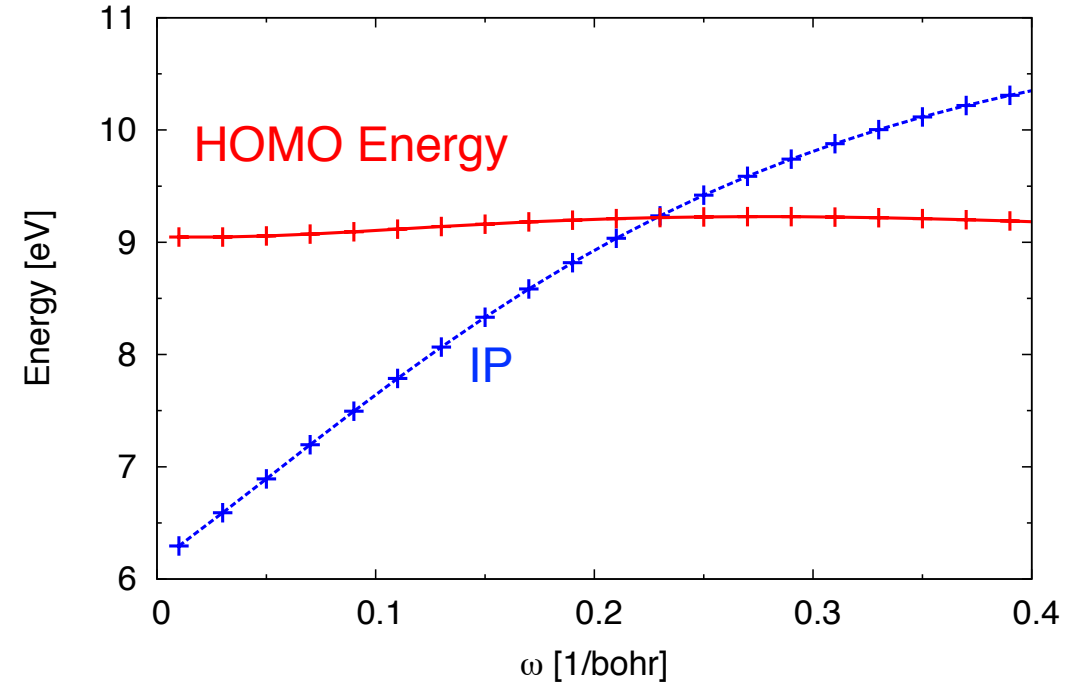
Tuning the range-separation parameter

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.

This IP exchange tuning method is currently quite popular for TDDFT excitation energies.

Tuning the range-separation parameter

In an exact theory, the energy of the HOMO is equal to the ionization potential
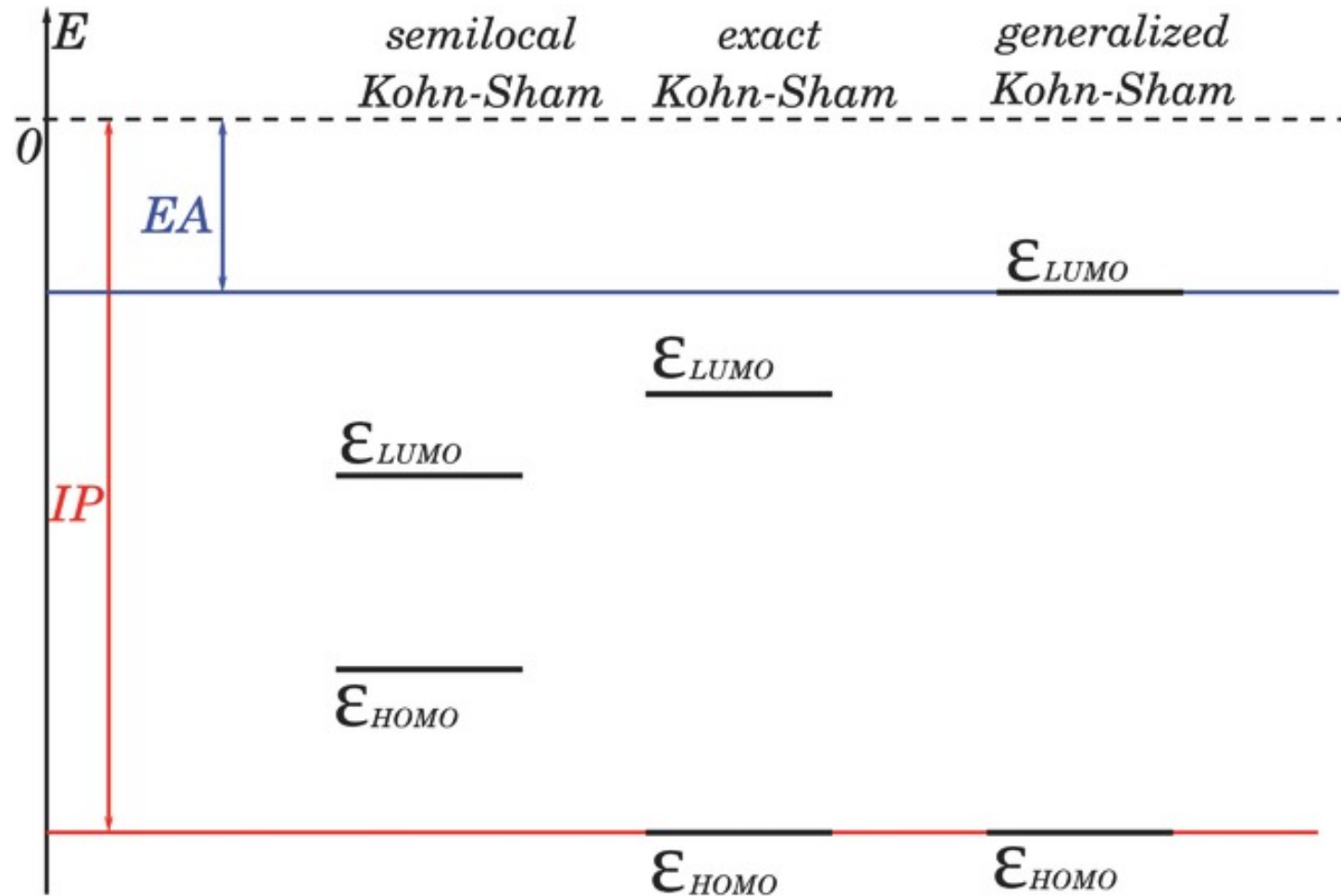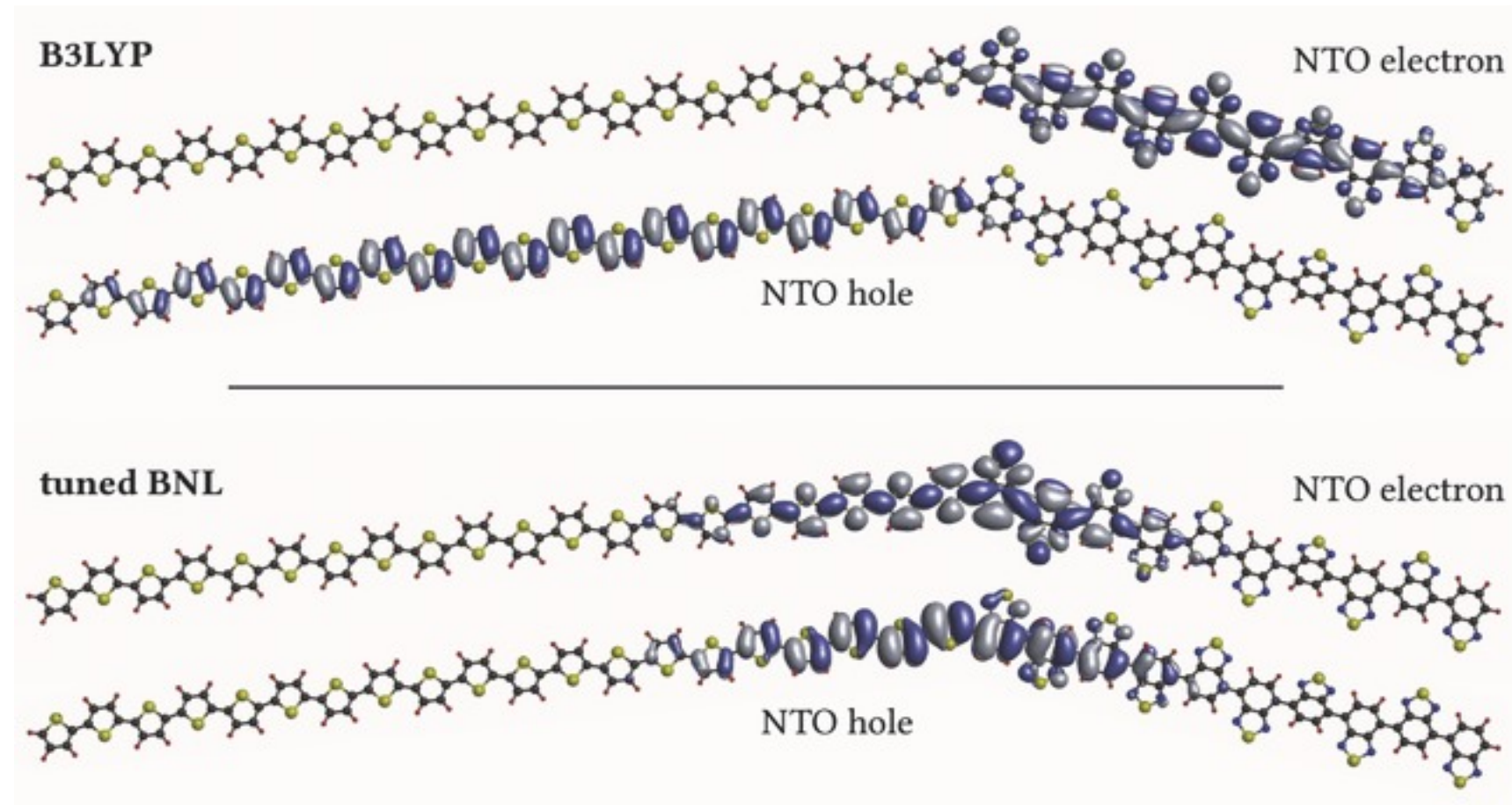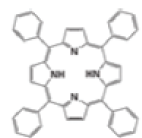
Koopmans' theorem:

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

Choose the ω that enforces Koopmans' theorem.

Plus: Non-empirical tuning procedure.

Minus: Not size-consistent

Kümmel Adv. Energy Mat. 2017, 7, 1700440.

Tuning the range-separation parameter

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

Koopmans' theorem:

$$\varepsilon_{HOMO} = -IP$$
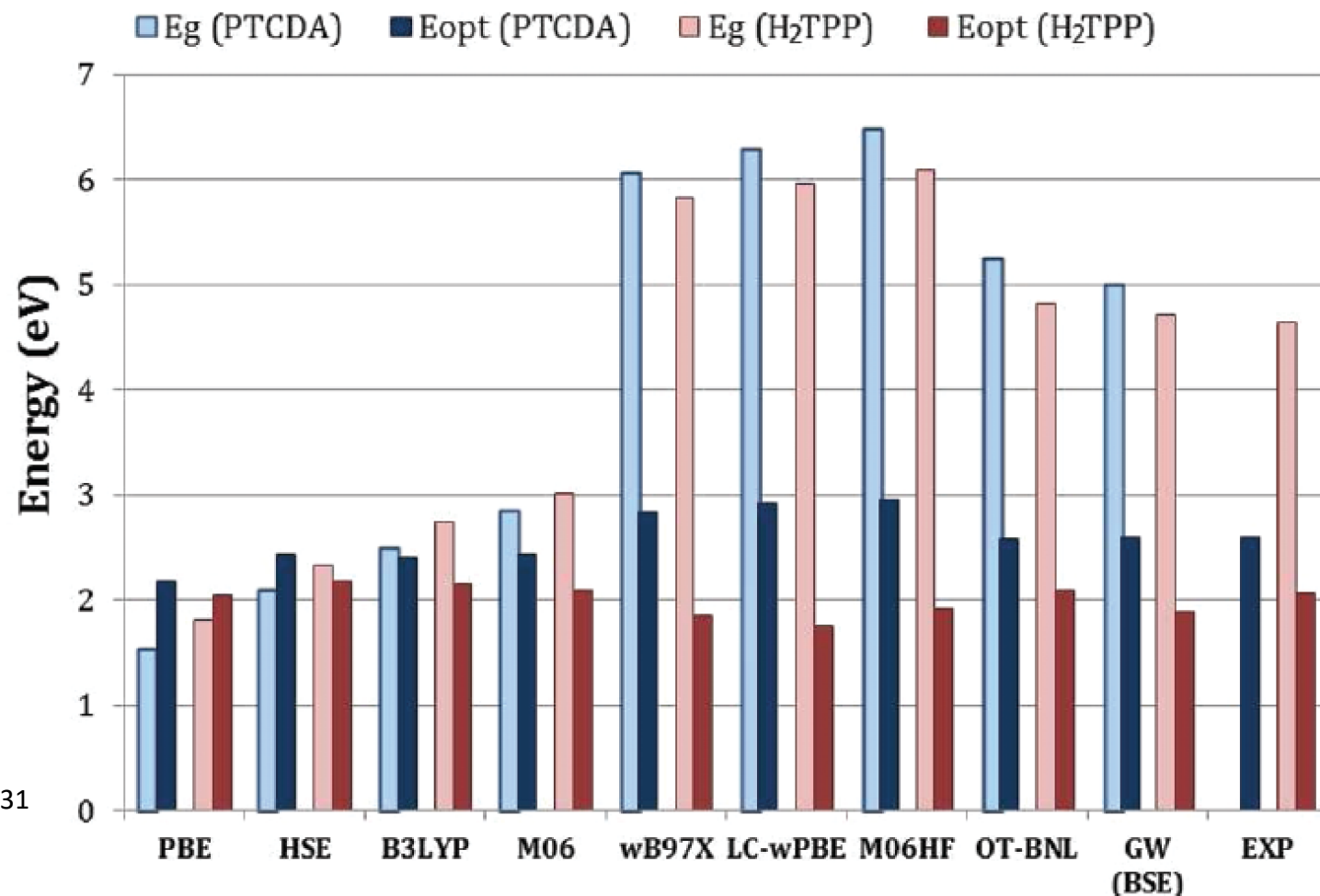
Choose the ω that enforces Koopmans' theorem.

Plus: Non-empirical tuning procedure.

Minus: Not size-consistent

B3LYP — NTO electron, NTO hole

tuned BNL — NTO electron, NTO hole

Kümmel Adv. Energy Mat. 2017, 7, 1700440.

(a) H2TPP

Fundamental and optical gaps for PTCDA and H2TPP, compared to many-body perturbation theory and experimental values
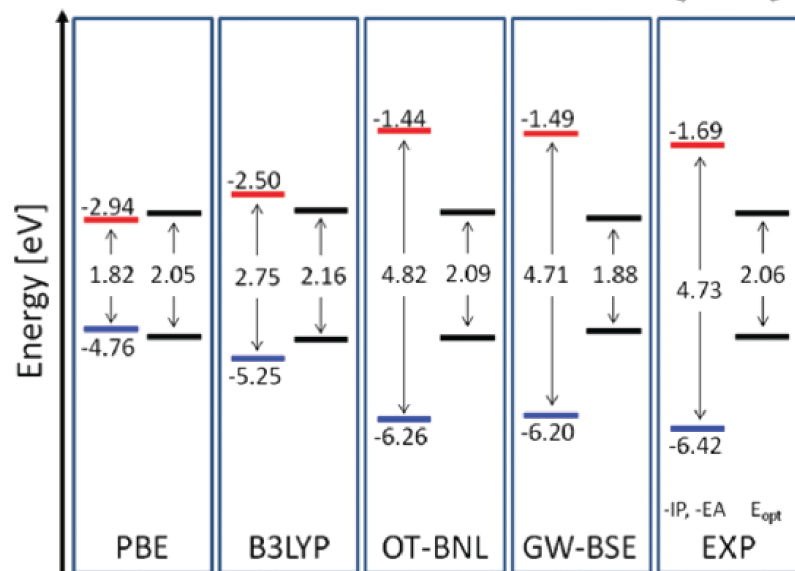
Kronik, Stein, Refaely-Abramson, and Baer
dx.doi.org/10.1021/ct2009363 | J. Chem. Theory Comput. 2012, 8, 1515–1531

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[1], Leeor Kronik[2], and Stephan Kümmel[1]
The Journal of Chemical Physics **138**, 204115 (2013); doi: http://dx.doi.org/10.1063/1.4807325

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.

Size-Dependent Exchange Tuning

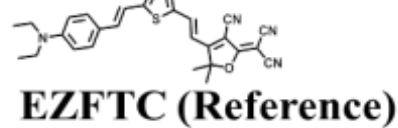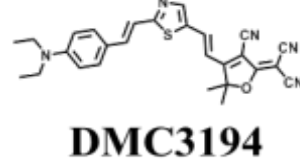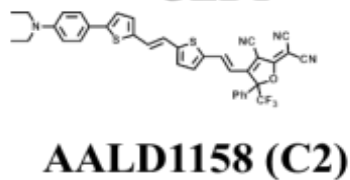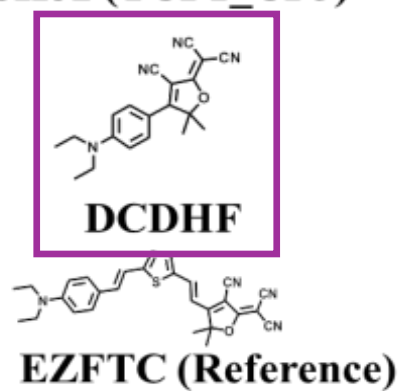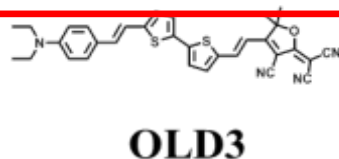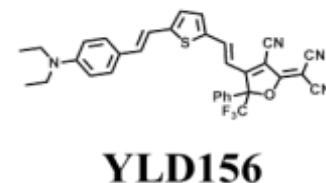Create system dependent exchange by tuning the range-separation parameter
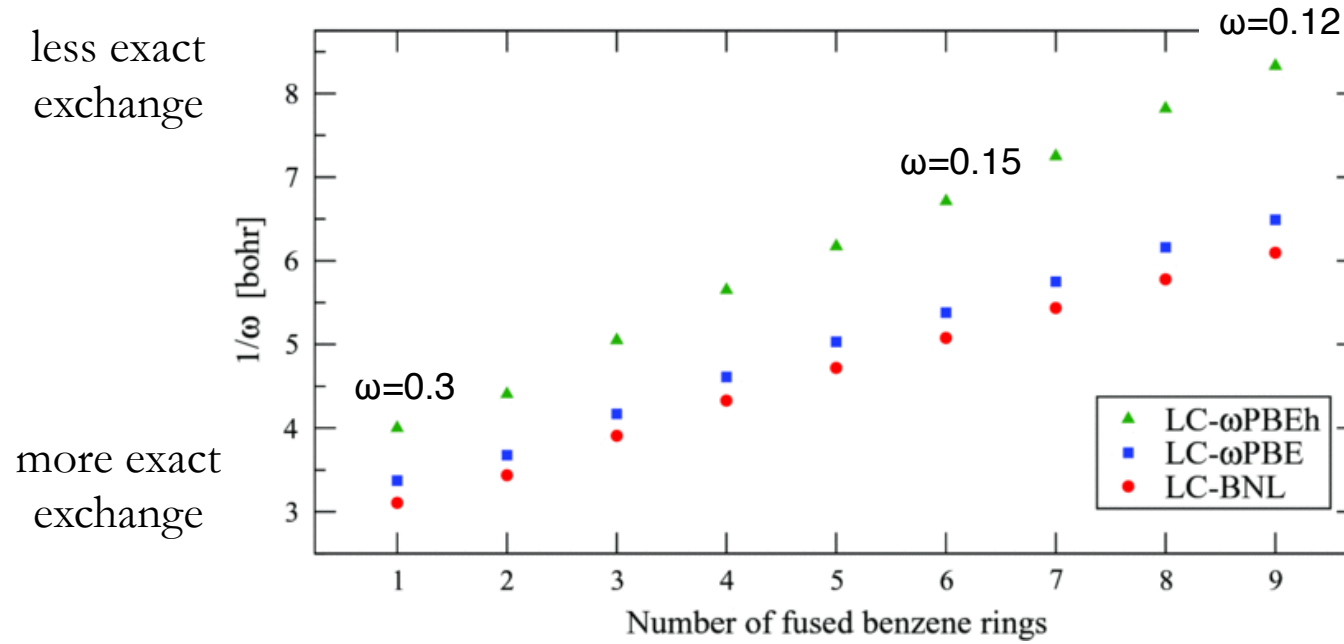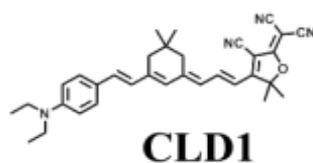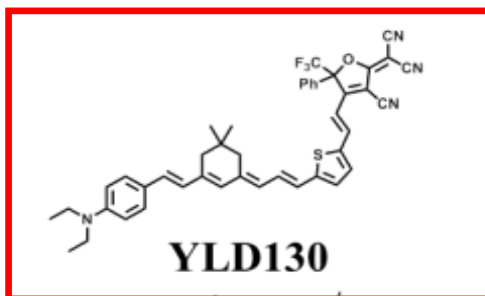

Körzdörfer, Sears, Sutton, and Brédas
J. Chem. Phys., 135, 204107, 2011

Optimal tuning predicts less exact exchange for larger systems

Size-Dependent Exchange Tuning

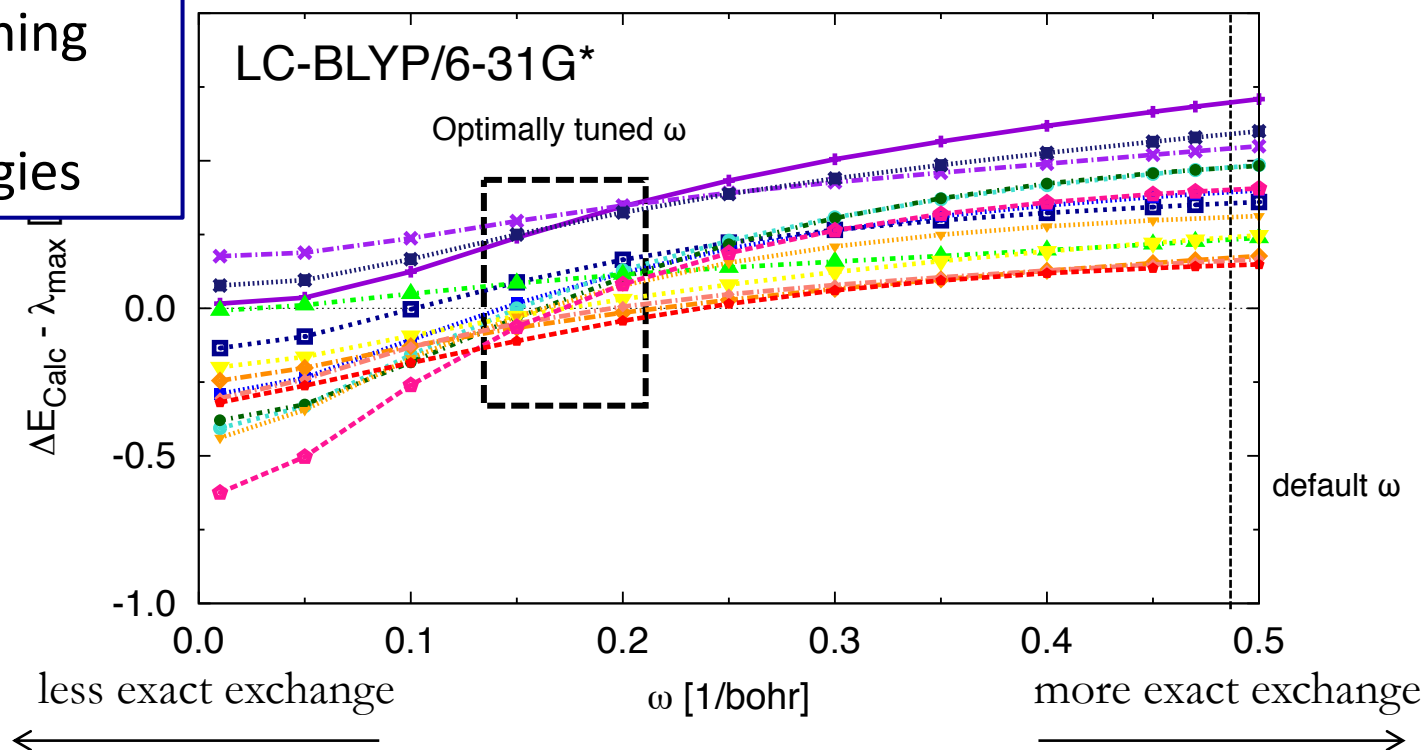We wanted good excitation energies for this set of charge transfer chromophores
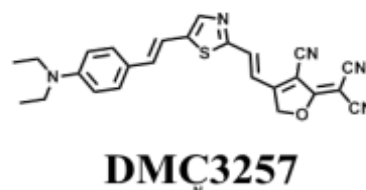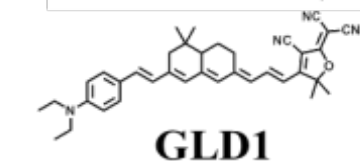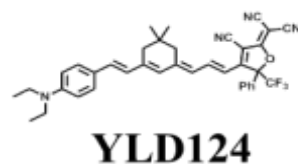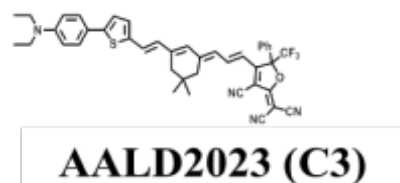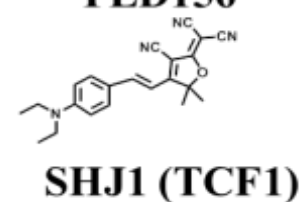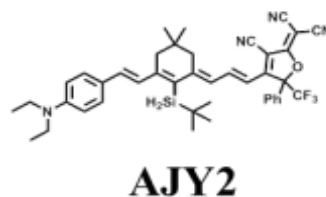
C. M. Isborn

Size-Dependent Excitation Energy Accuracy

Does optimal tuning of exchange improve the excitation energies?
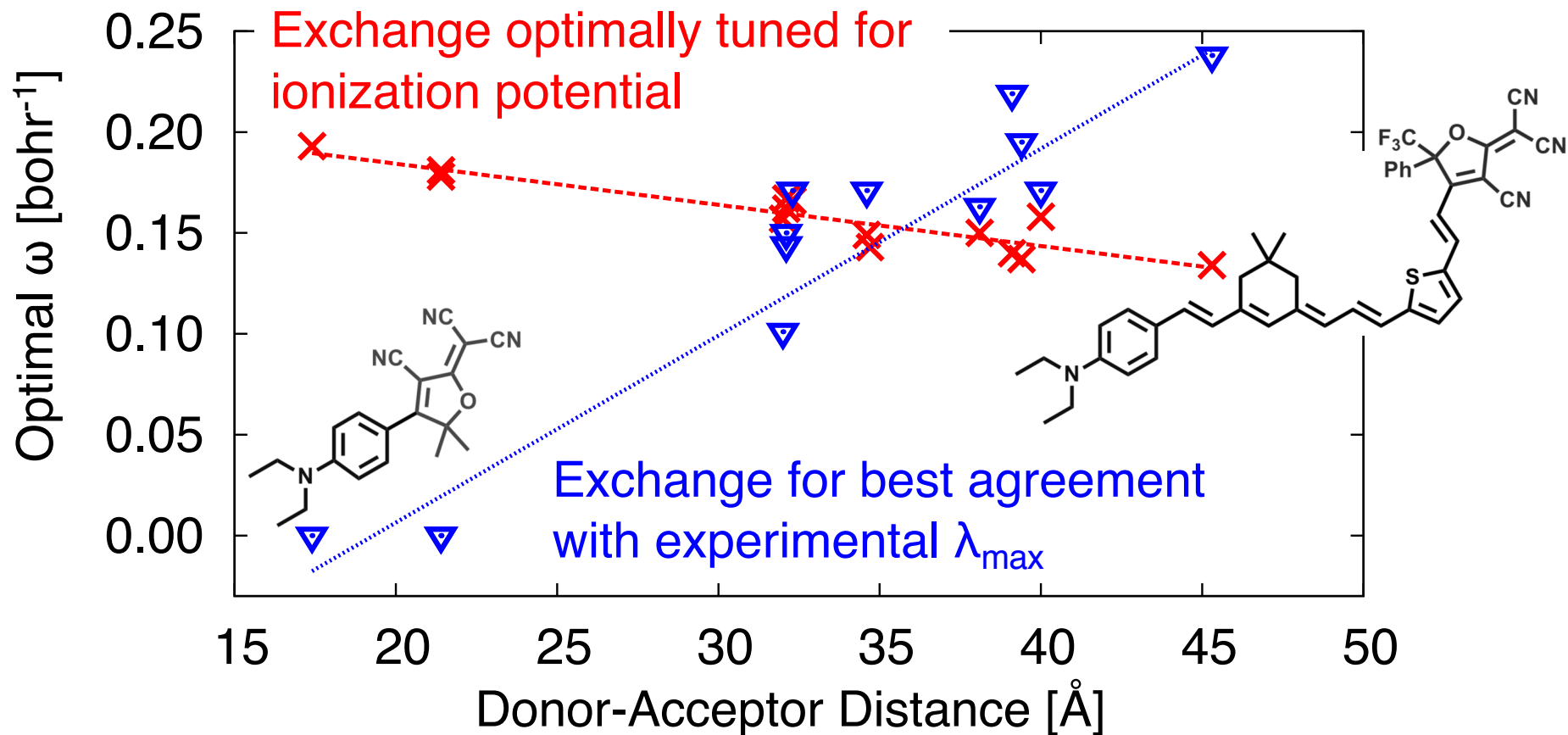
Yes, optimal tuning improves the excitation energies

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

Optimal ω [bohr⁻¹] — Exchange optimally tuned for ionization potential

Exchange for best agreement with experimental λ_{max}

Donor-Acceptor Distance [Å]

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

Size-Dependent TDDFT Errors
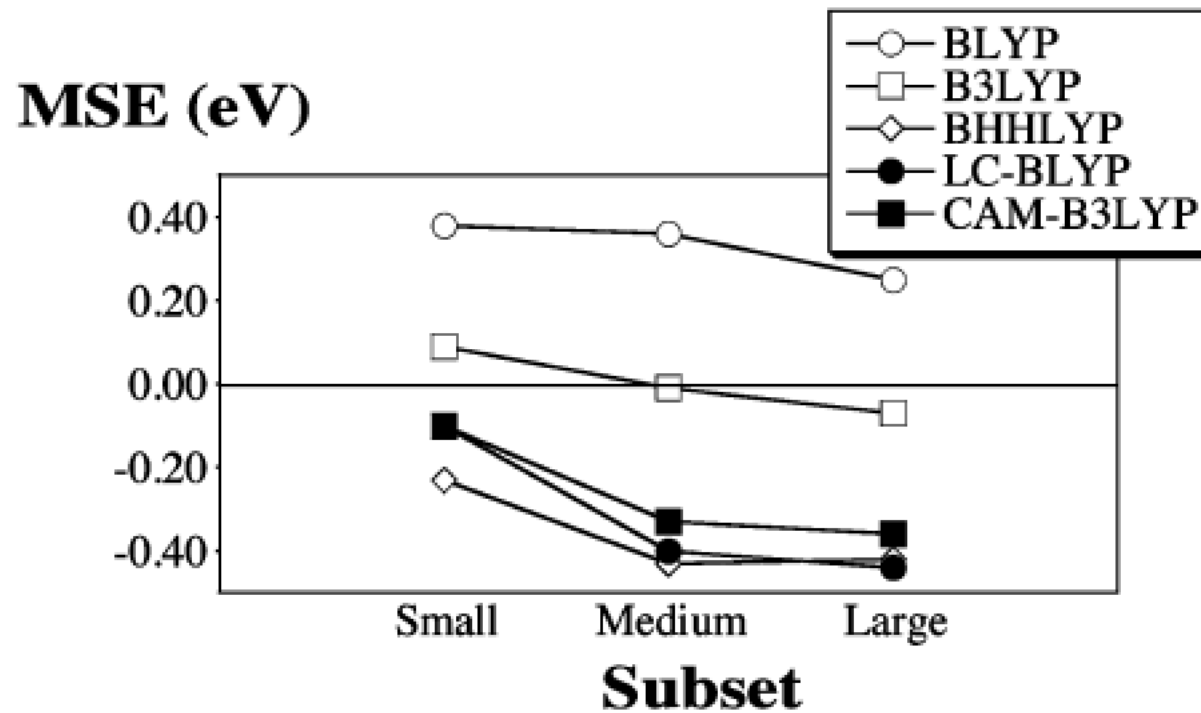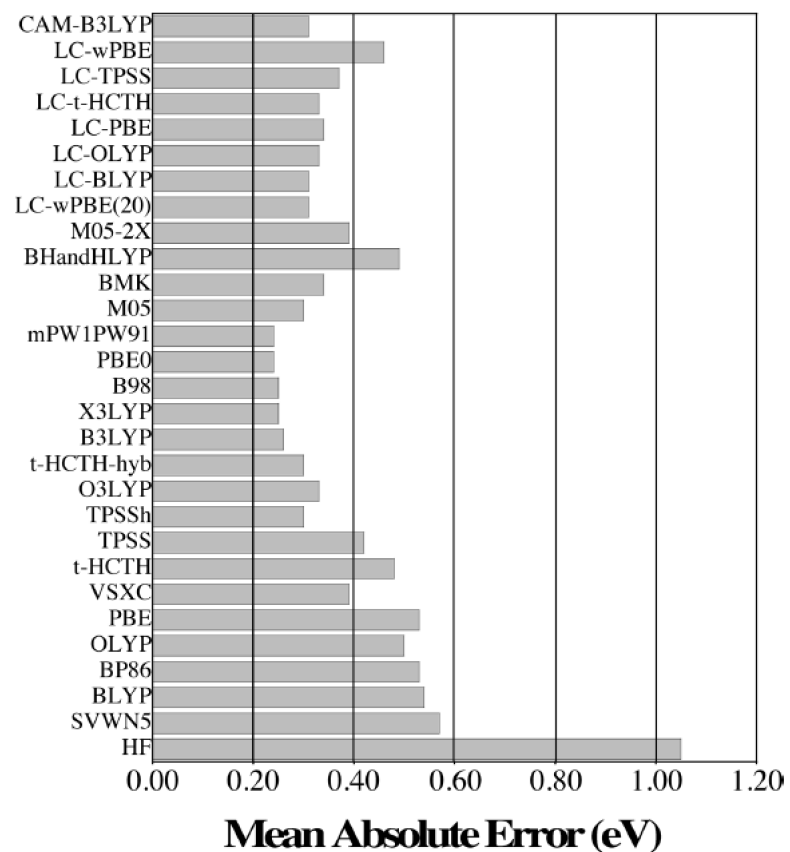
the VT set contains 28 molecules and 103 excited
states (not a significant number of CT states)

Jacquemin, Wathelet, Perpete, 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

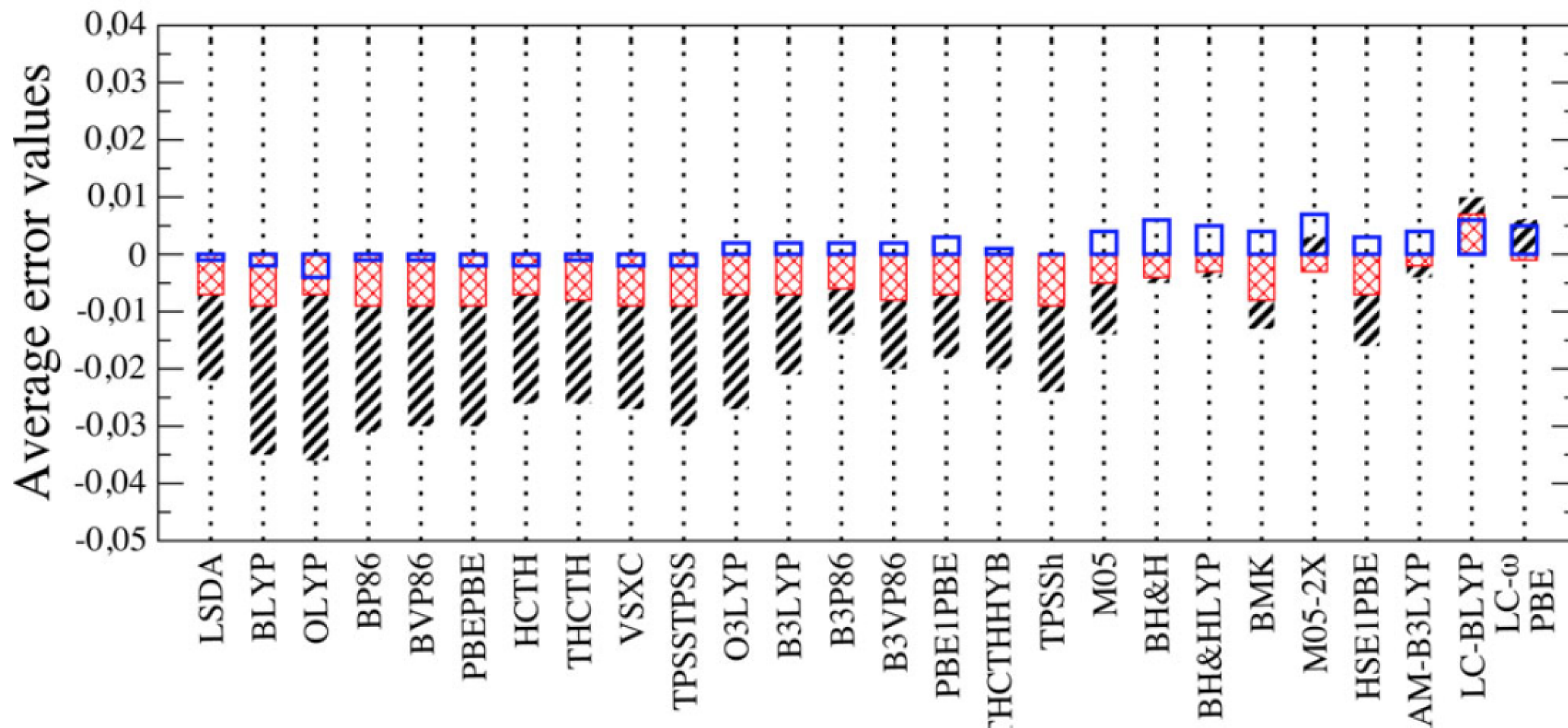*** Has incorrect exact exchange trend with system size compared to experiment!**

TDDFT seems to have different errors with systems of different size?
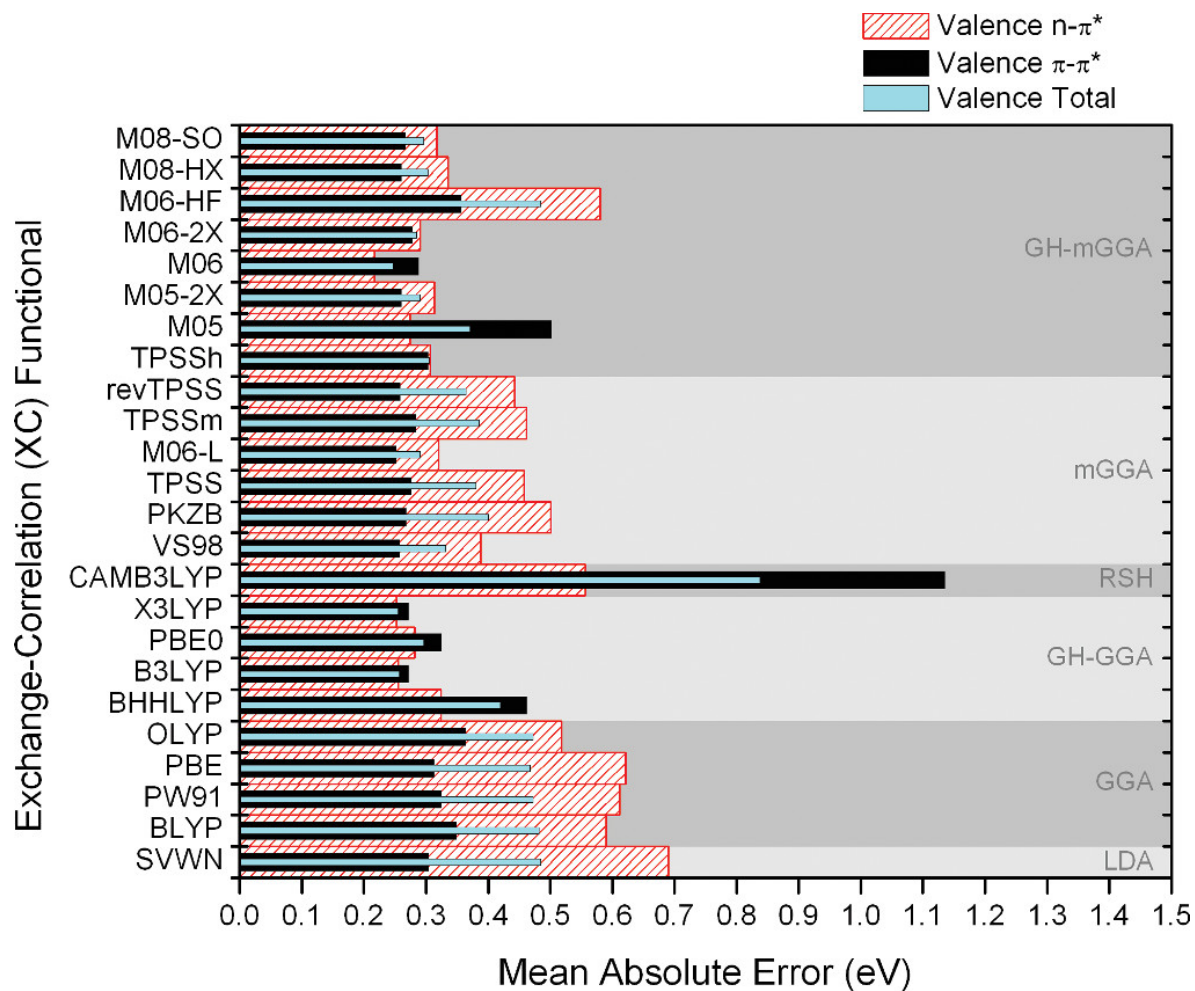
Does tuning improve Rydberg transitions?
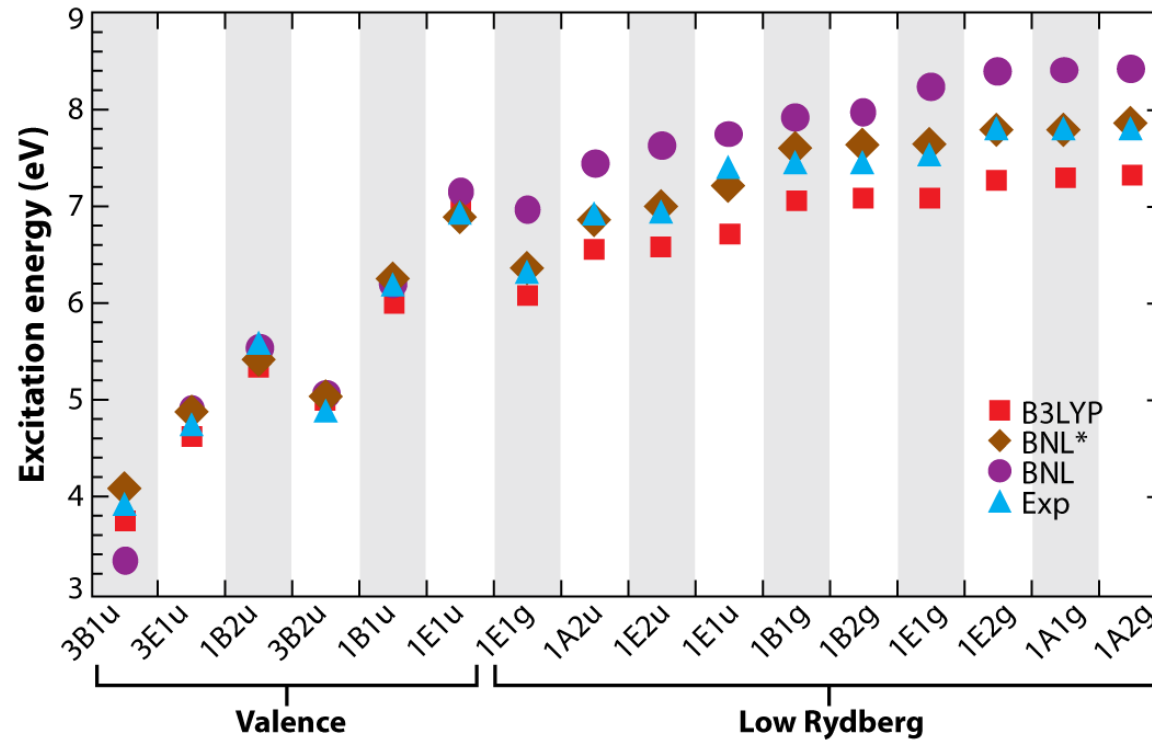
Baer R, et al. 2010.
Annu. Rev. Phys. Chem. 61:85–109
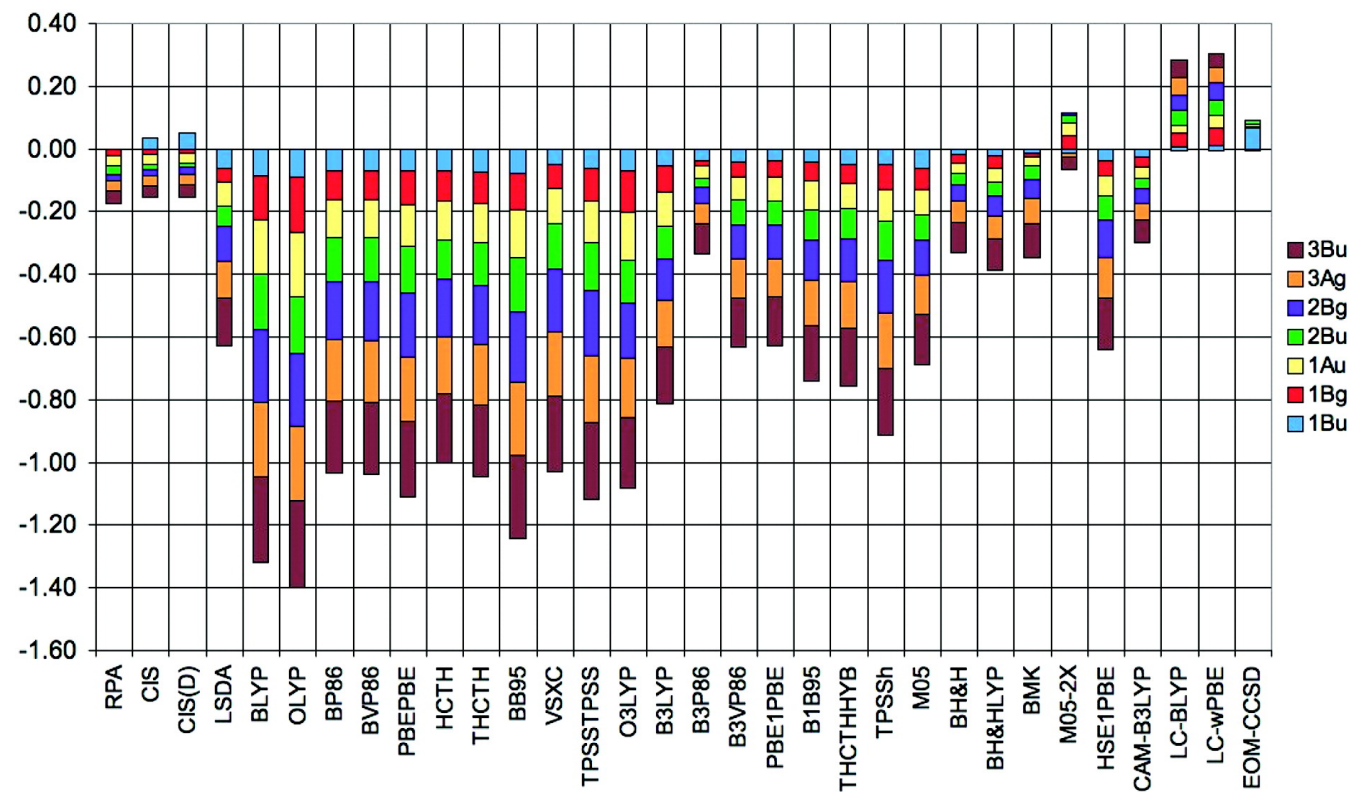
TDDFT oscillator strengths

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

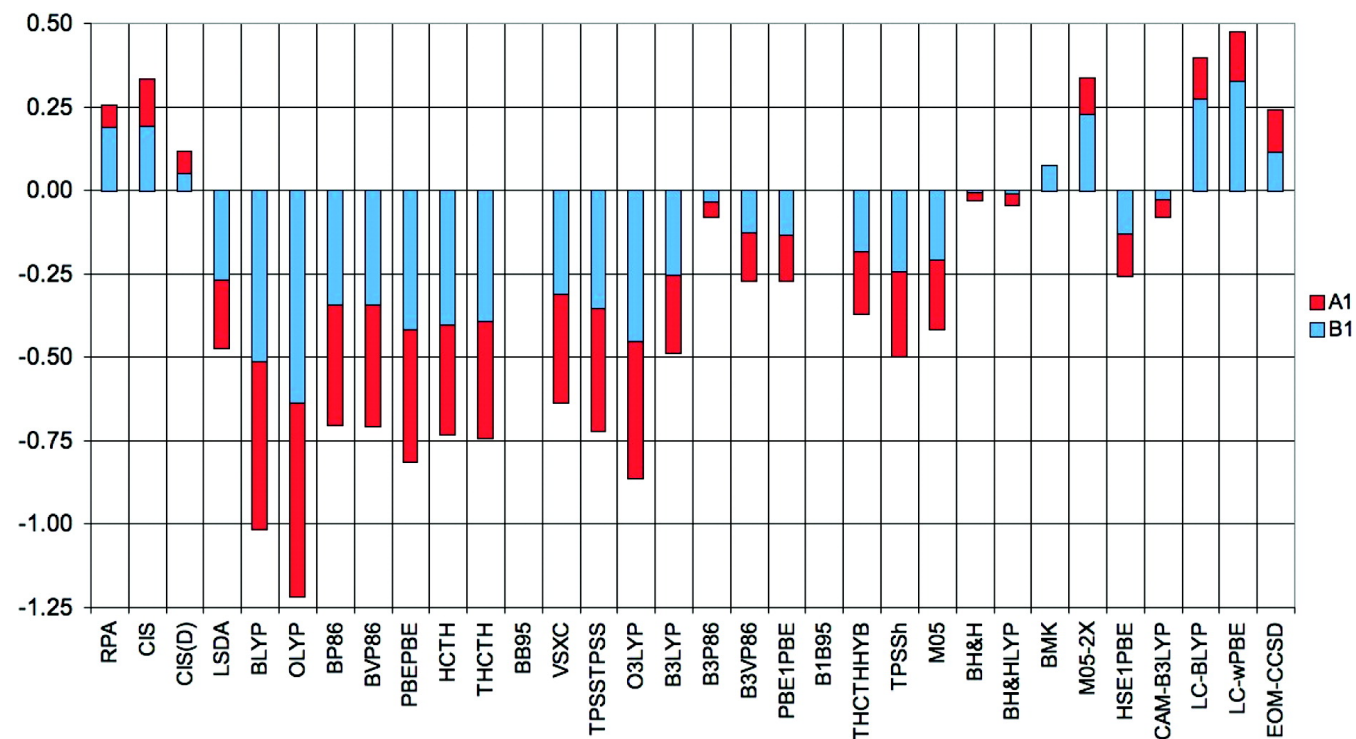# What kinds of transitions does TDDFT get correct?

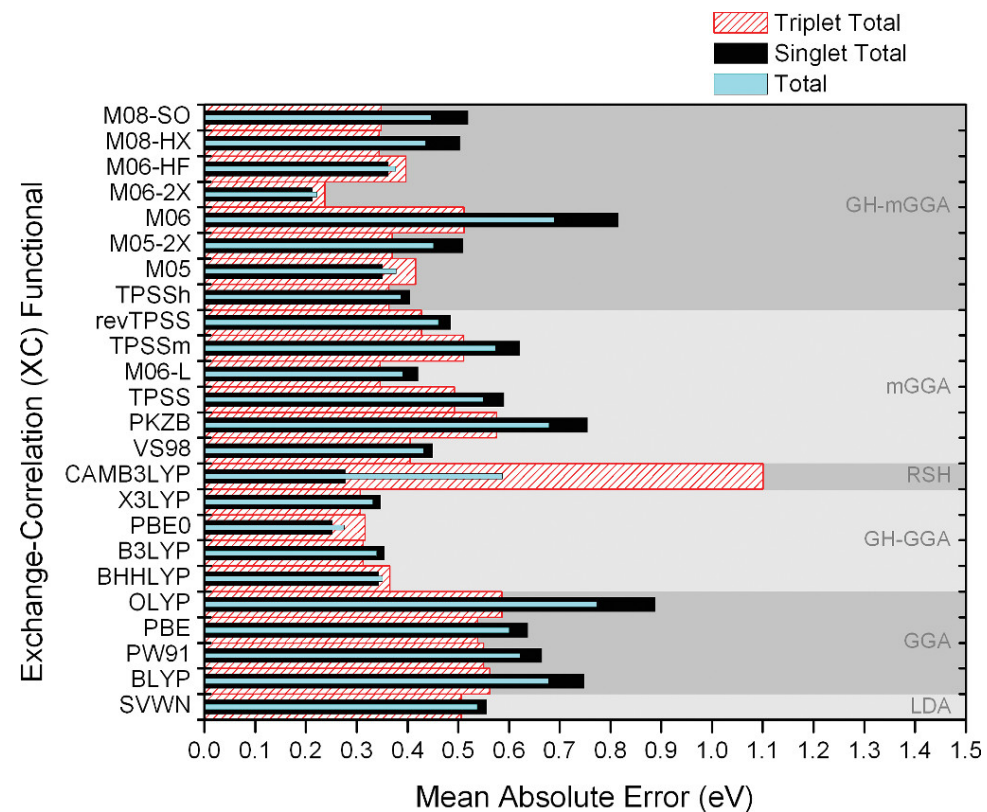14 small- to medium-sized compounds with 60 valence experimental excited state energies

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

Errors (eV) for trans-1,3-butadiene. The 1*Bu* transition is π → π*, the rest are Rydberg.

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

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

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