On the Road to the Modeling of Resonance UV/vis Spectroscopic Properties

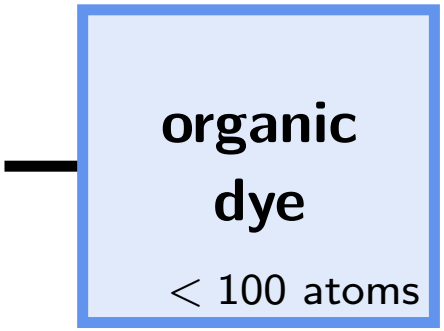
Éric Brémond, Philippe Lainé, François Maurel

ITODYS UMR CNRS 7086, Université de Paris,
Paris, France

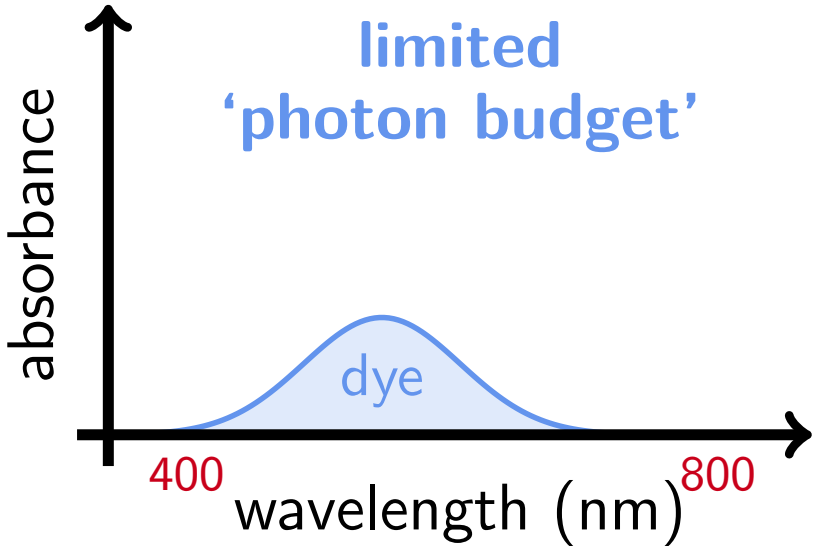
Lille, January 9, 2020

Molecular Resonance: Dye → 'Super' Dye

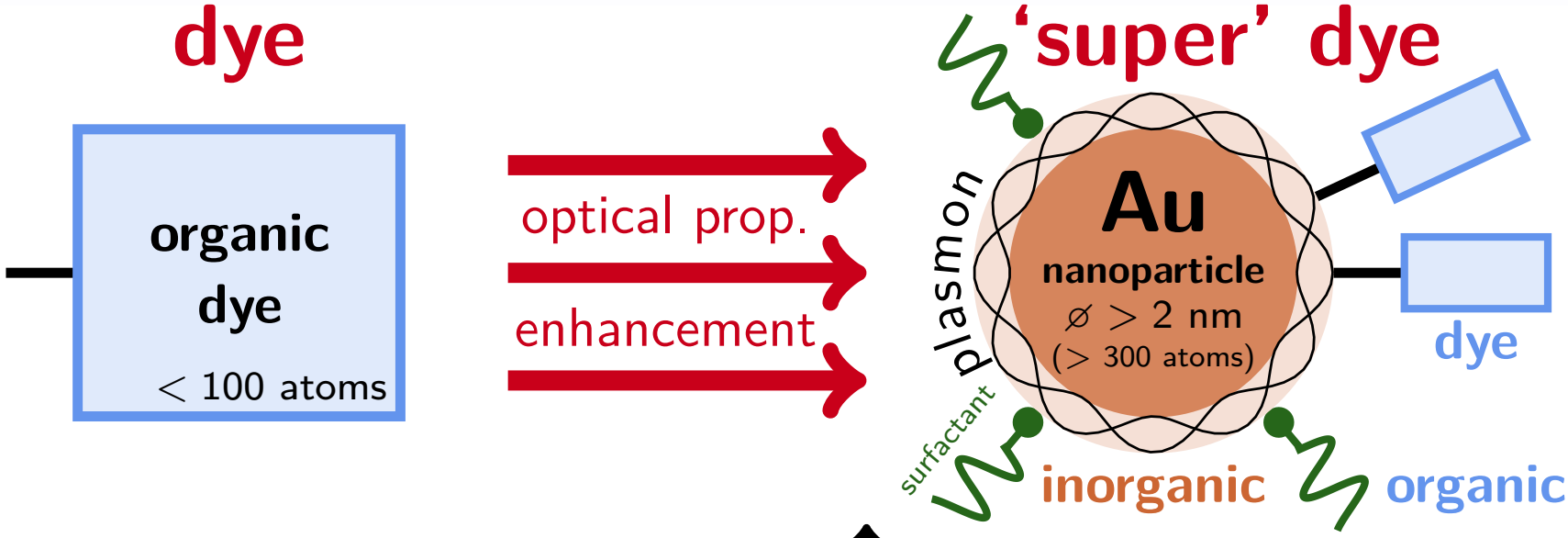
dye

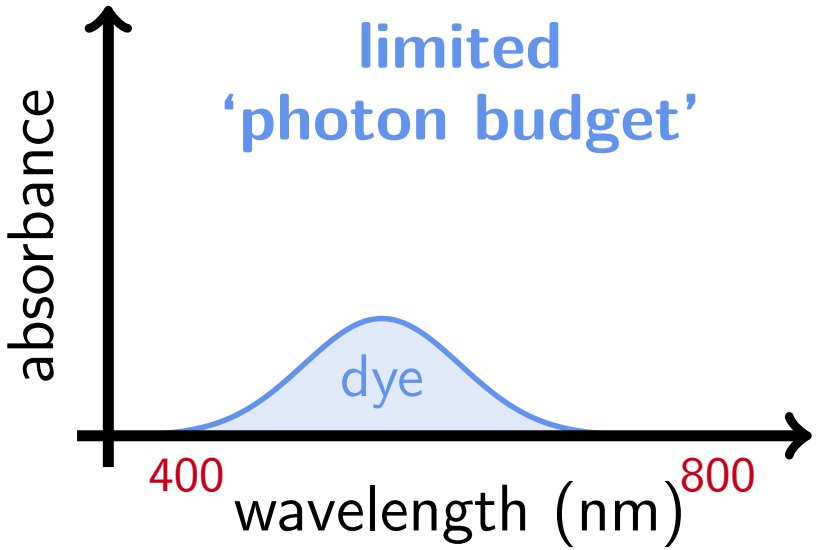


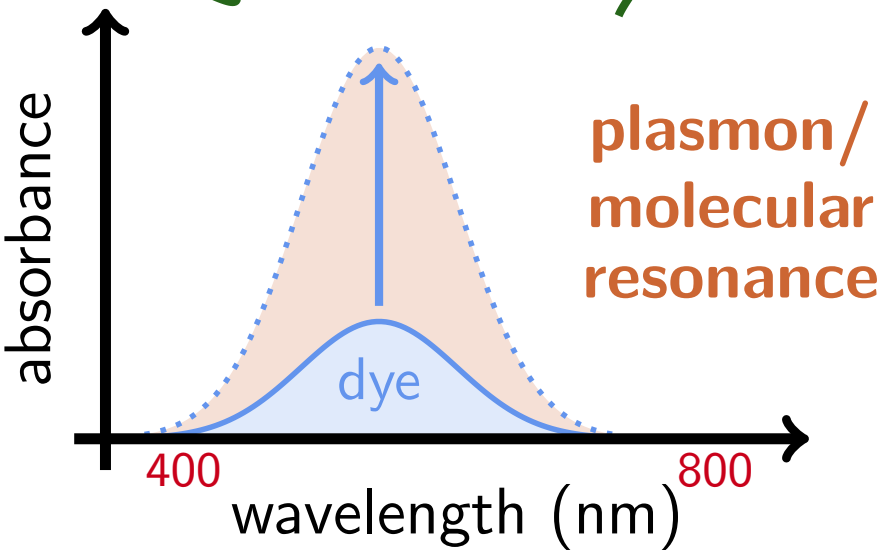
limited 'photon budget'



Molecular Resonance: Dye → 'Super' Dye

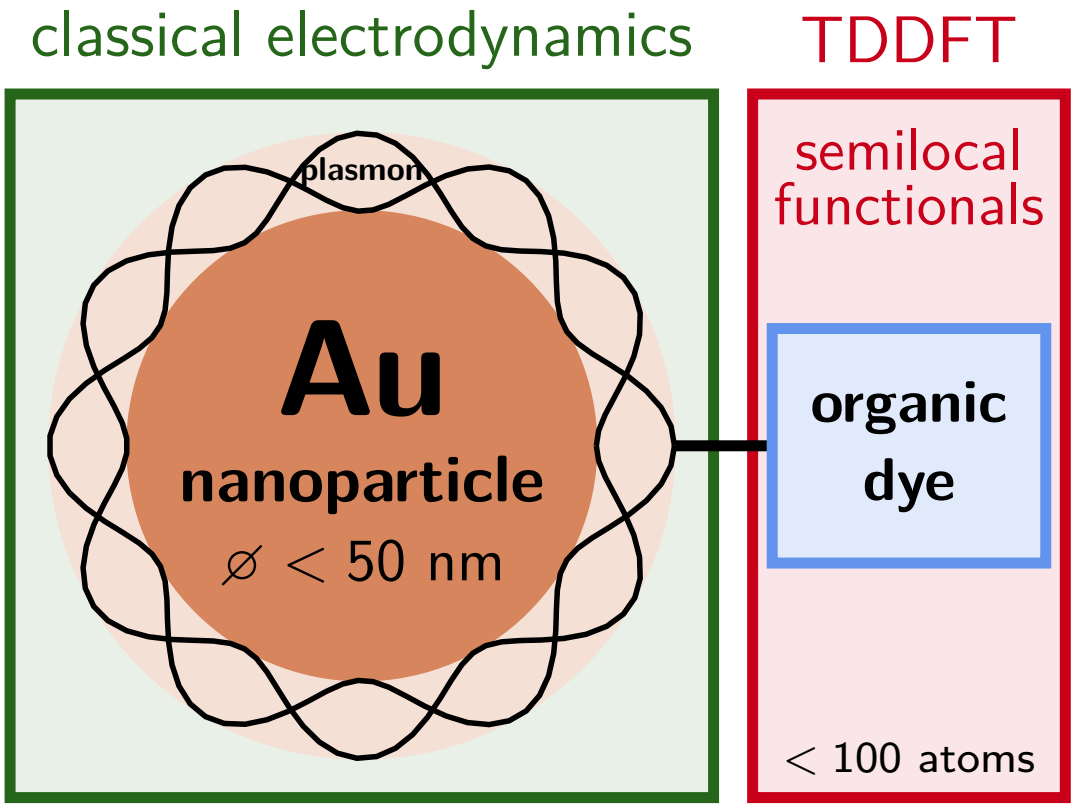






State of Art: Plasmon/Molecular Resonance

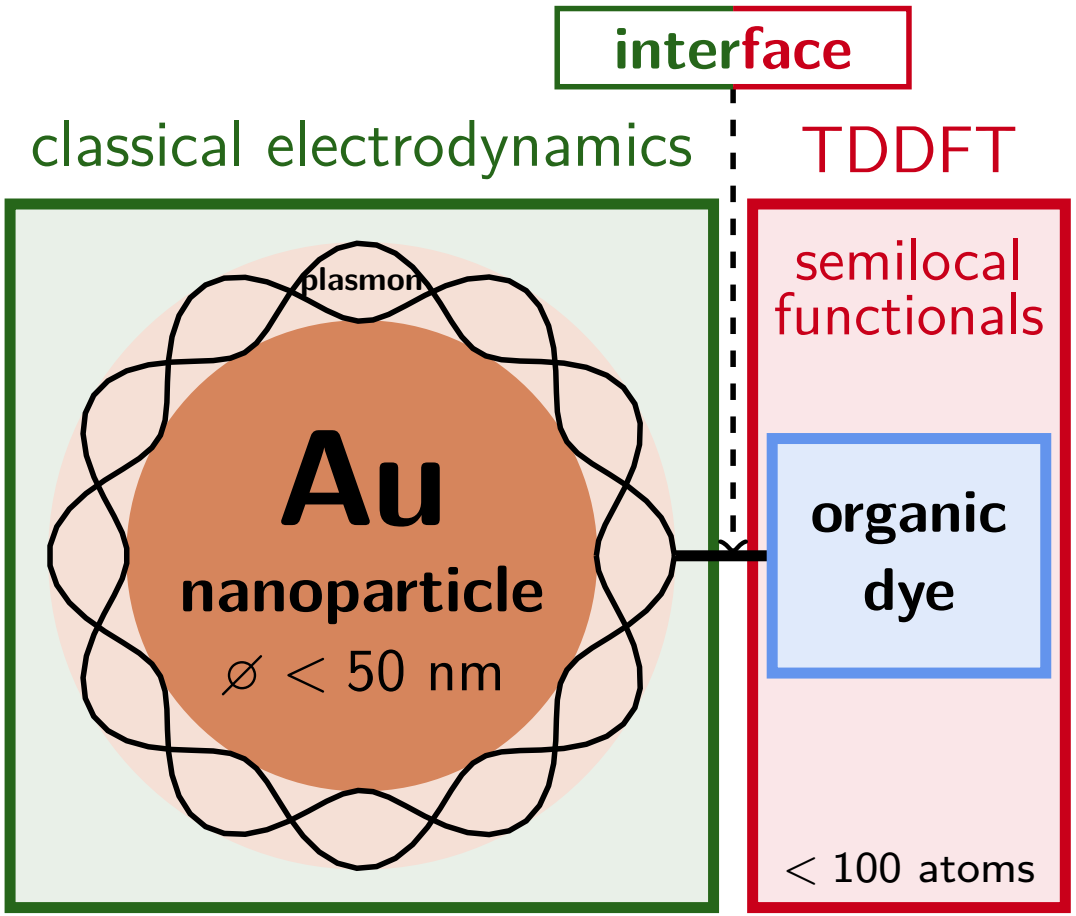
hybrid model (DIM/QM)



State of Art: Plasmon/Molecular Resonance

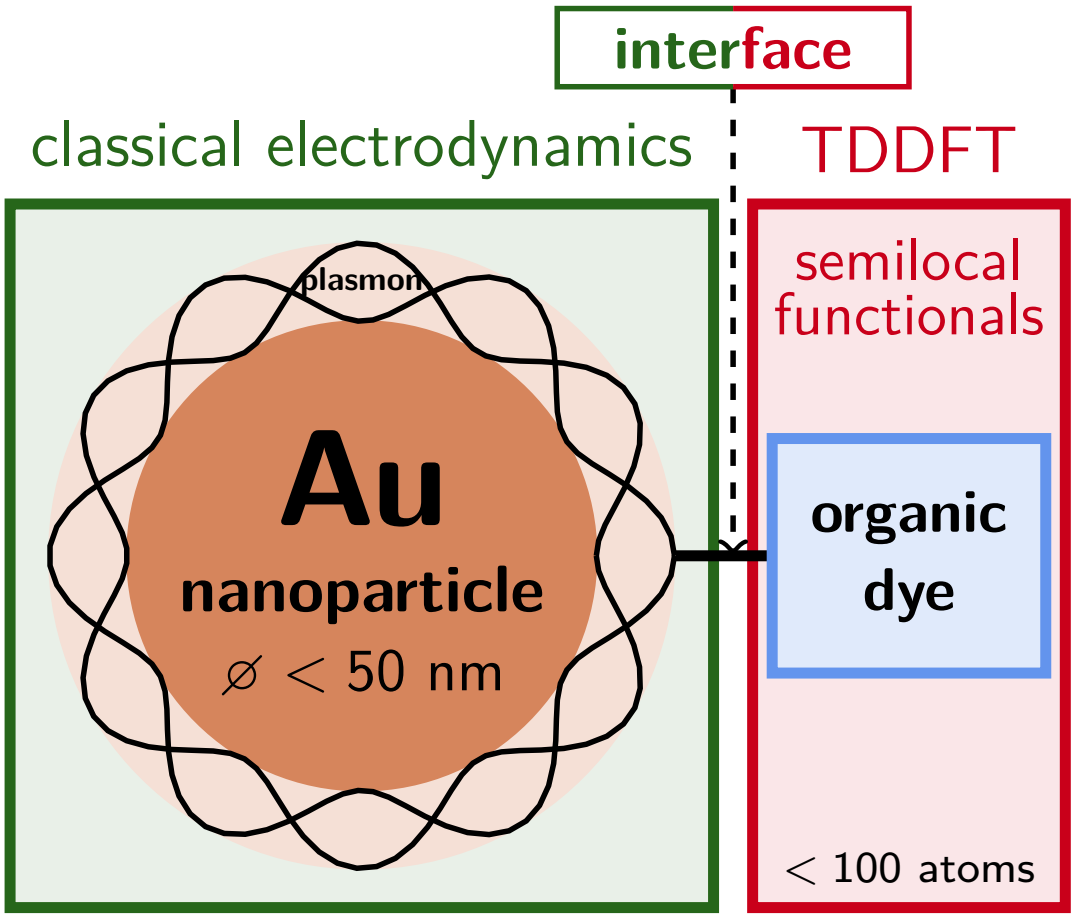
hybrid model (DIM/QM)

LIMITATION!



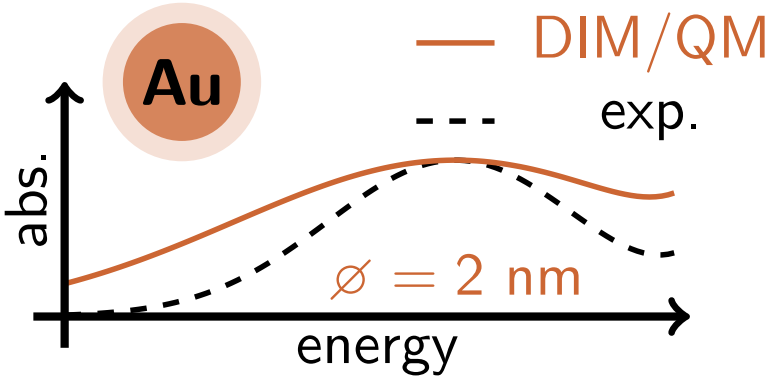
State of Art: Plasmon/Molecular Resonance

hybrid model (DIM/QM)



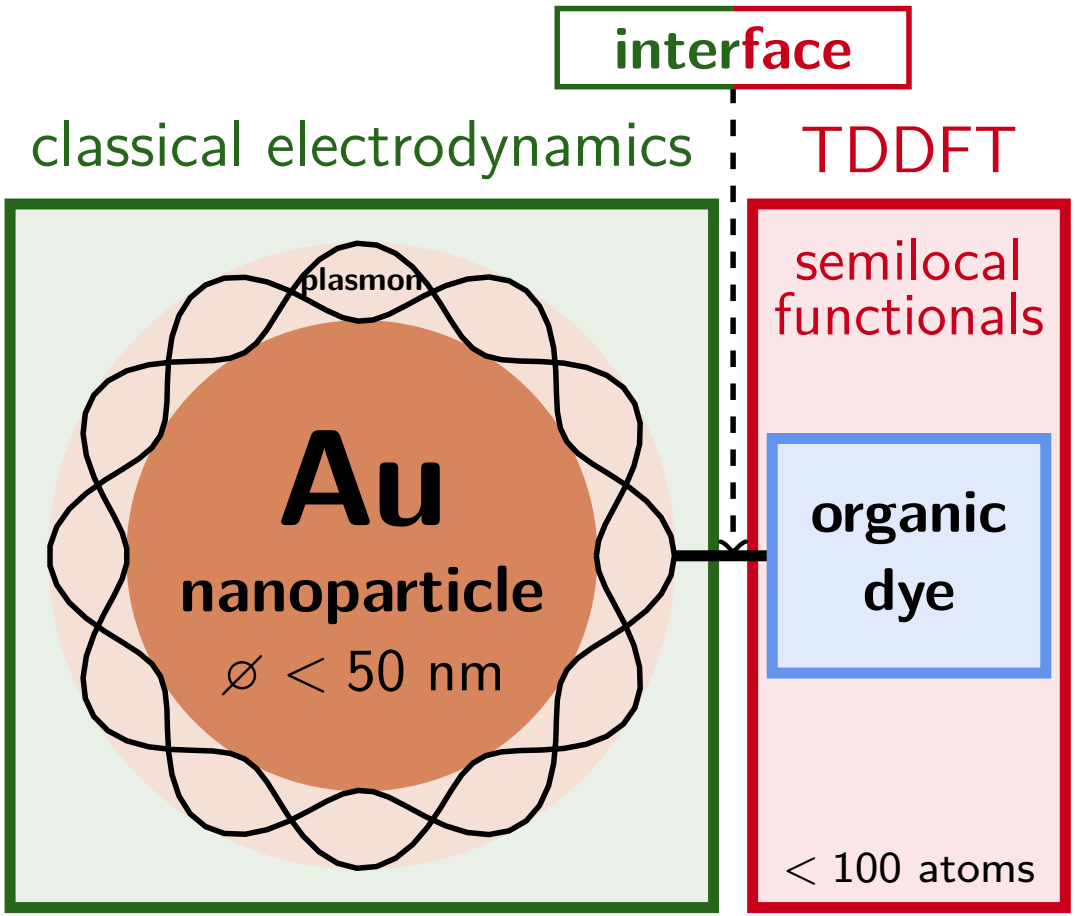
LIMITATION!

classical electrodynamics



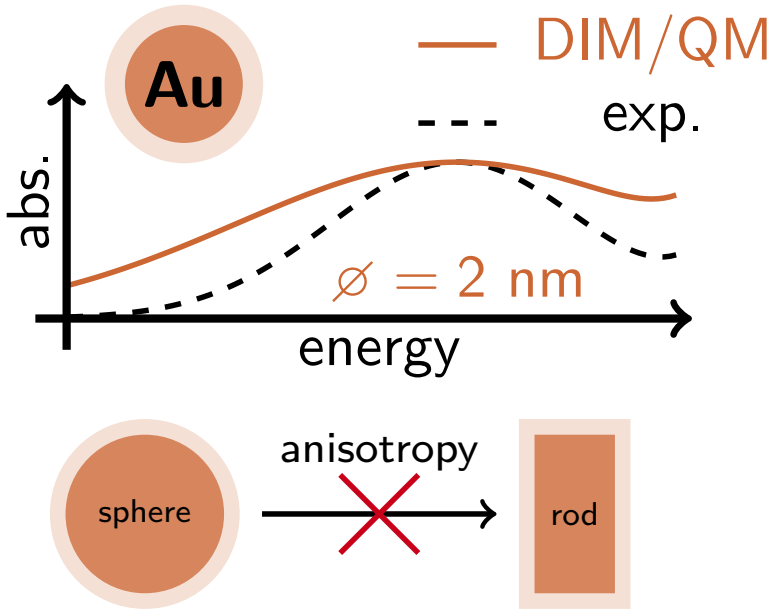
State of Art: Plasmon/Molecular Resonance

hybrid model (DIM/QM)



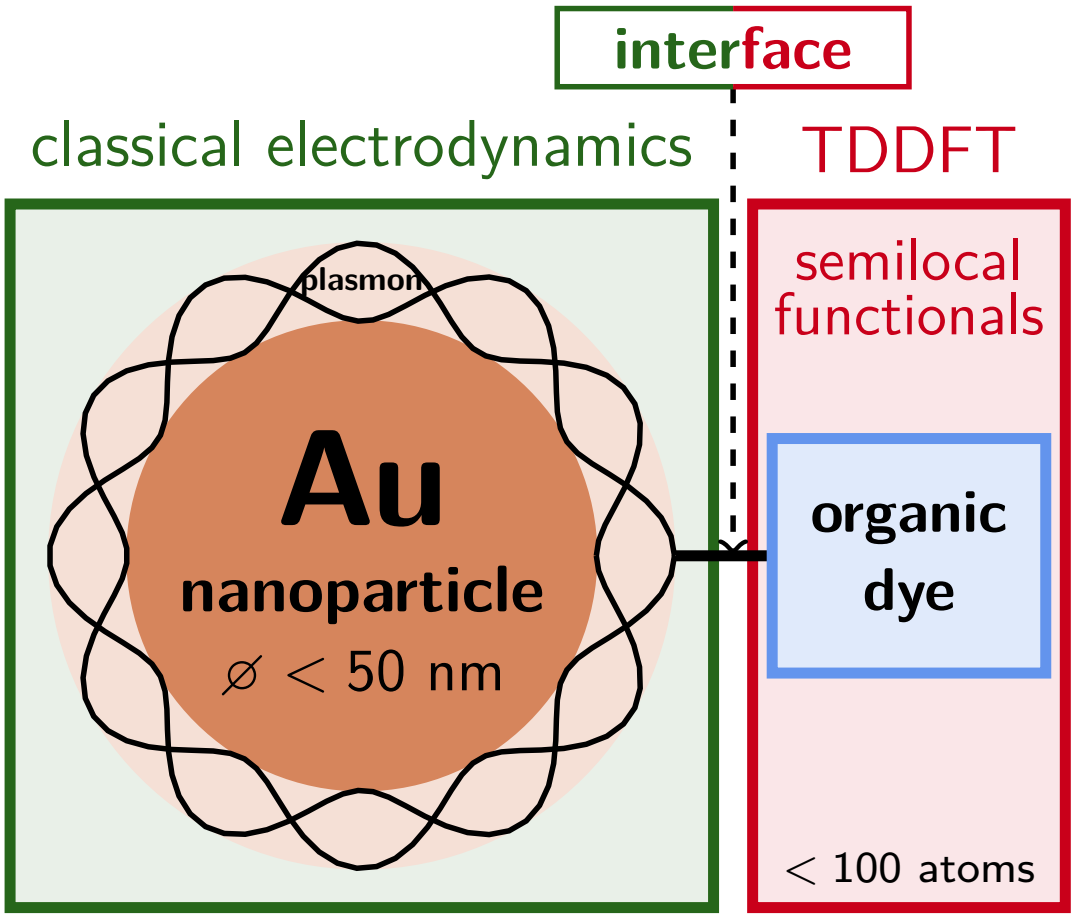
LIMITATION!

classical electrodynamics



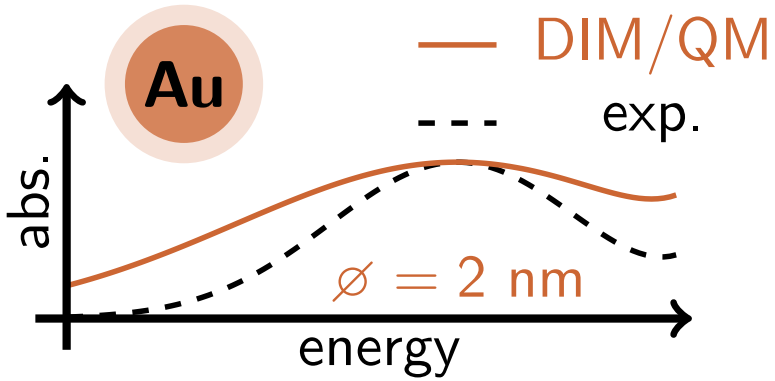
State of Art: Plasmon/Molecular Resonance

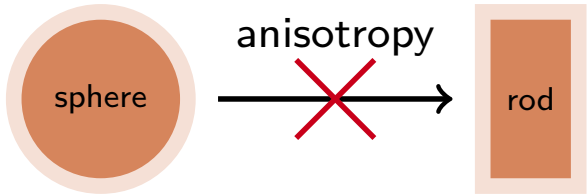
hybrid model (DIM/QM)



LIMITATION!

classical electrodynamics

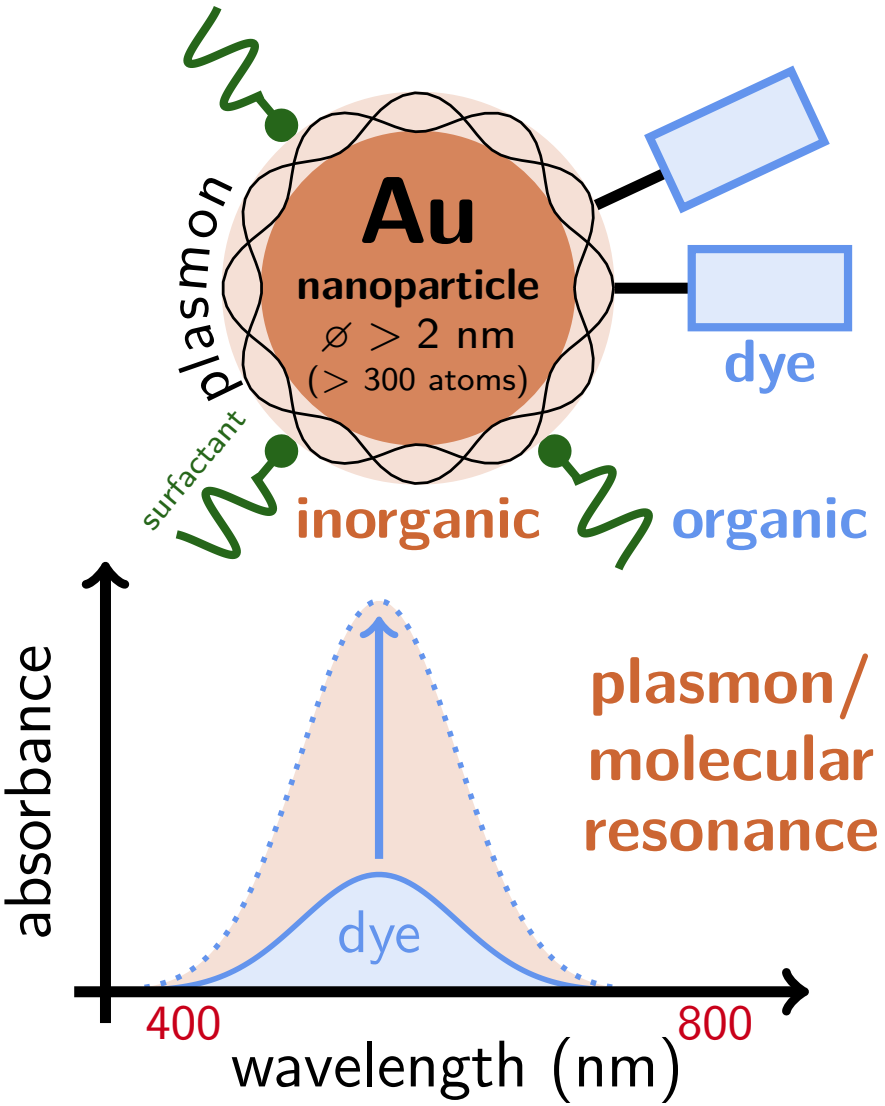




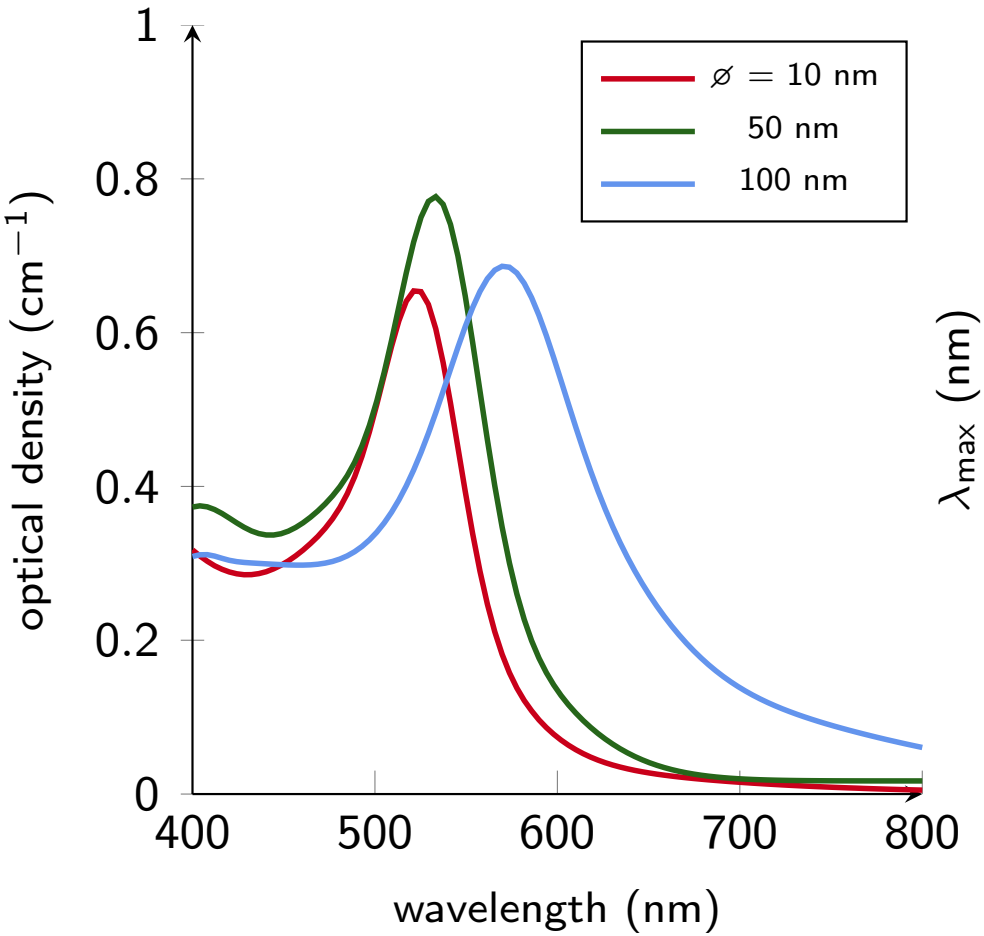
TDDFT(semilocal)

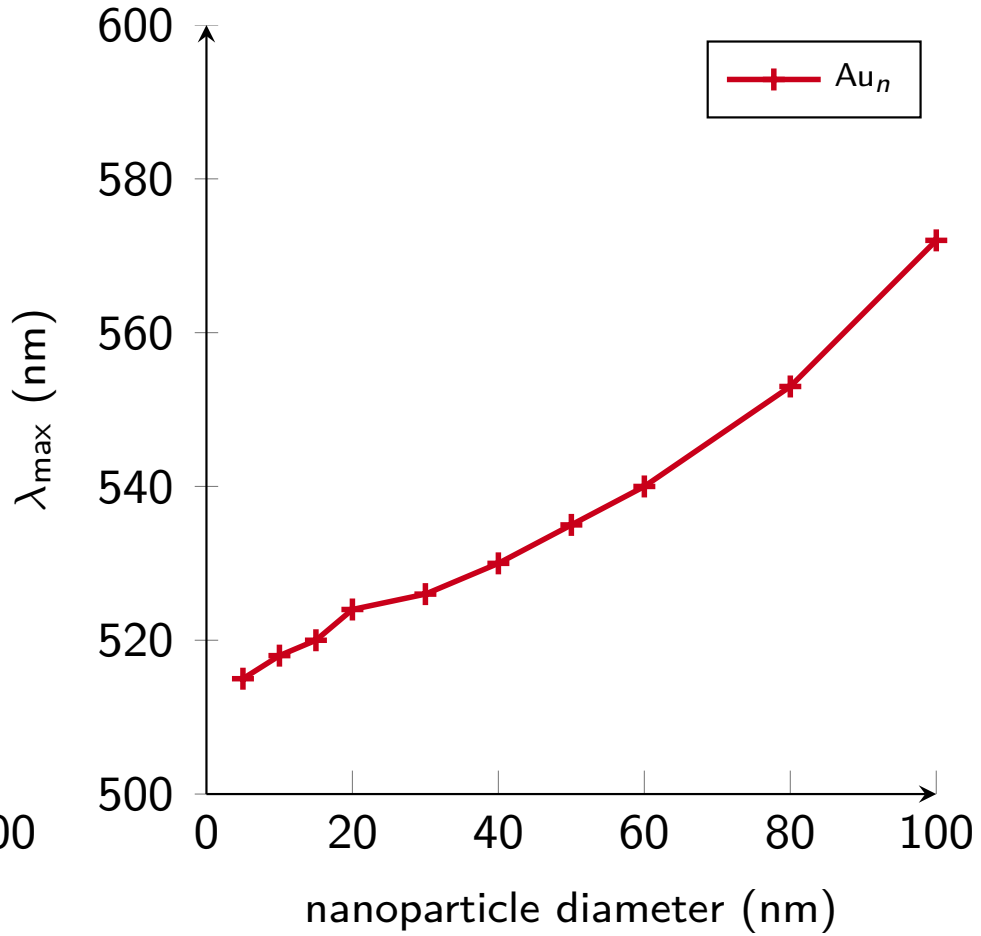
→ charge-transfer issue

Looking For an Organic Dye



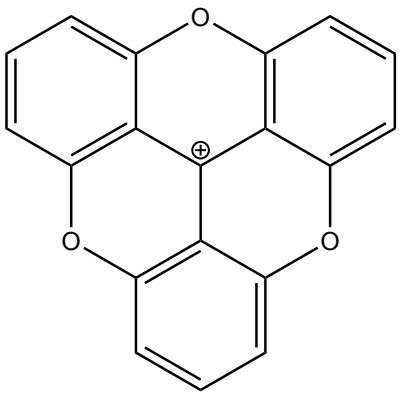
Gold Nanoparticle UV/vis Abs. Spectra





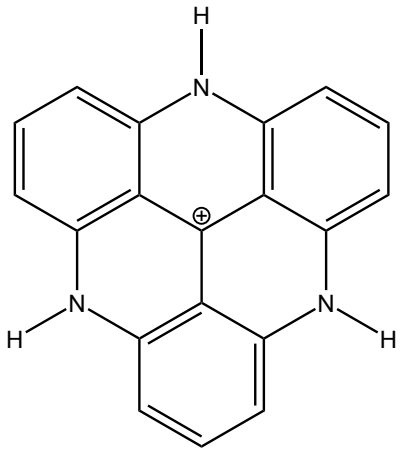
Sigma-Aldrich

The Triangulenium Family



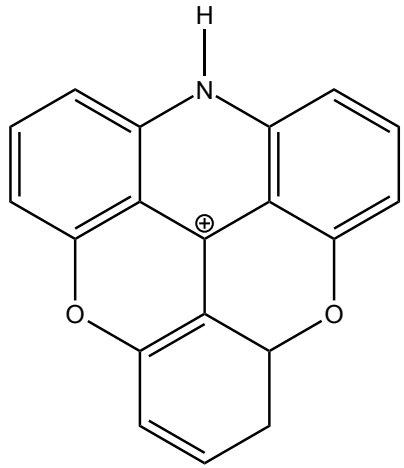
TOTA

$\lambda_{max} = 450$ **nm**



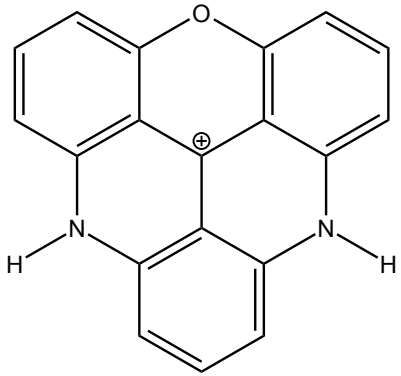
TATA

$\lambda_{max} = 525$ **nm**



ADOTA

$\lambda_{max} = 550$ **nm**

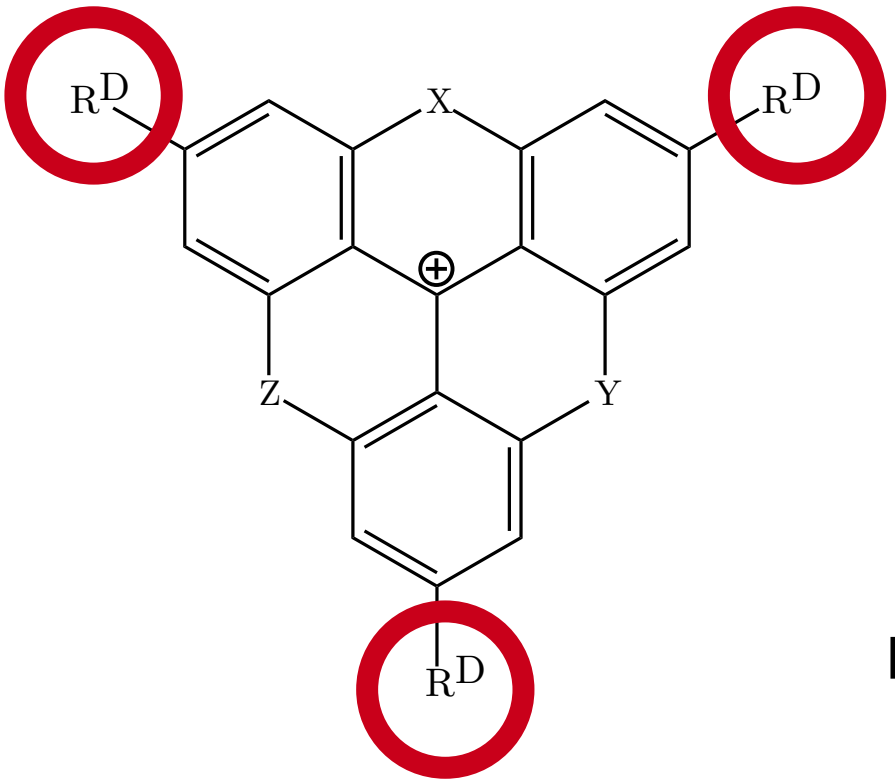


DAOTA

$\lambda_{max} = 575$ **nm**

Laursen *et al.* **Eur. Chem. J. 2001** 7, 1773.

The Triangulenium Family



in addition to

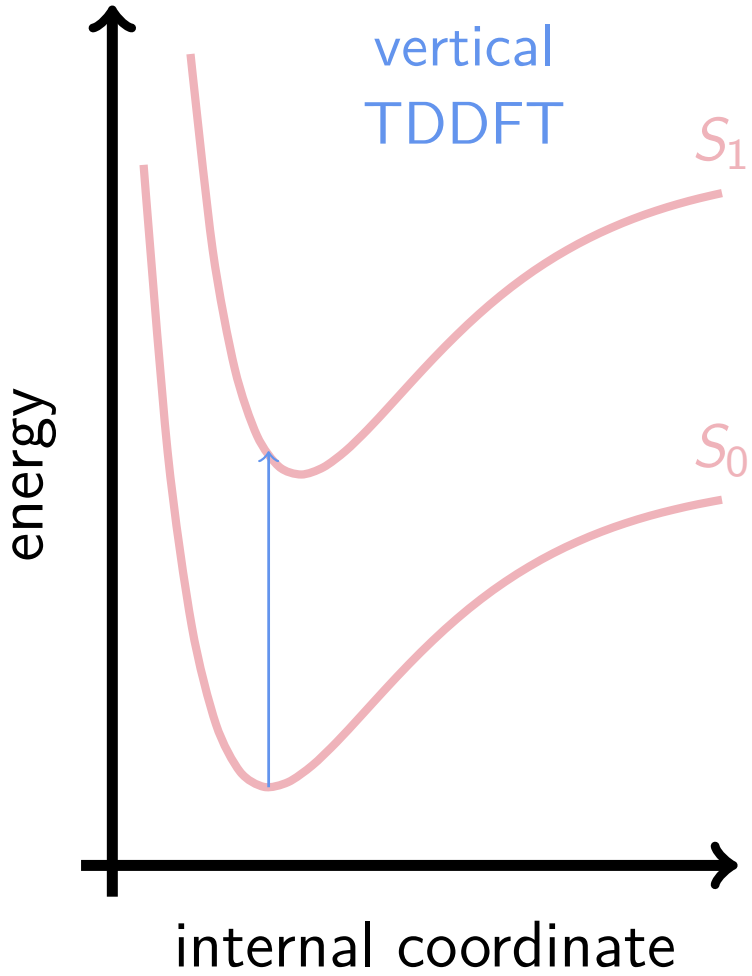
X, Y, Z = O, NR', ...

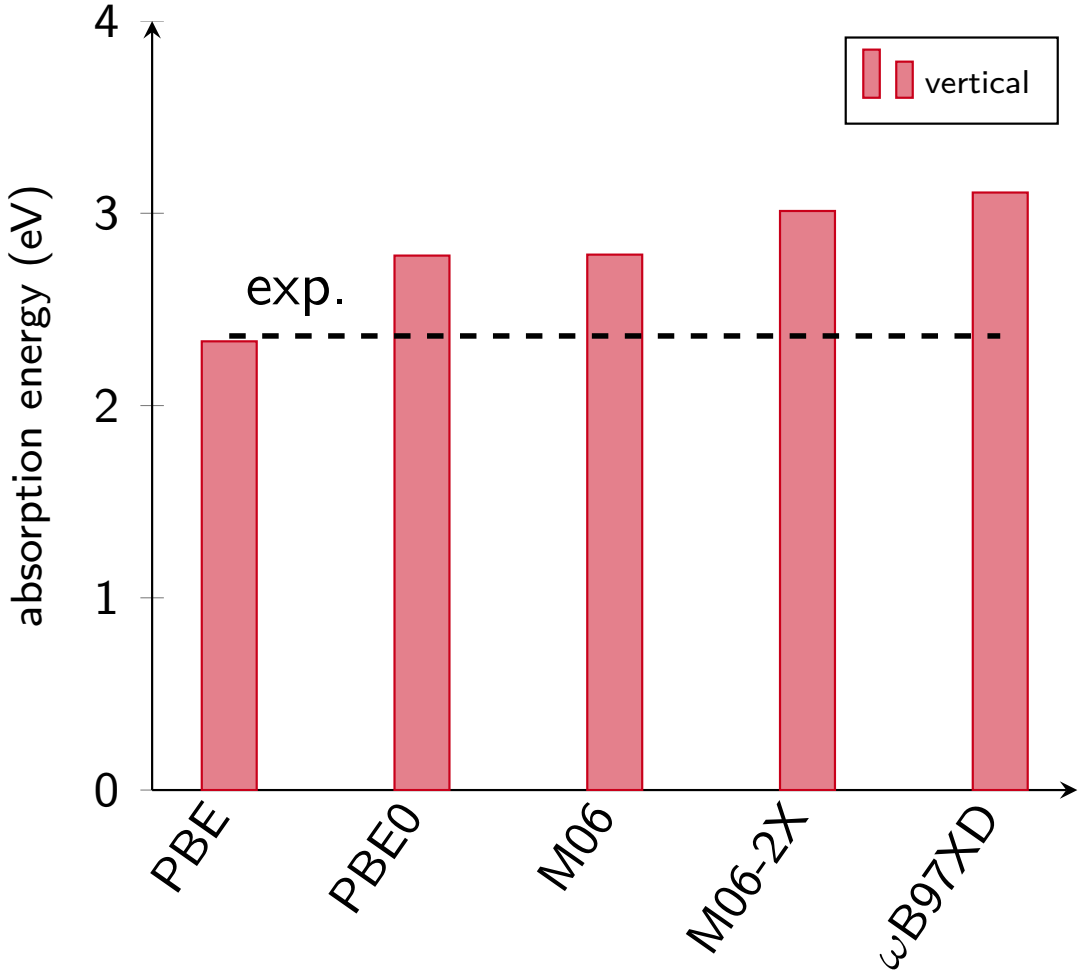
fine tuning of λ_{max} with

R^D = electron donor group

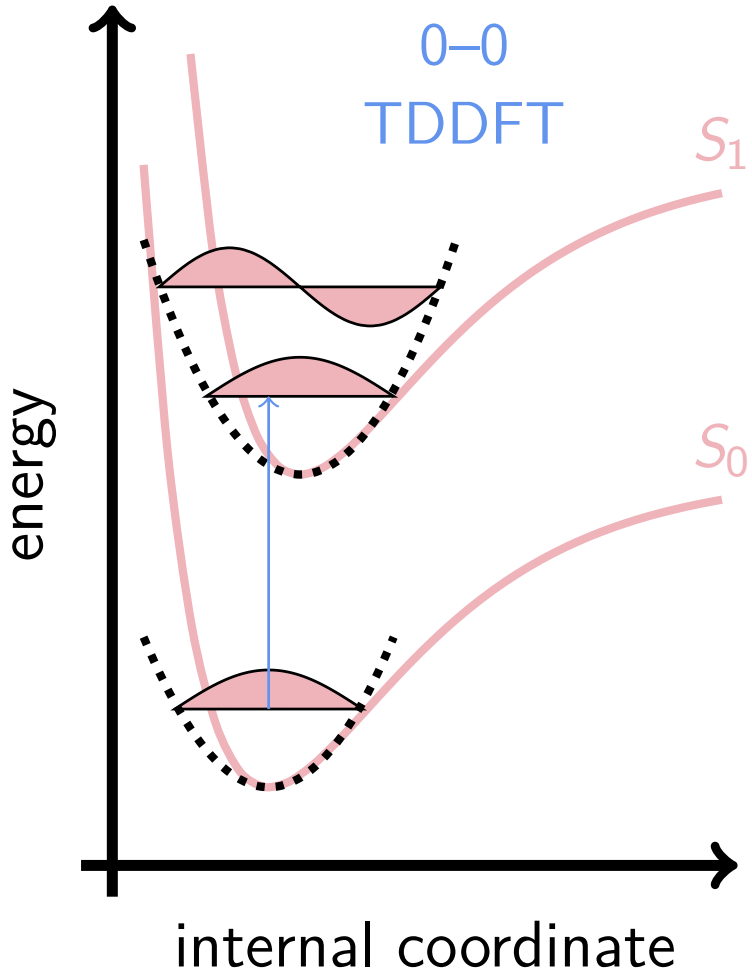
Gueret *et al.* **ACS Catal.** **2018** 8, 3792.

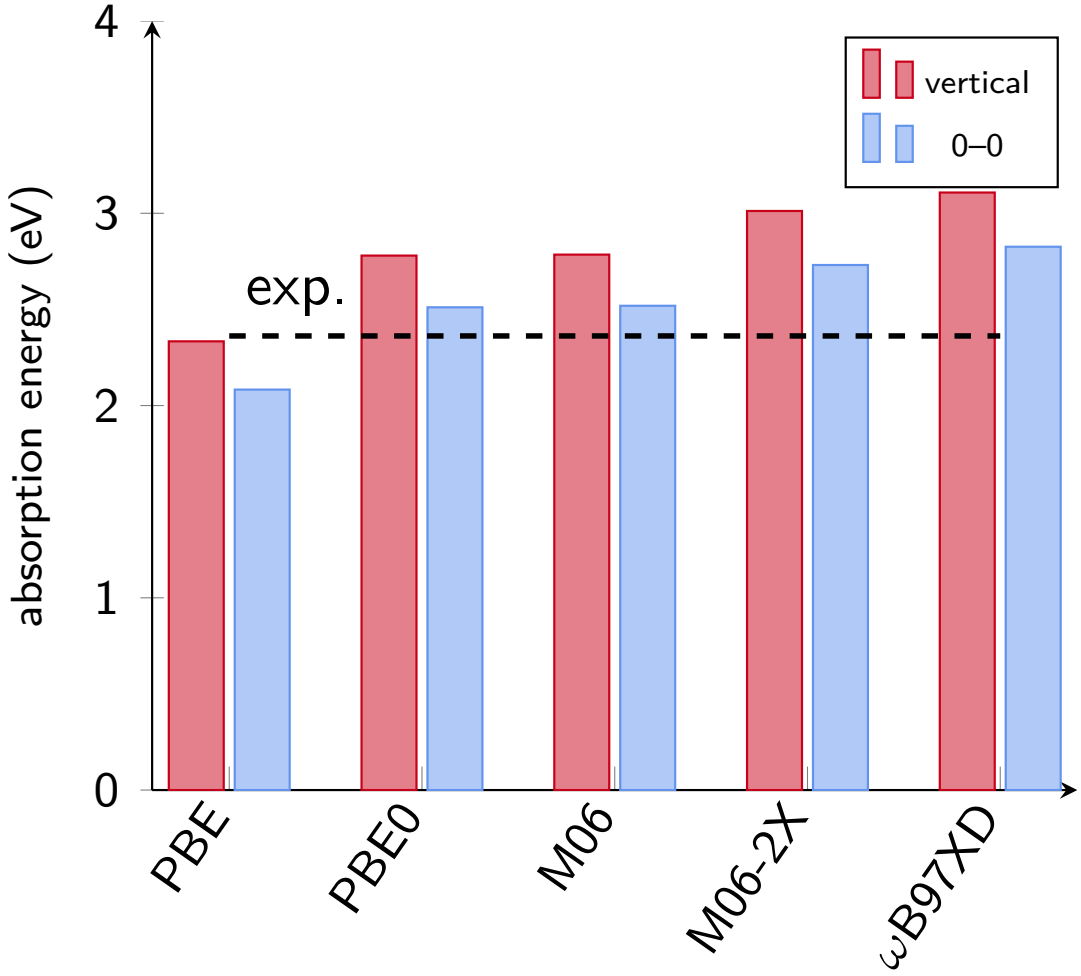
UV/vis Spectrum of the TATA Dye



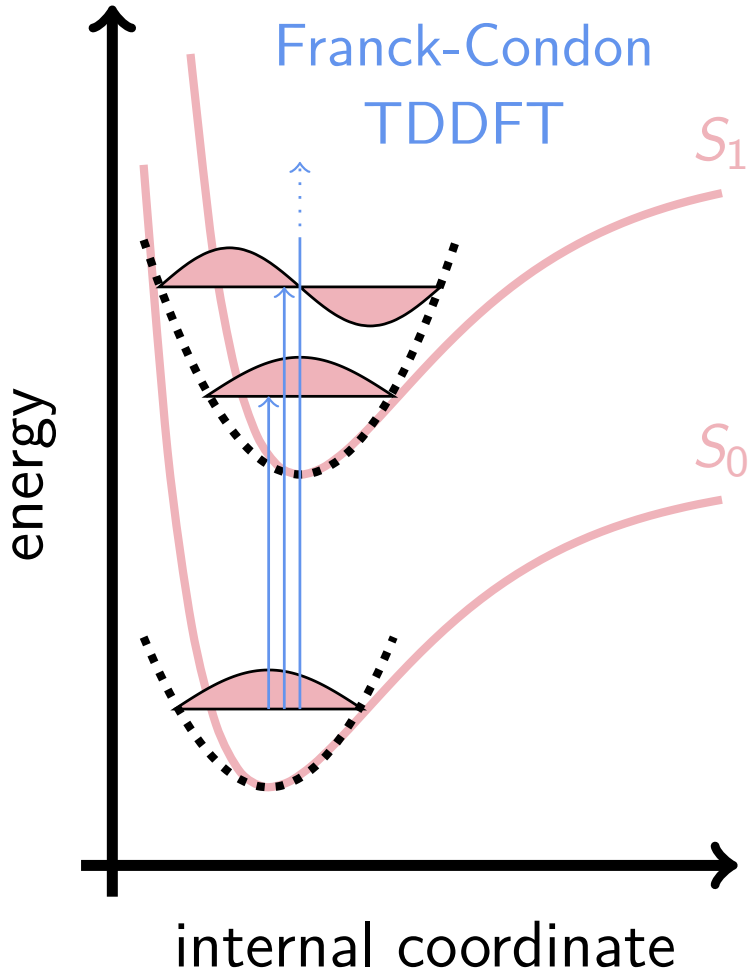


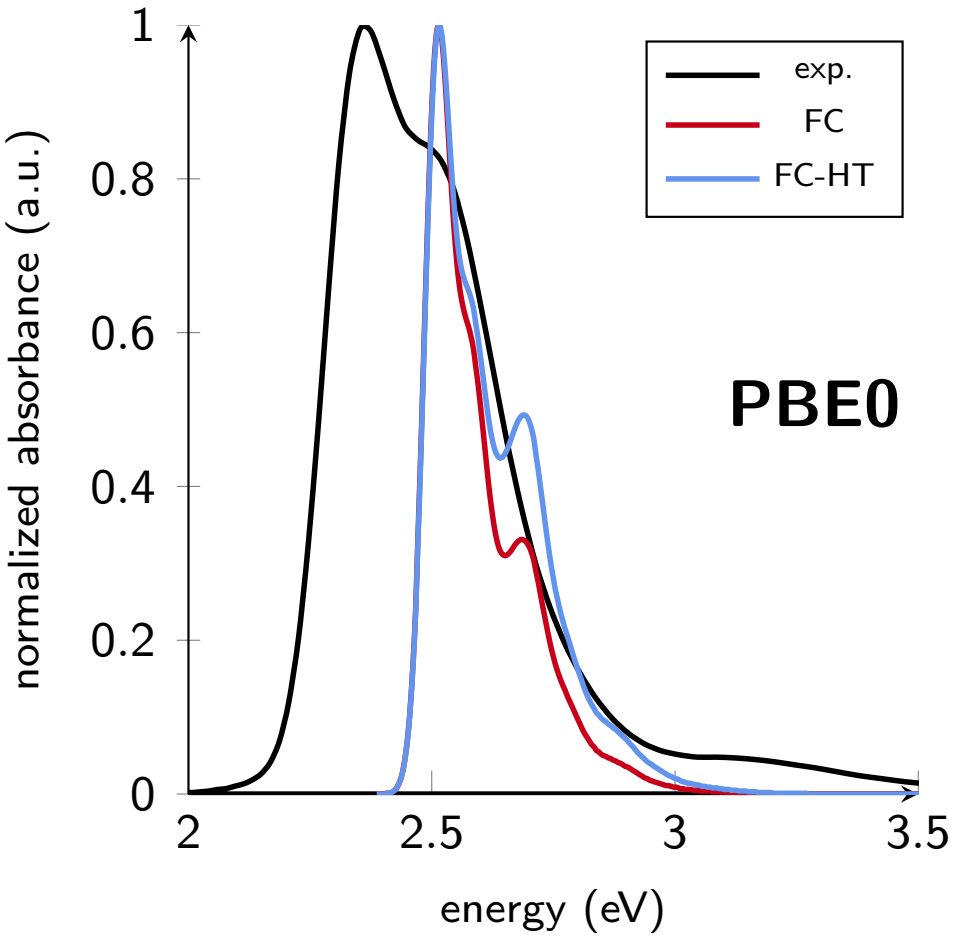
UV/vis Spectrum of the TATA Dye



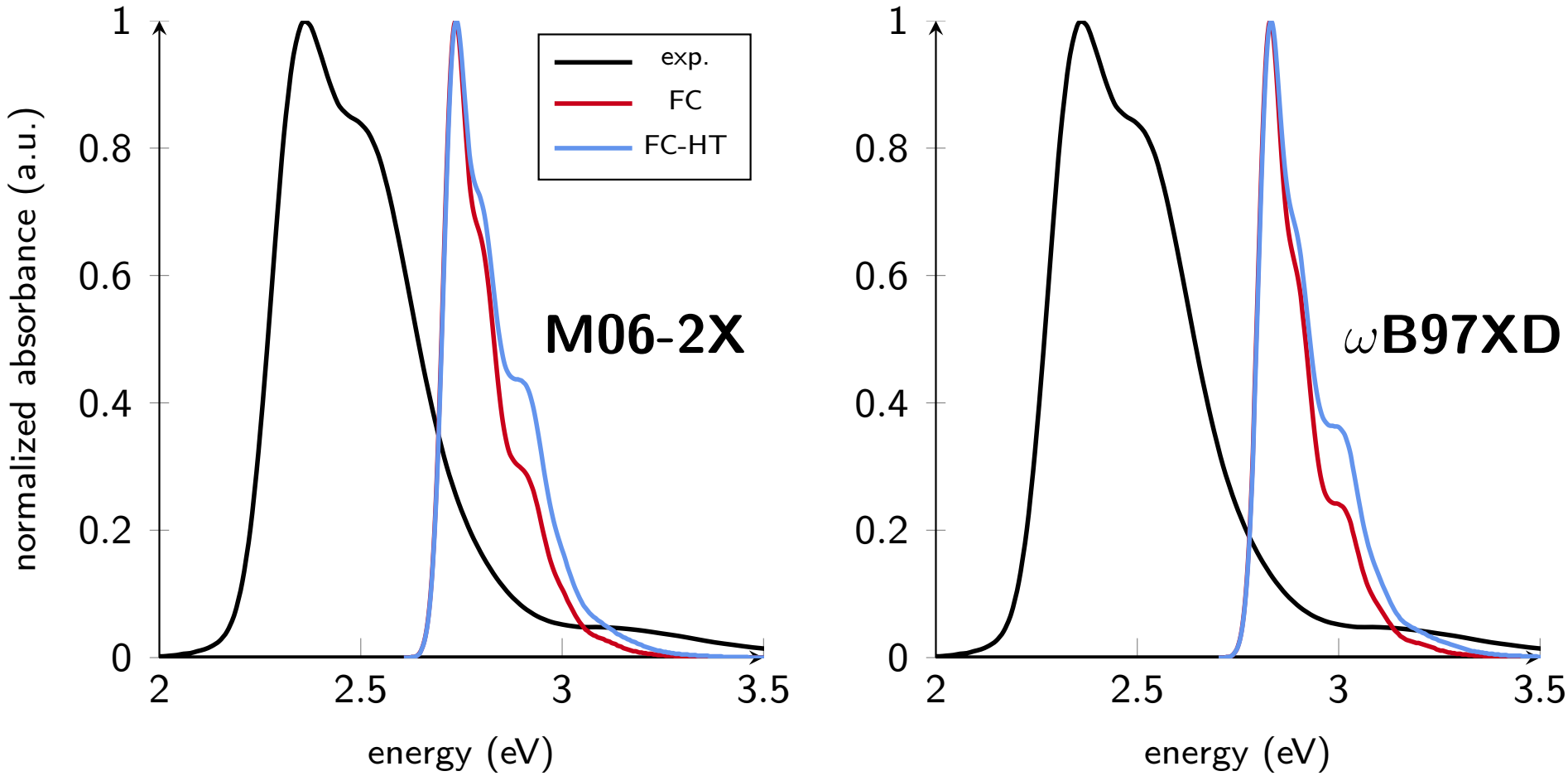


UV/vis Spectrum of the TATA Dye



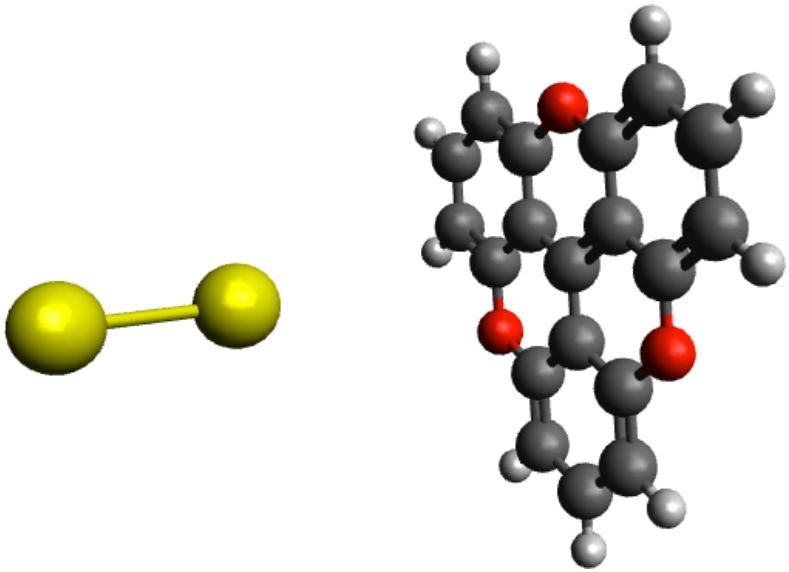


UV/vis Spectrum of the TATA Dye

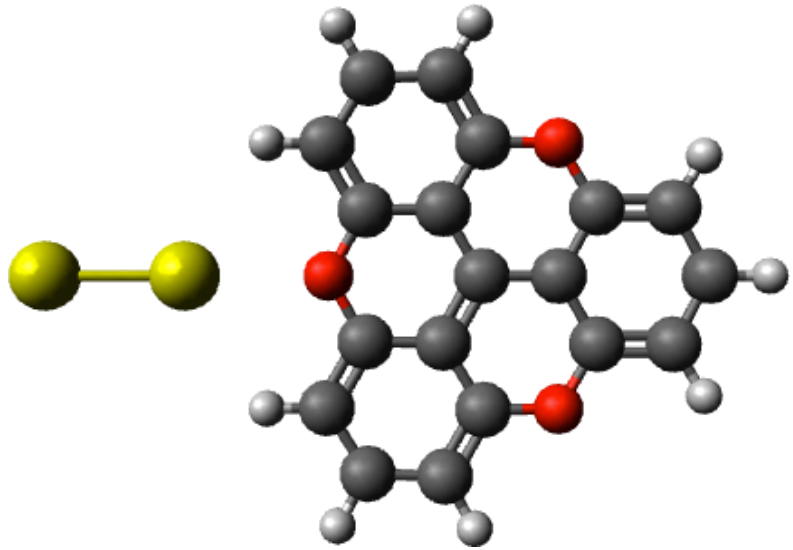


TOTA – Au_2 Interaction

T-shape

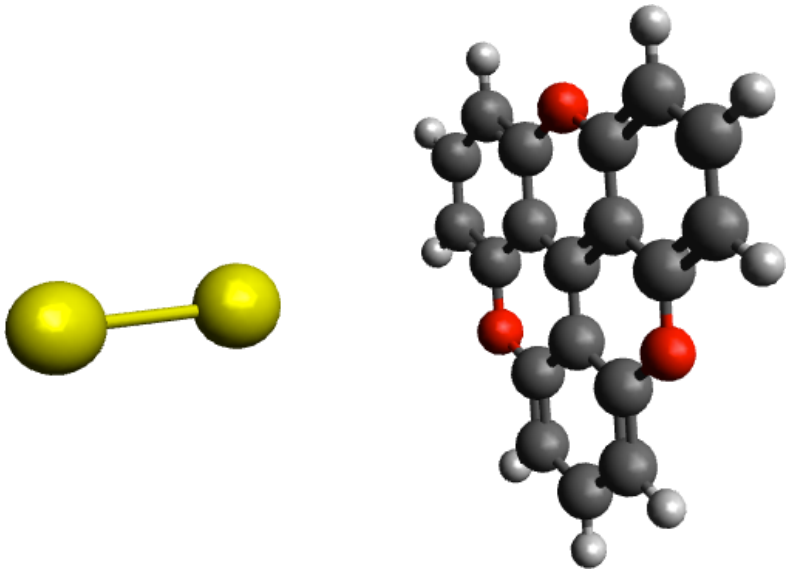


in plane



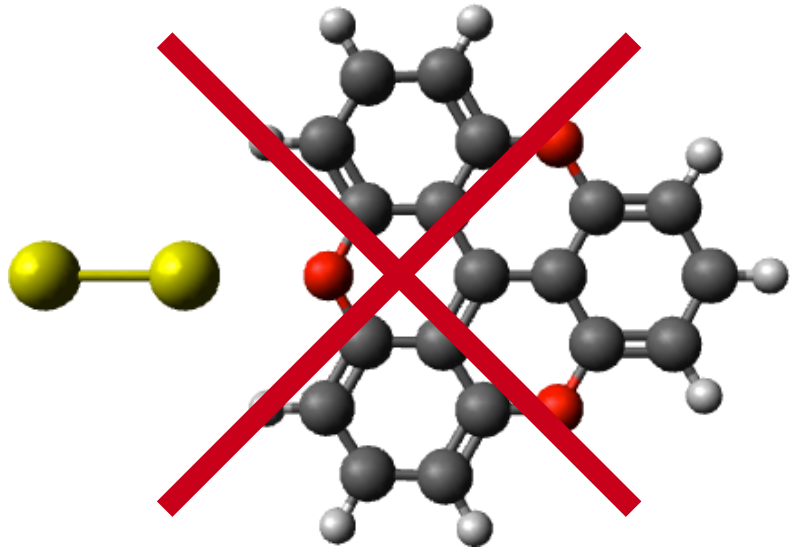
TOTA – Au_2 Interaction

T-shape



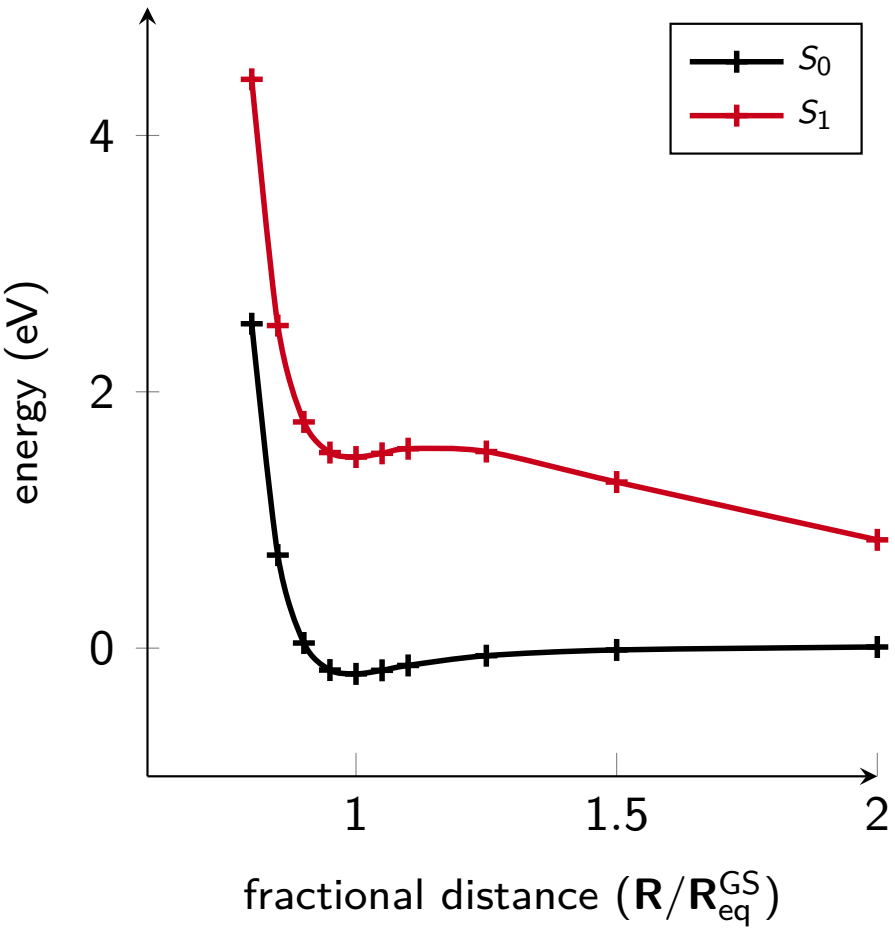
charge-transfer

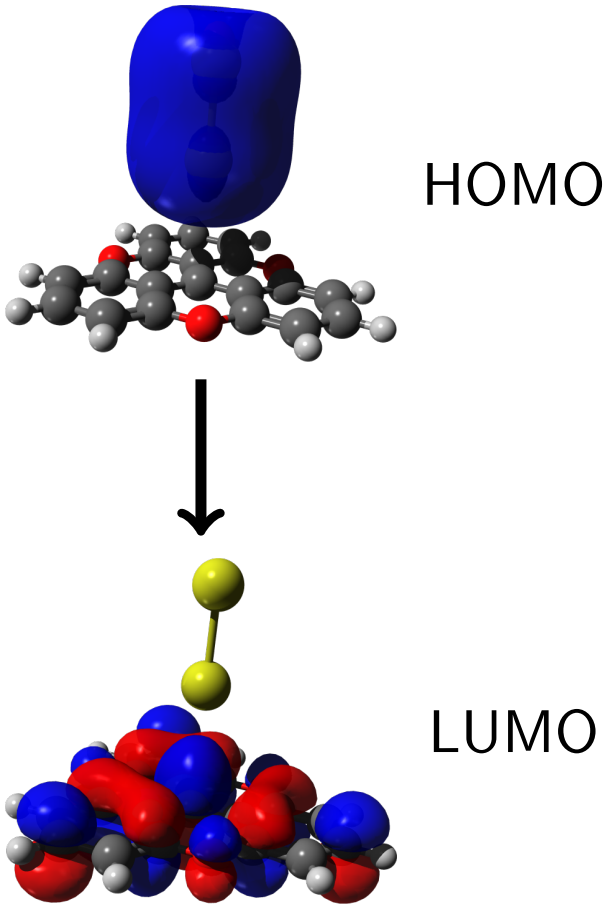
in plane



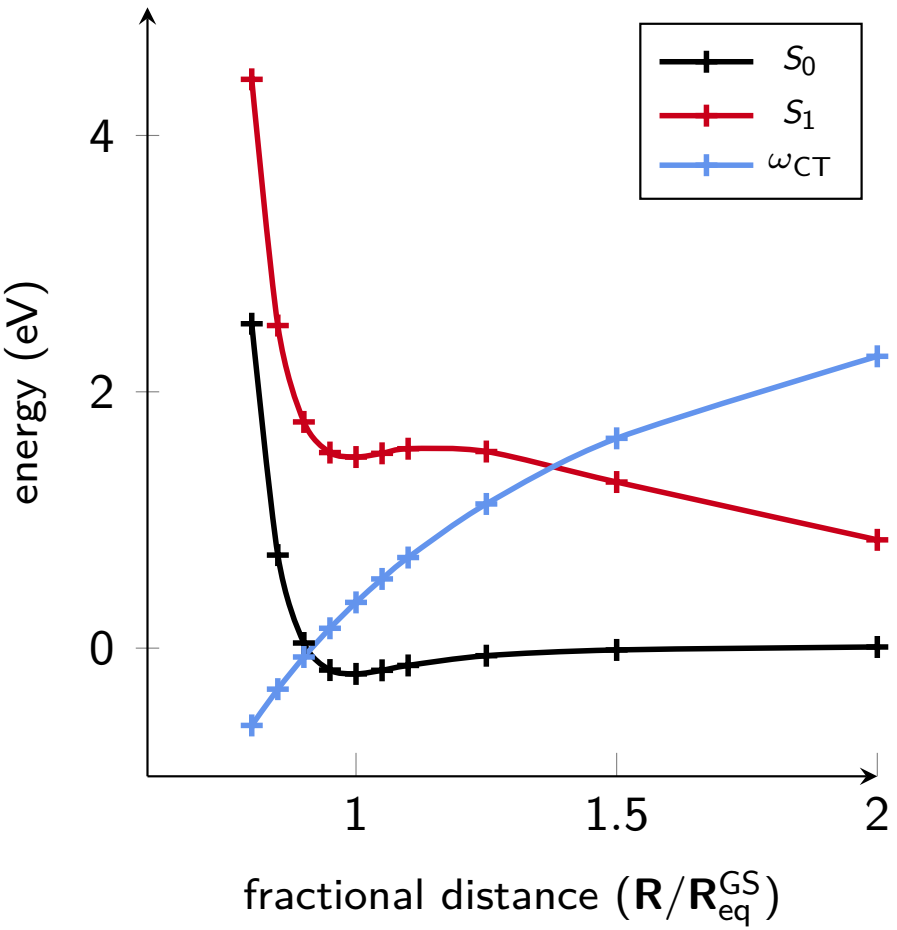
monomer-like

TOTA – Au_2 Interaction @TD-PBE level



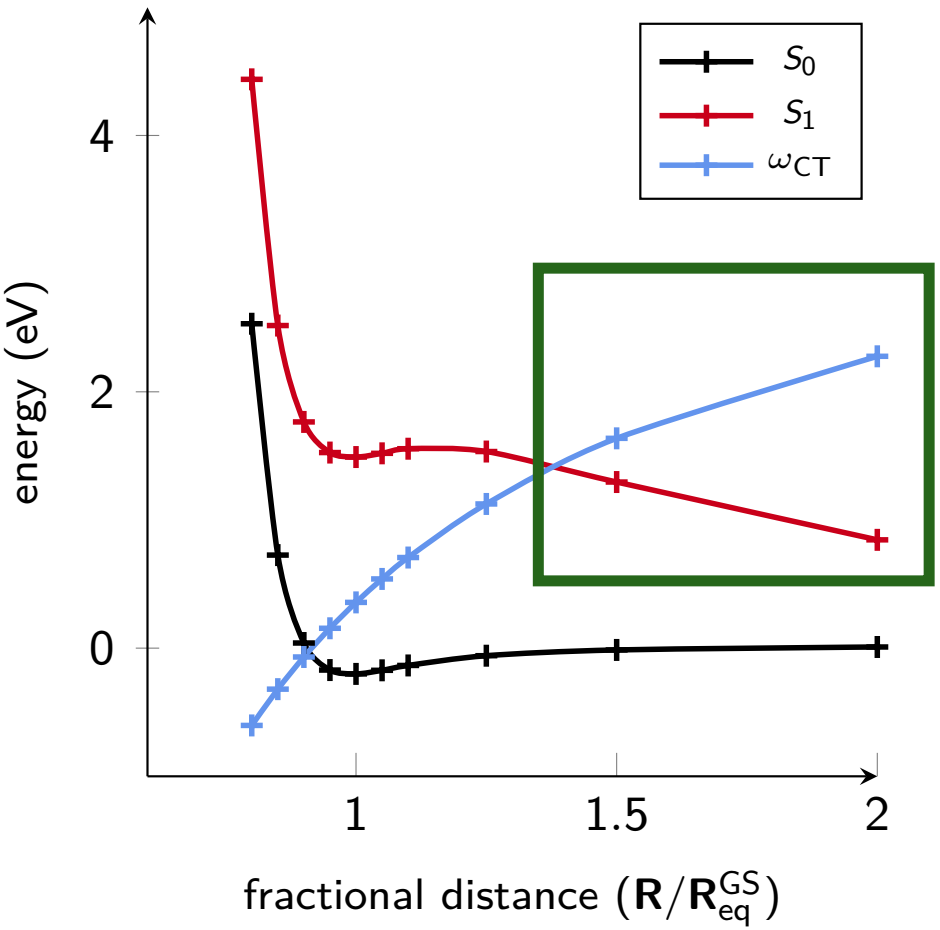


TOTA – Au_2 Interaction @TD-PBE level



$$\omega_{CT} = IP_{donor} - EA_{acceptor} - \frac{1}{\mathbf{R}}$$

TOTA – Au_2 Interaction @TD-PBE level



$$\omega_{CT} = IP_{donor} - EA_{acceptor} - \frac{1}{\mathbf{R}}$$

$$\omega_{CT} < e_{S_1}$$

PBE failure

Asymptote of the Exchange Potential

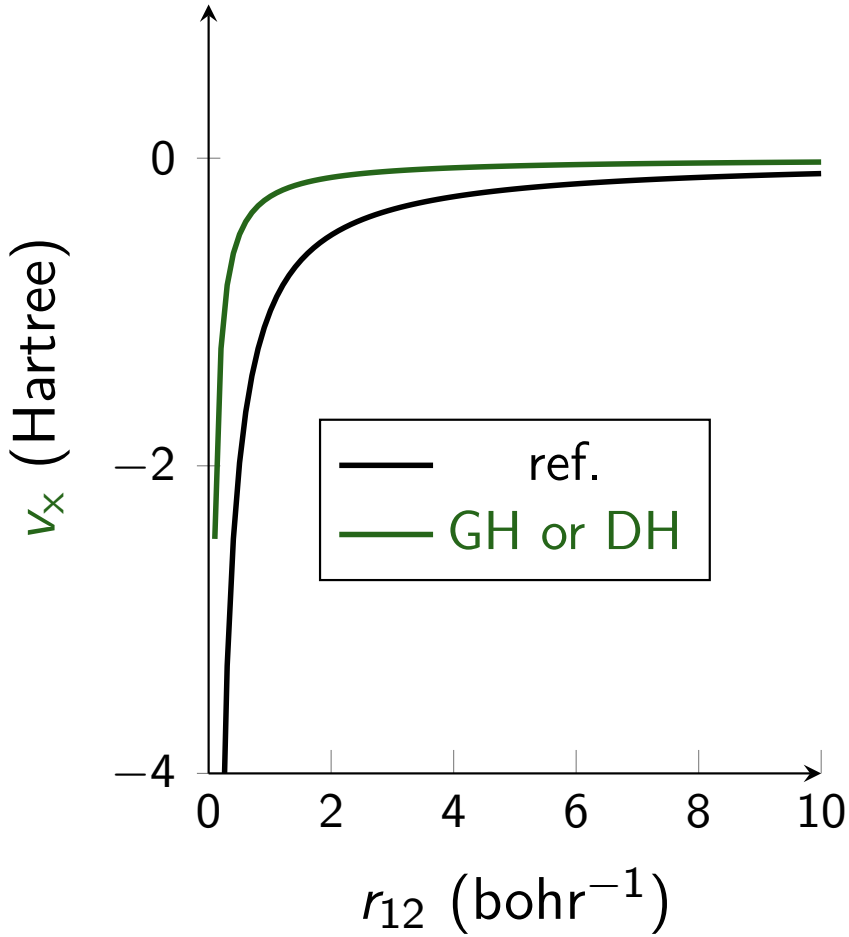
in the long-range (LR) regime

$$v_{\mathbf{x}}(r_{12}) \rightarrow -r_{12}^{-1}$$

while

$$v_{\mathbf{x}}^{\mathbf{GH}}(r_{12}) \rightarrow -a_x r_{12}^{-1}$$

$$v_{\mathbf{x}}^{\mathbf{DH}}(r_{12}) \rightarrow -a_x r_{12}^{-1}$$



Savin **Recent Dev. & App. of Modern DFT** **1996** 327.

Asymptote of the Exchange Potential

in the long-range (LR) regime

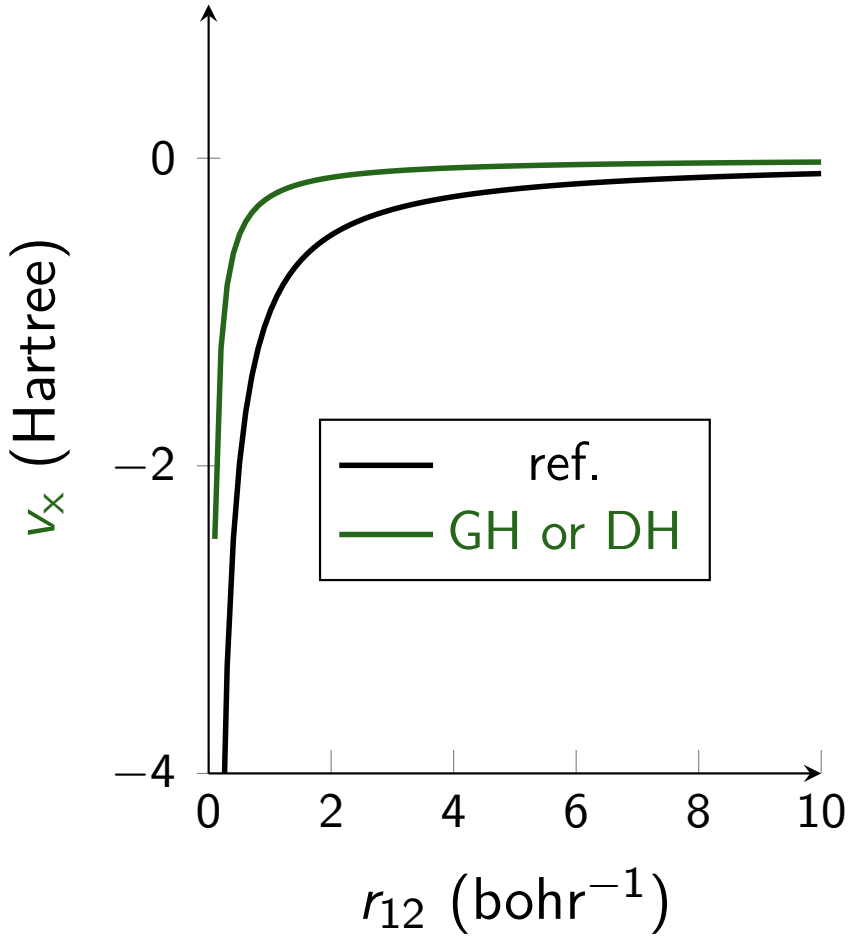
$$v_{\mathbf{x}}(r_{12}) \rightarrow -r_{12}^{-1}$$

while

$$v_{\mathbf{x}}^{\mathbf{GH}}(r_{12}) \rightarrow -a_x r_{12}^{-1}$$

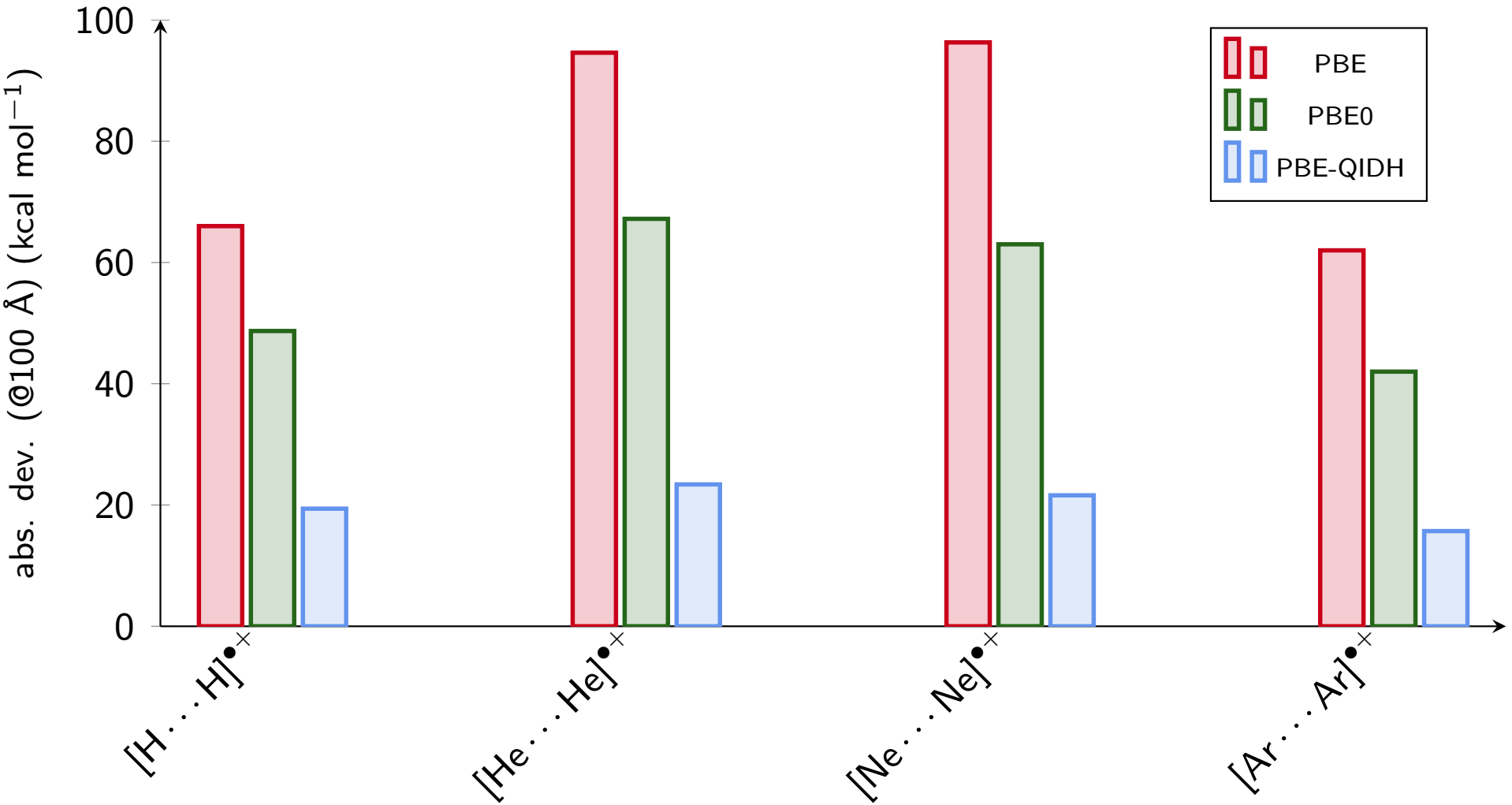
$$v_{\mathbf{x}}^{\mathbf{DH}}(r_{12}) \rightarrow -a_x r_{12}^{-1}$$

underestimation of energy properties



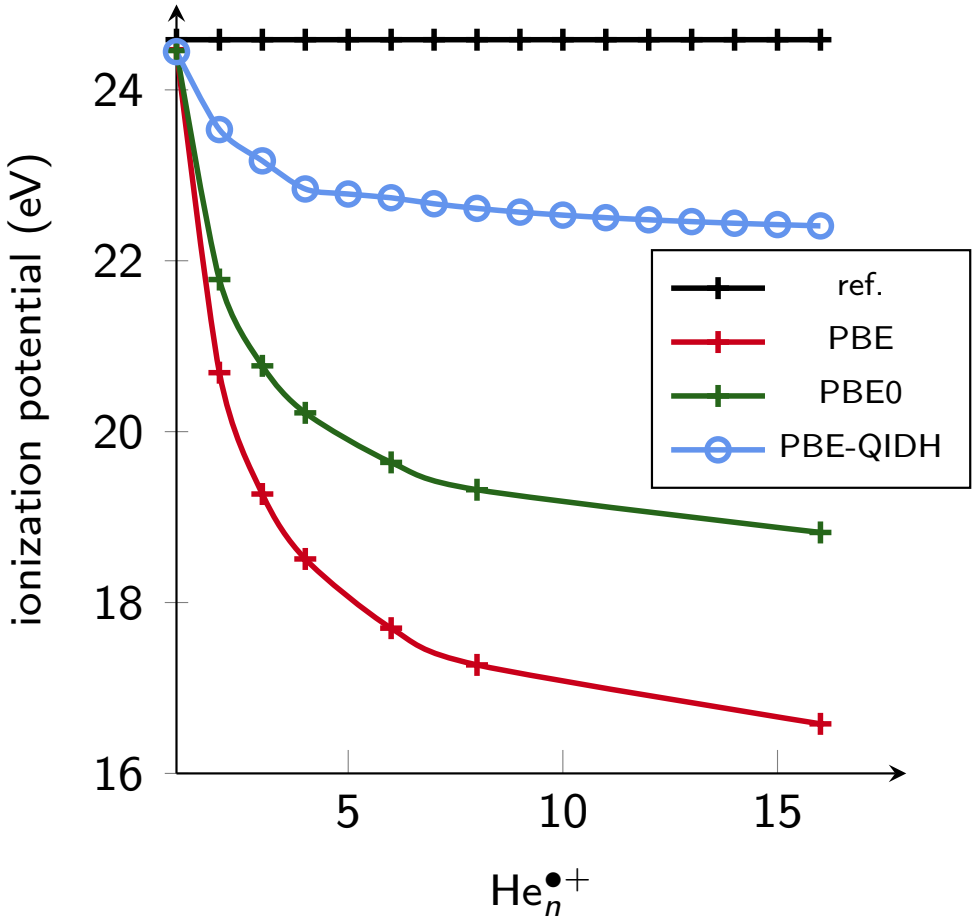
Savin **Recent Dev. & App. of Modern DFT** **1996** 327.

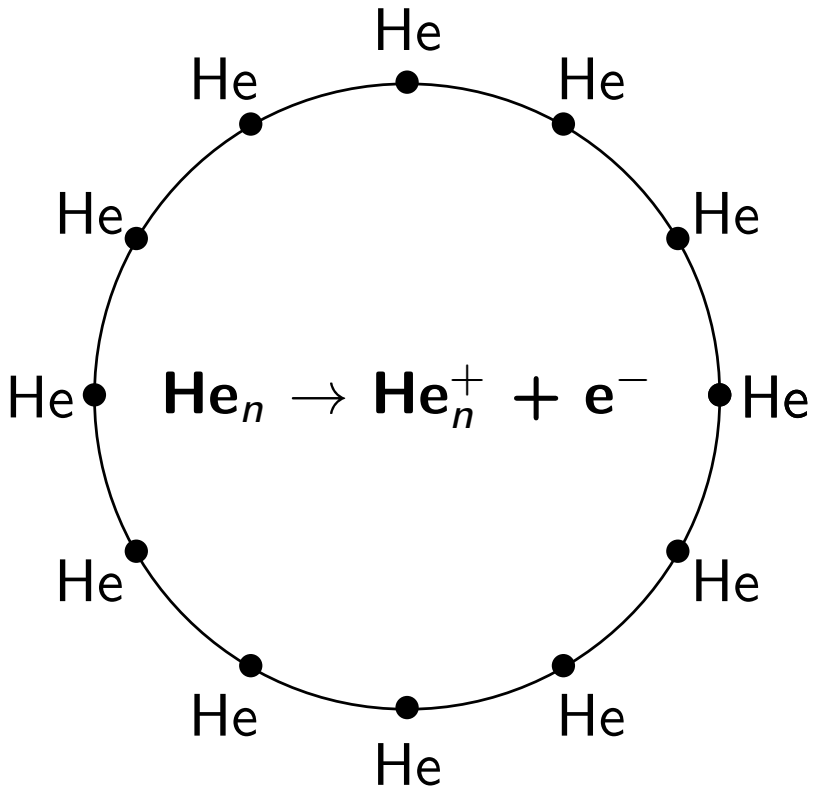
Long-Range Energy Properties



Brémond *et al.* **J. Chem. Theory Comput.** **2018** 14, 4052.

Long-Range Energy Properties





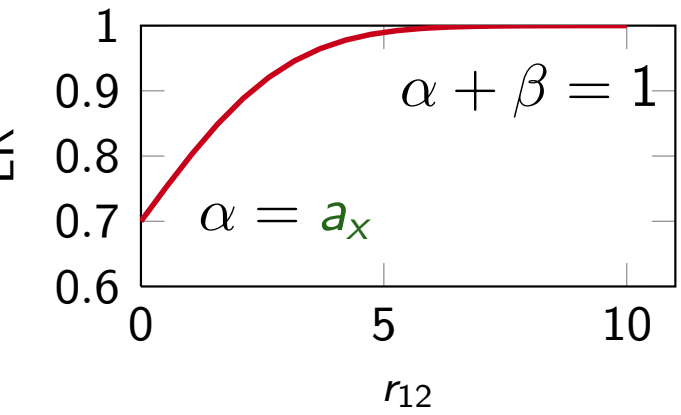
Brémond *et al.* **J. Chem. Theory Comput.** **2018** 14, 4052.

The RSX Models: Tentative of Rationalization

The RSX-H and RSX-DH Models

range-separation model

$$\frac{1}{r_{12}} = \underbrace{\frac{1-[\alpha+\beta\mathrm{erf}(\omega r_{12})]}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\alpha+\beta\mathrm{erf}(\omega r_{12})}{r_{12}}}_{\text{LR}}$$

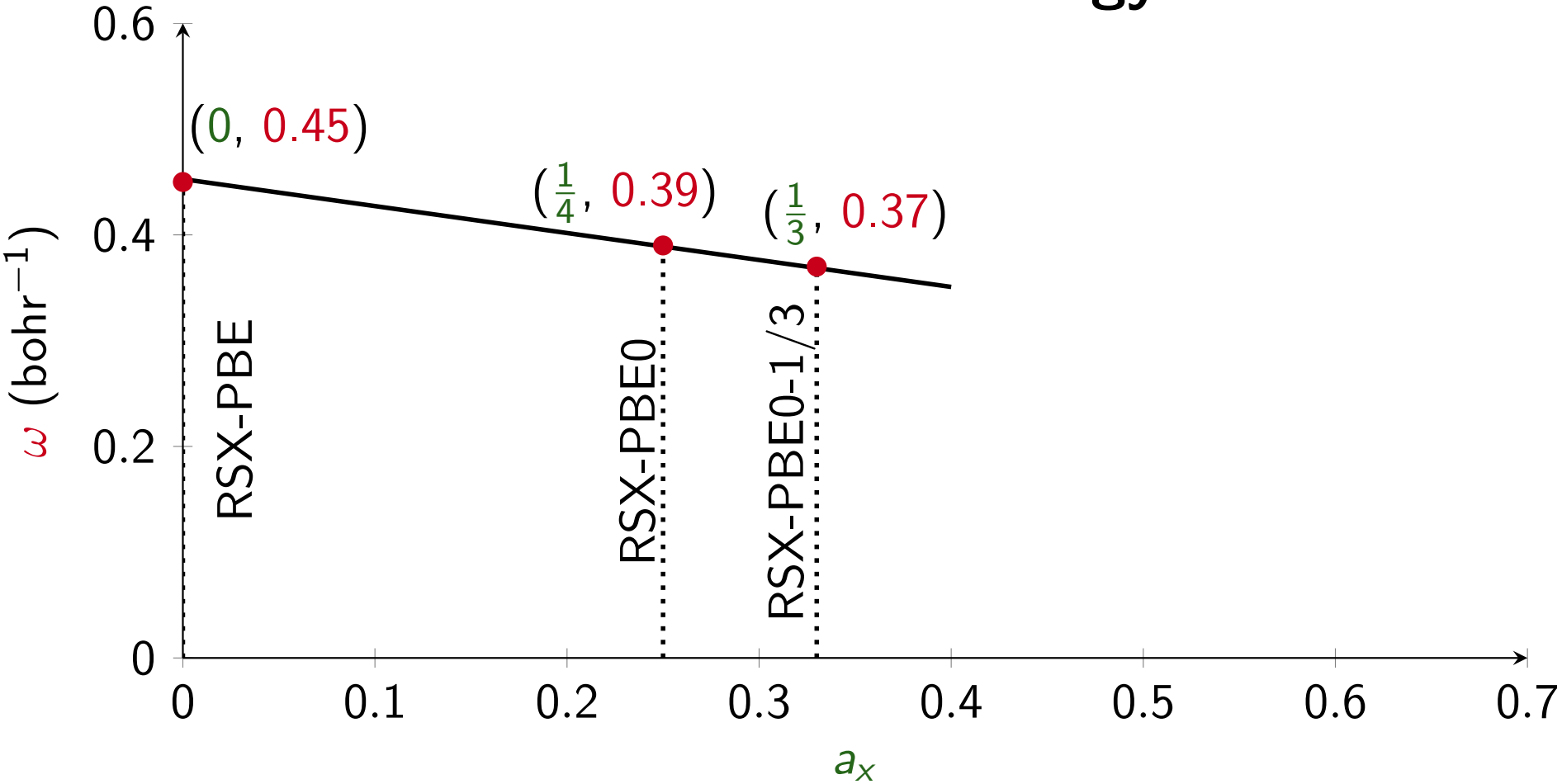


$$E_{xc}^{\text{RSX-DH}} = E_{xc}^{\text{DFA}} + a_x\left(E_x^{\text{EXX}} - E_x^{\text{DFA}}\right) + a_c\left(E_c^{\text{PT2}} - E_c^{\text{DFA}}\right) + (1-a_x)\left(E_x^{\text{LR-EXX}}[\omega] - E_x^{\text{SR-DFA}}[\omega]\right)$$

Brémond *et al.* **J. Chem. Phys.** **2019** 150, 201102.

The RSX Models: Tentative of Rationalization

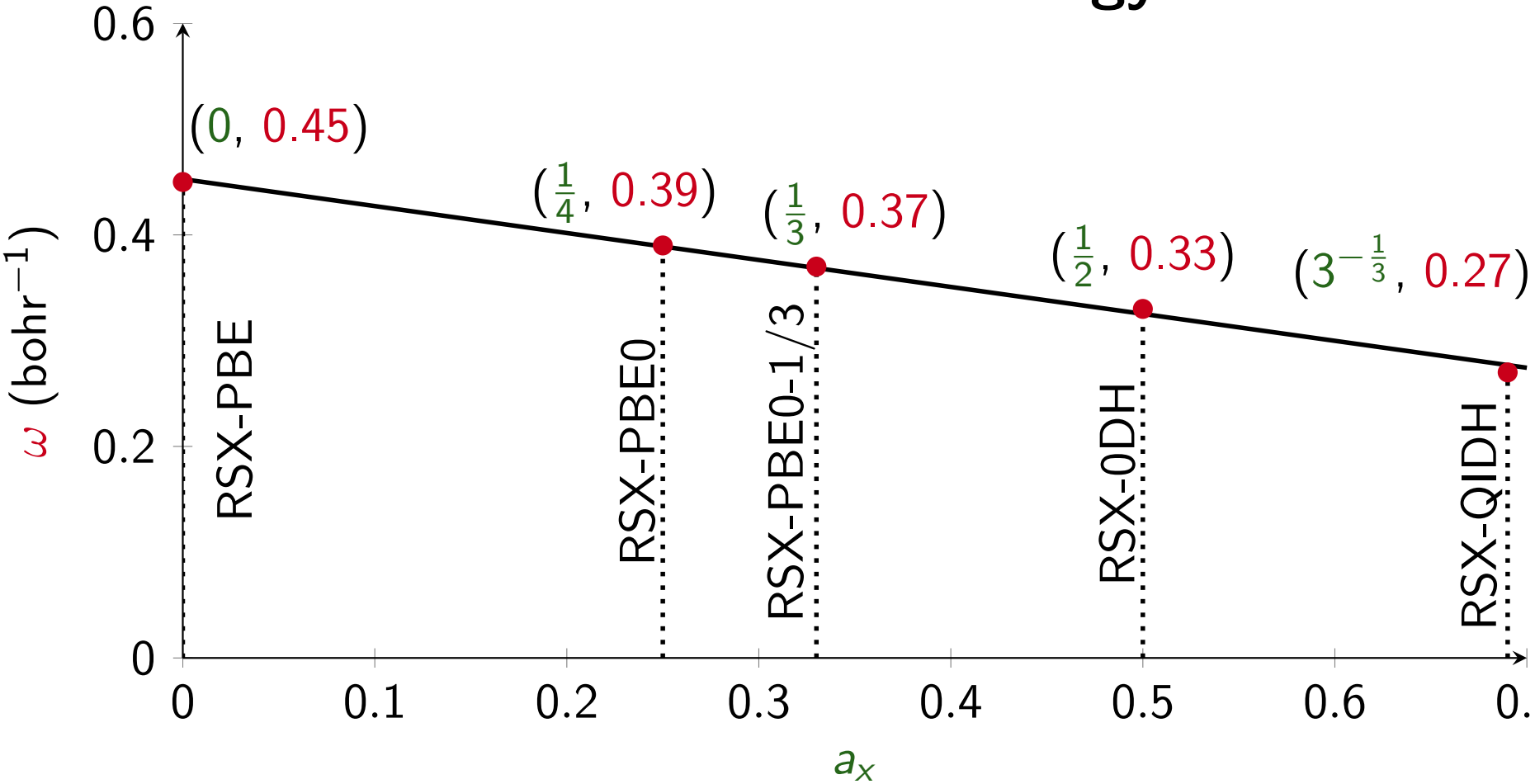
set ω to enforce the energy of H



Brémond *et al.* **J. Chem. Phys.** **2019** 150, 201102.

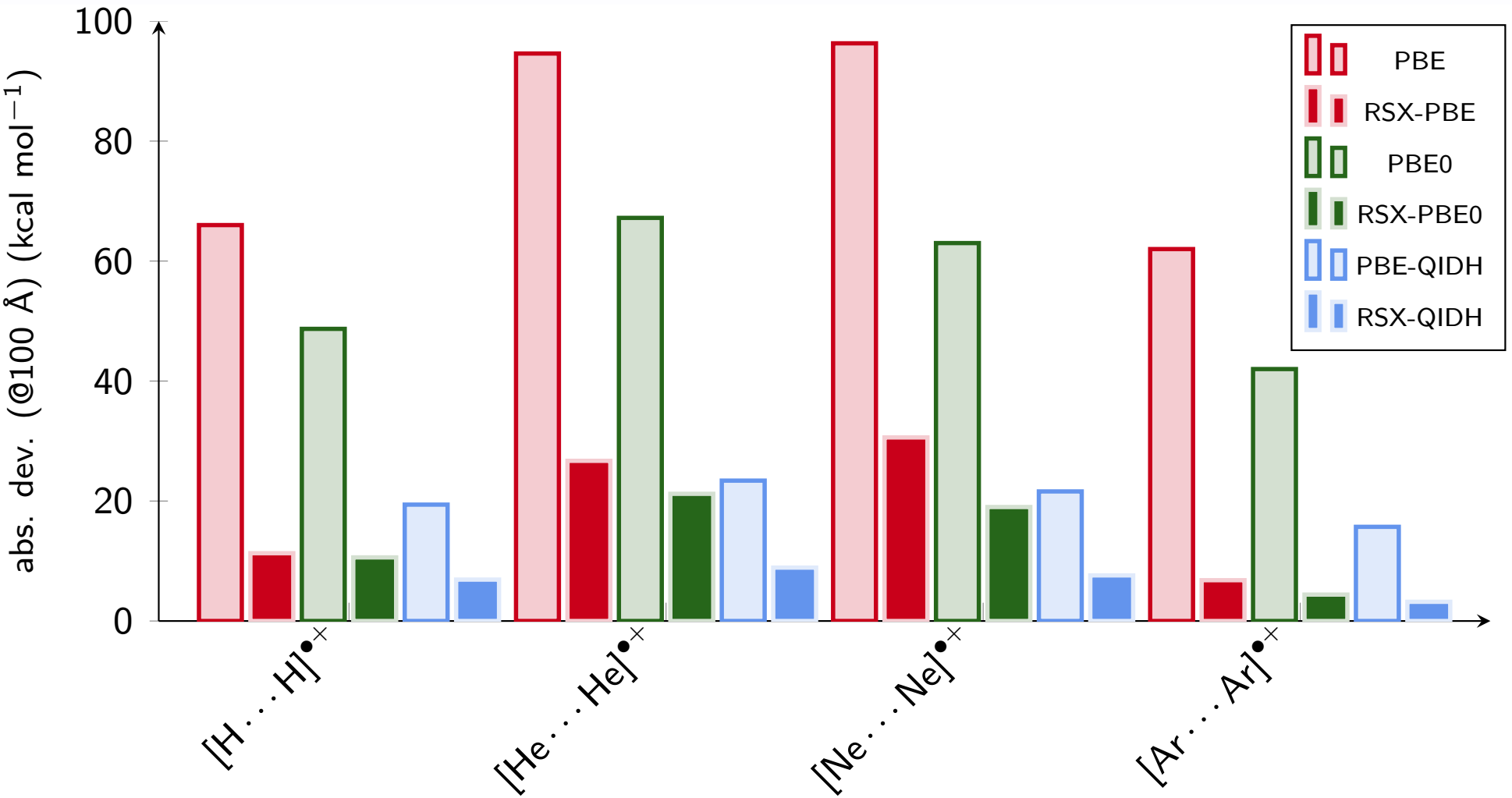
The RSX Models: Tentative of Rationalization

set ω to enforce the energy of H



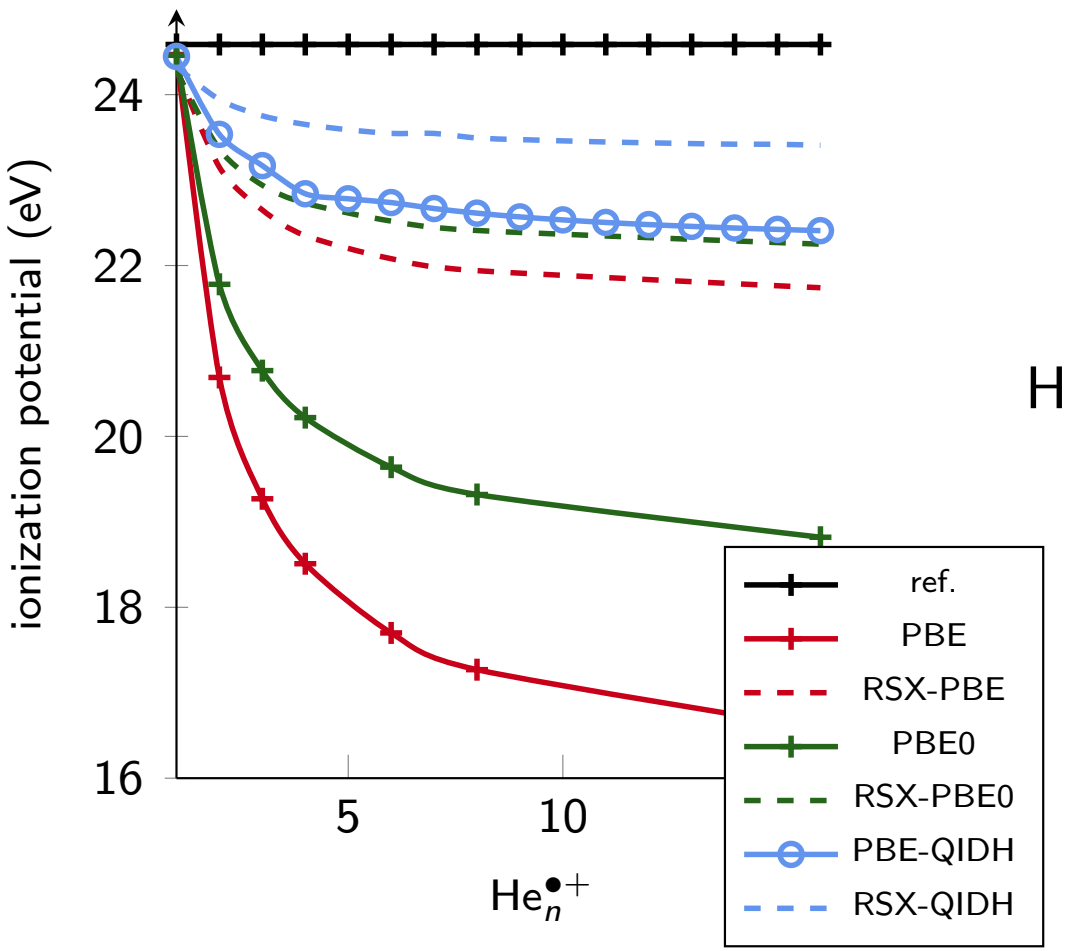
Brémond *et al.* **J. Chem. Phys.** **2019** 150, 201102.

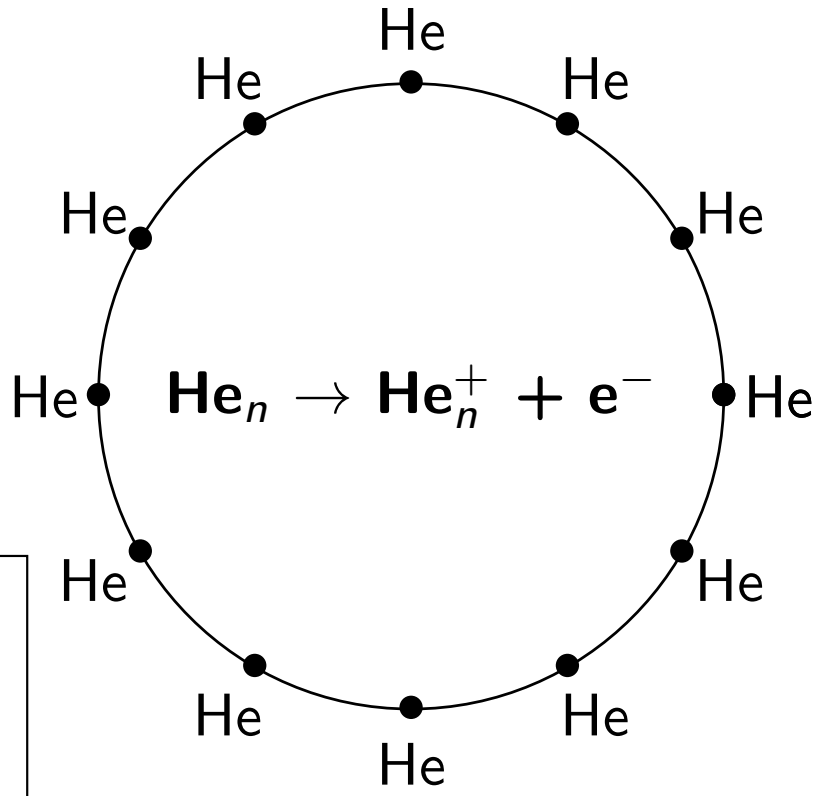
Rare Gas Cationic Dimers



Brémond *et al.* **J. Chem. Theory Comput.** **2018** 14, 4052.

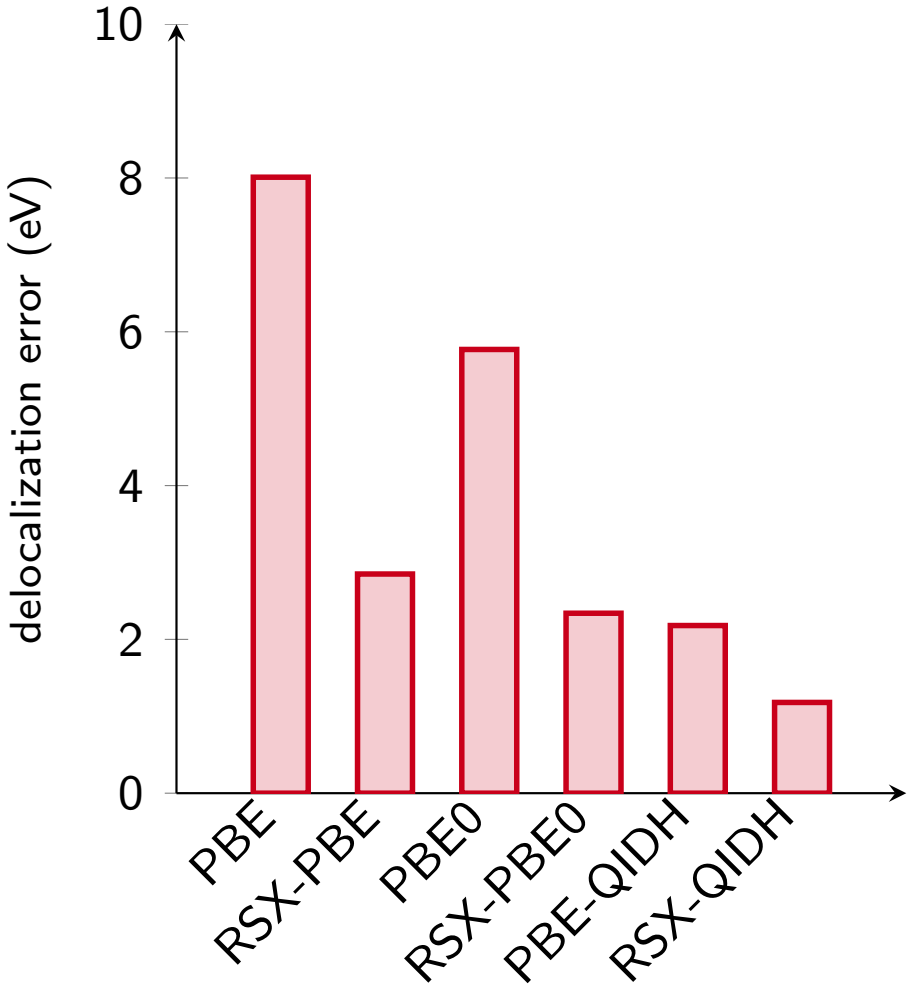
Delocalization Error in He Clusters

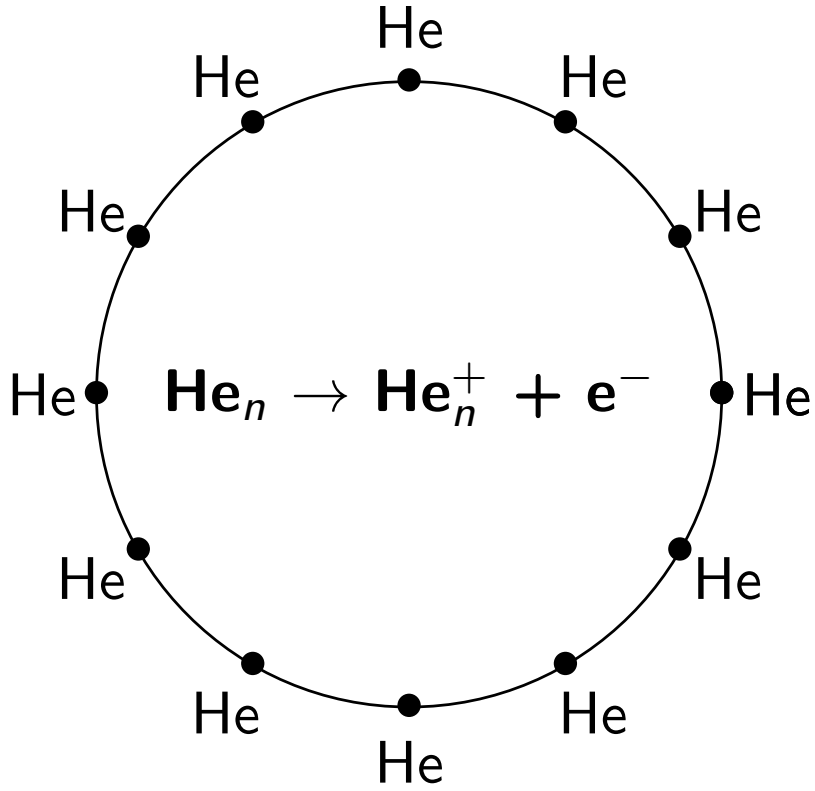




Brémond *et al.* **J. Chem. Theory Comput.** **2018** 14, 4052.

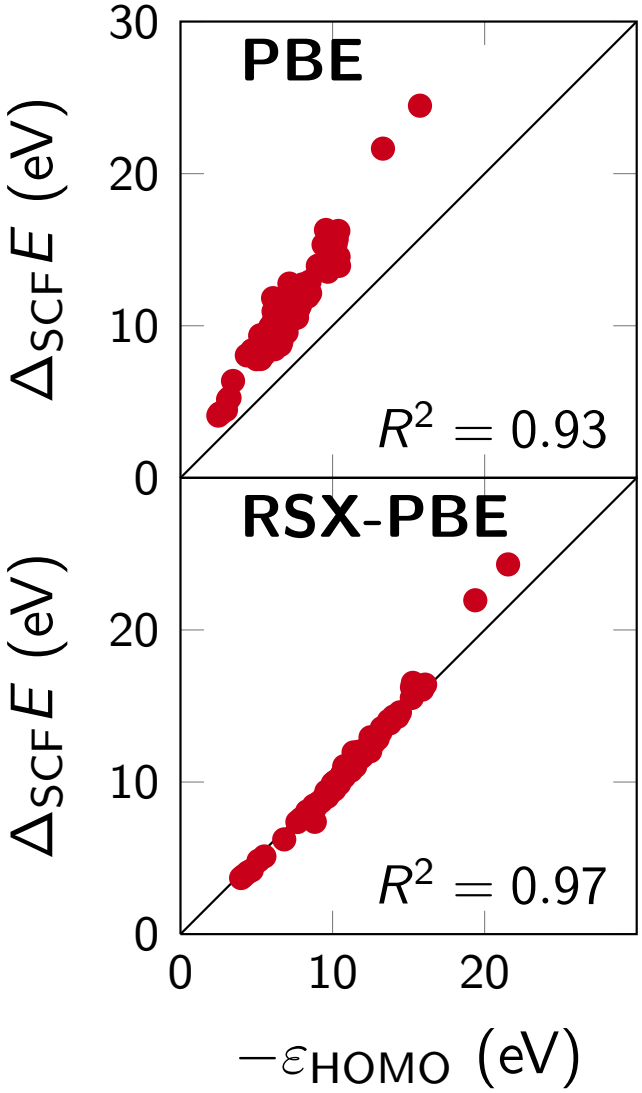
Delocalization Error in He Clusters





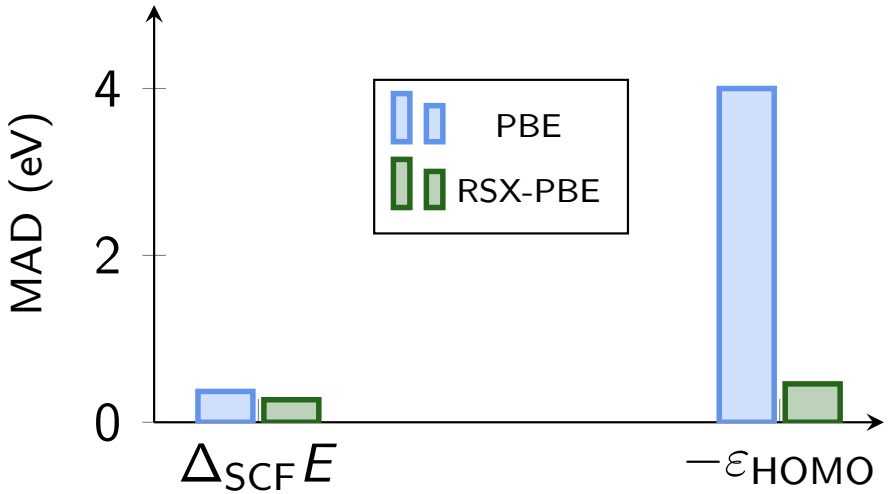
Brémond *et al.* **J. Chem. Theory Comput.** **2018** 14, 4052.

GW100: Ionization Potentials



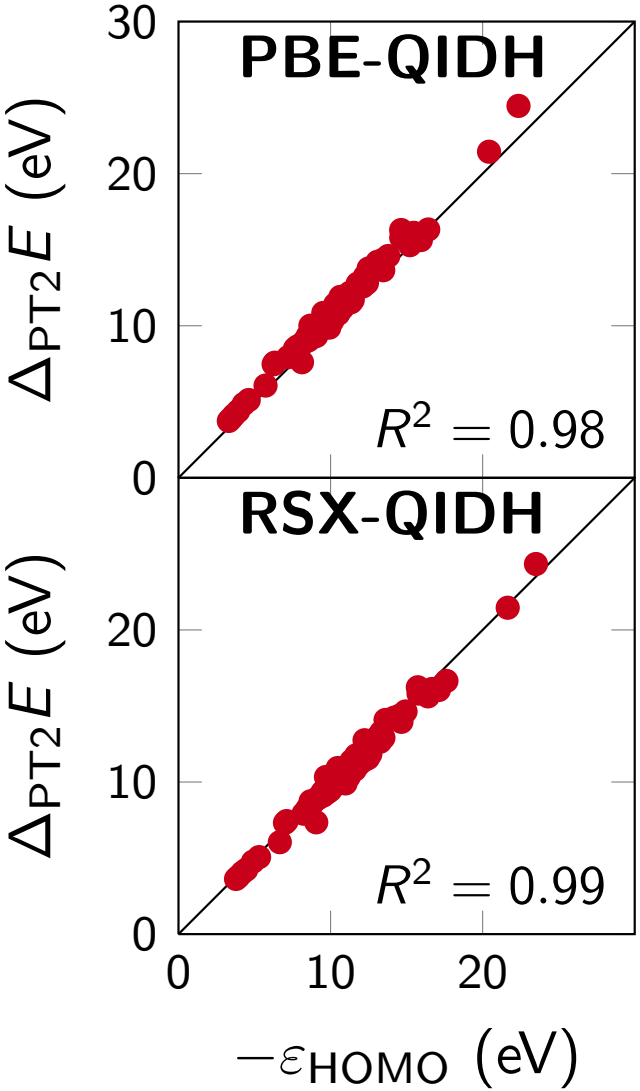
Koopman's Theorem?

$$\Delta_{SCF}E^{RSX\text{-}H} = -\varepsilon_{HOMO}$$



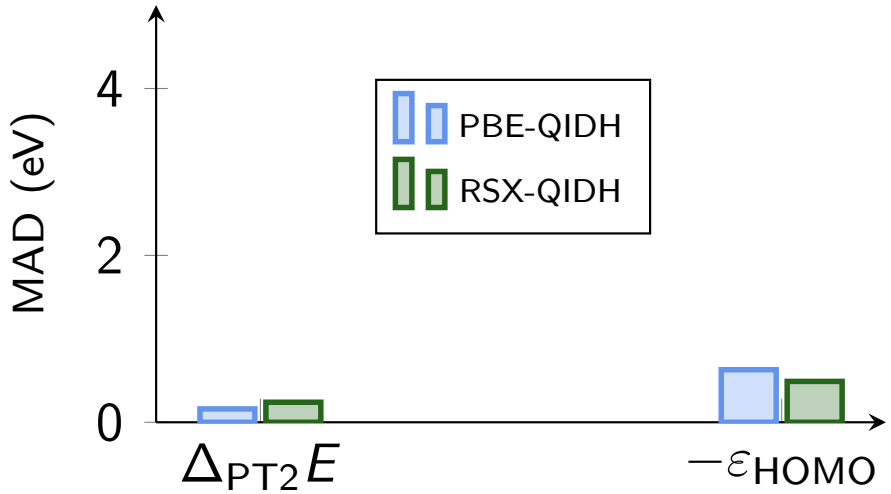
Brémond *et al.* **J. Chem. Phys.** **2019** 150, 201102.

GW100: Ionization Potentials



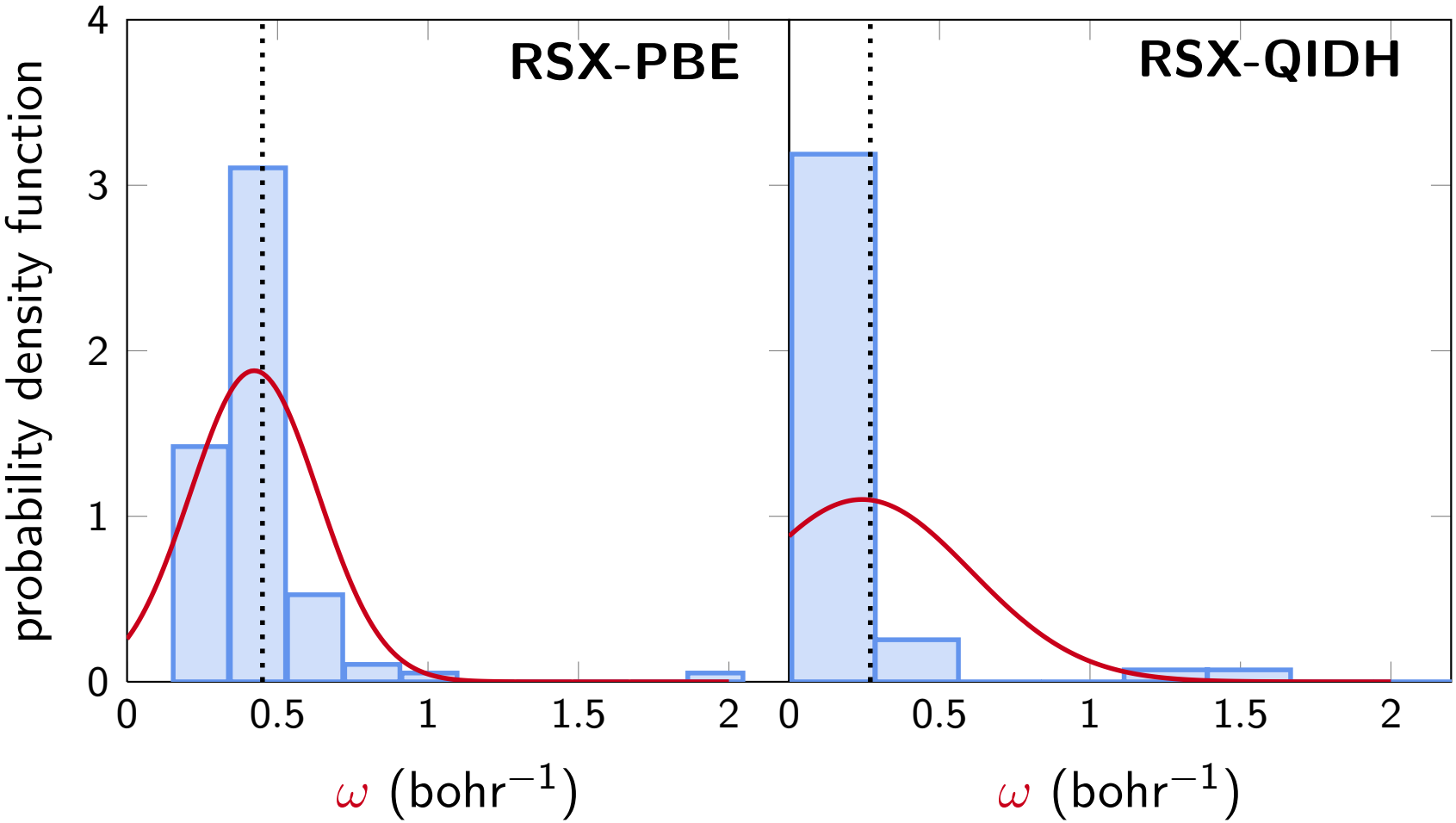
what about DHs?

$$\Delta_{\mathbf{PT2}}E^{\mathbf{RSX\text{-}DH}} = -\varepsilon_{\mathbf{HOMO}}$$



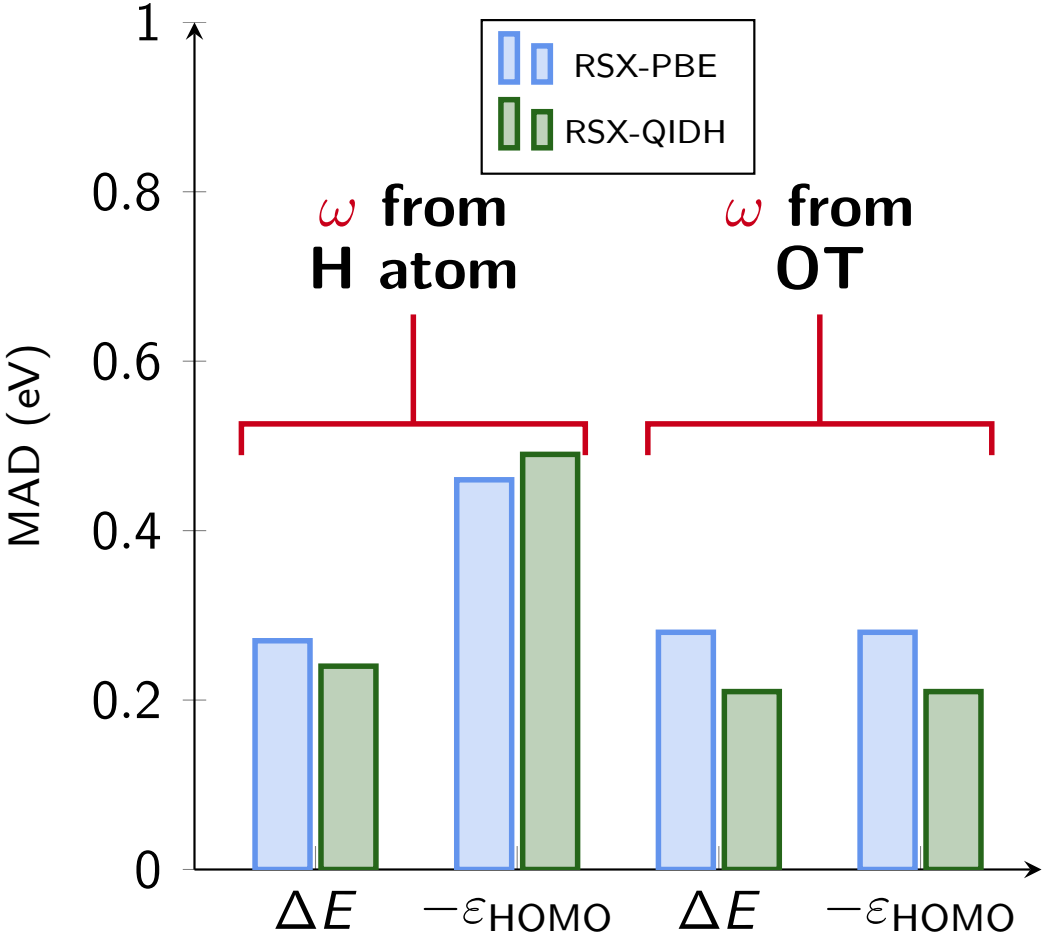
Brémond *et al.* **J. Chem. Phys.** **2019** 150, 201102.

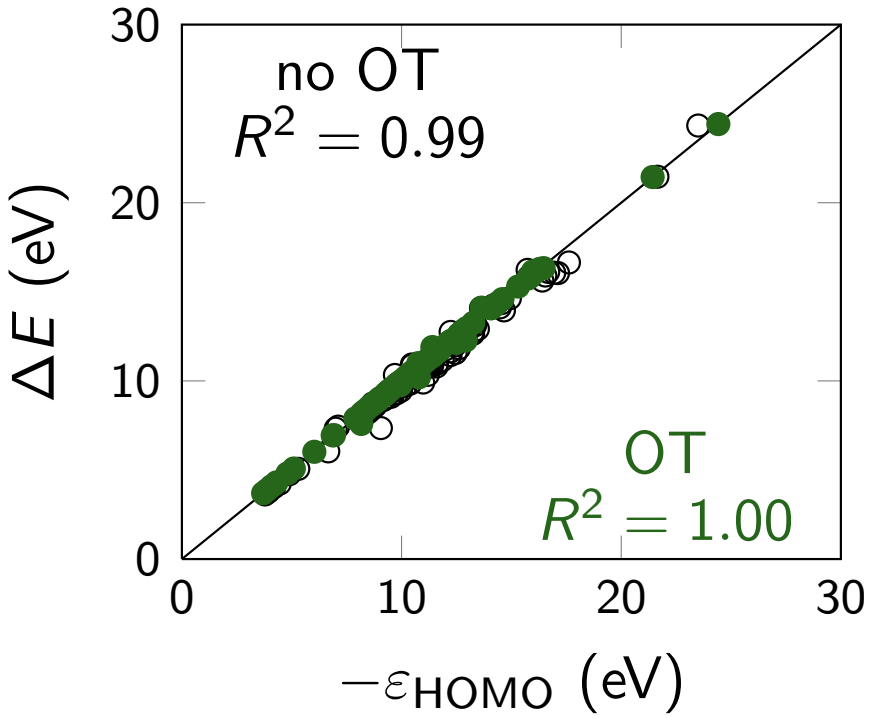
GW100: Optimal Tuning



Brémond *et al.* **J. Chem. Phys.** **submitted**.

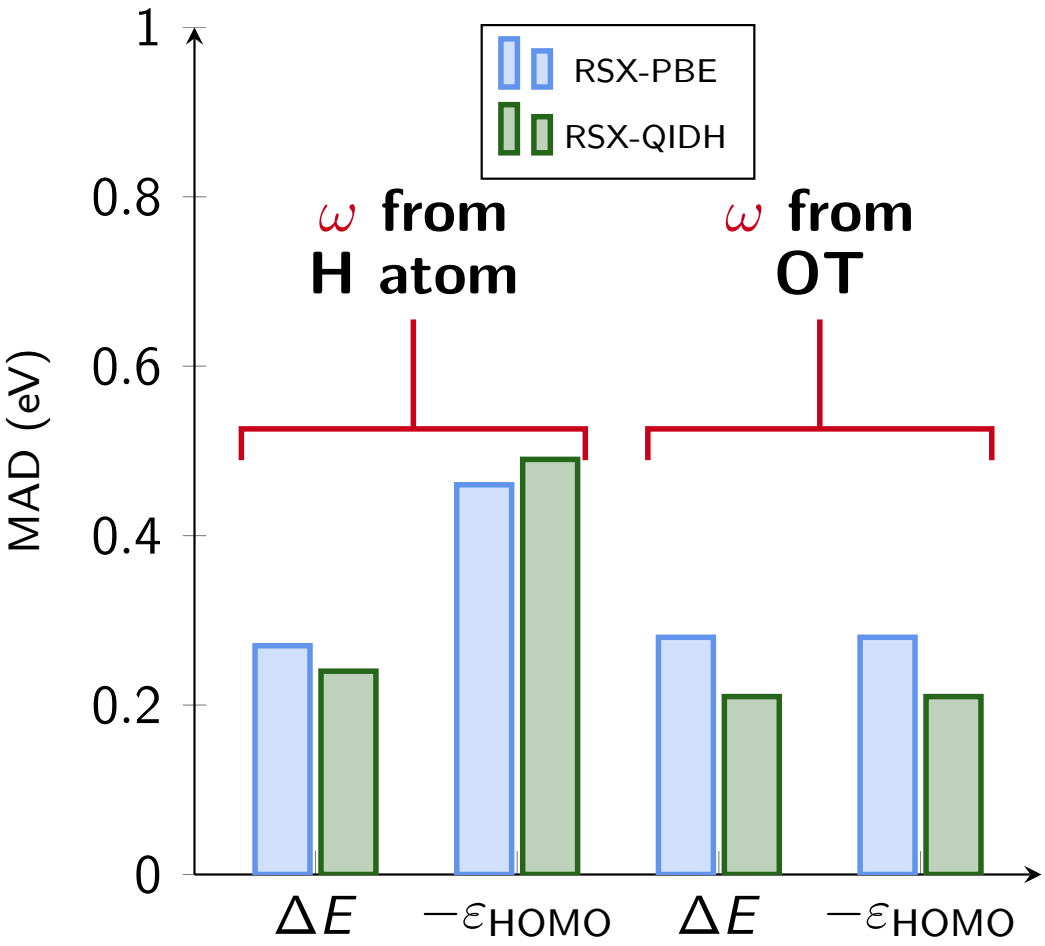
GW100: Optimal Tuning





Brémond *et al.* **J. Chem. Phys. submitted**.

GW100: Optimal Tuning



OT

better performance in average

however

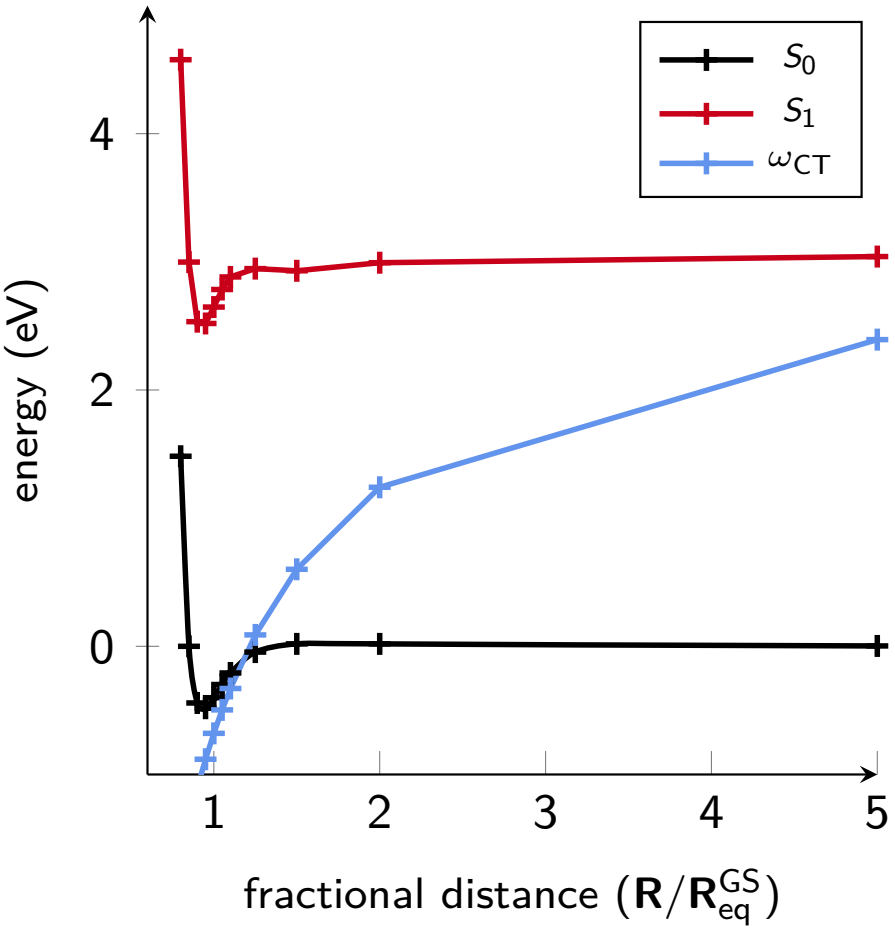
so

time-consuming. . .

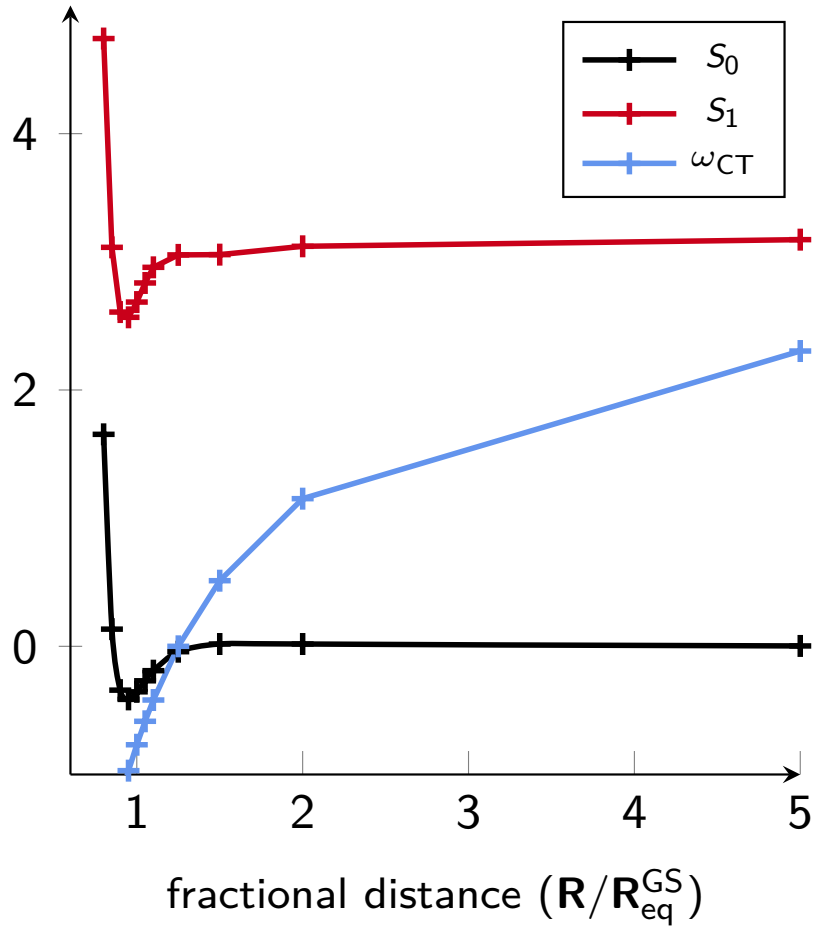
Brémond *et al.* **J. Chem. Phys.** **submitted**.

TOTA – Au_2 Interaction @TD-RSX-PBE level

RSX-PBE

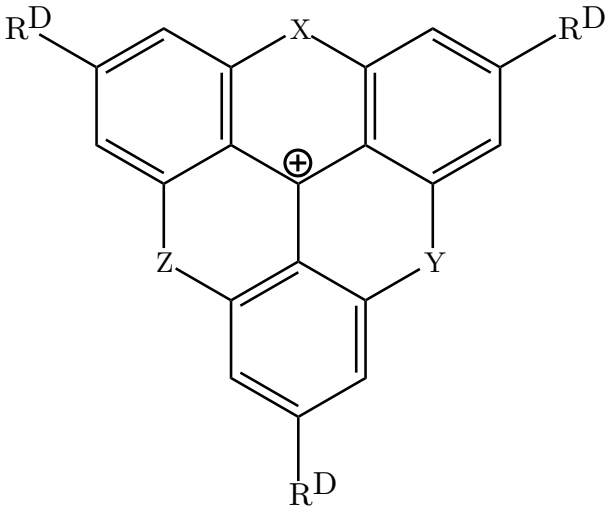


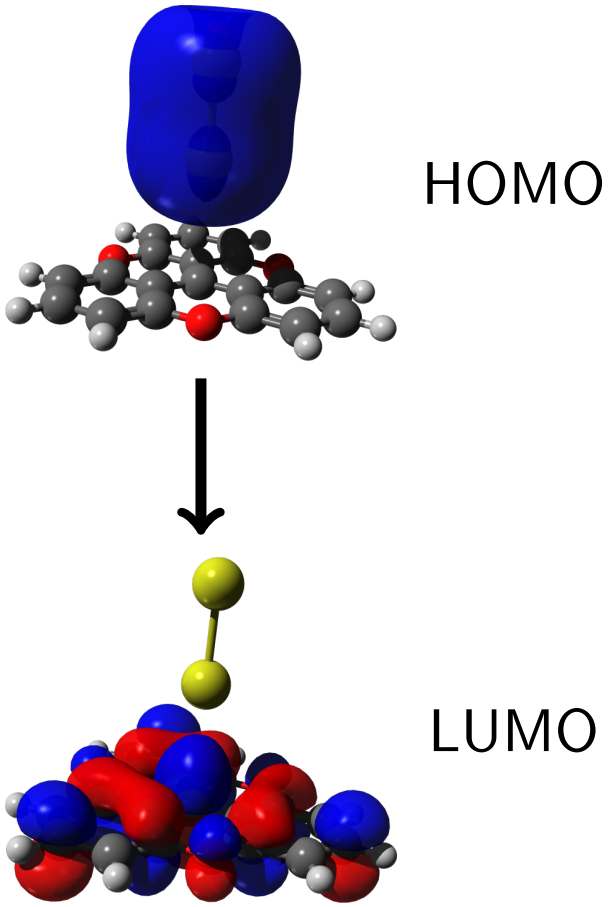
RSX-PBE0



Conclusions

identification of a full family of dyes

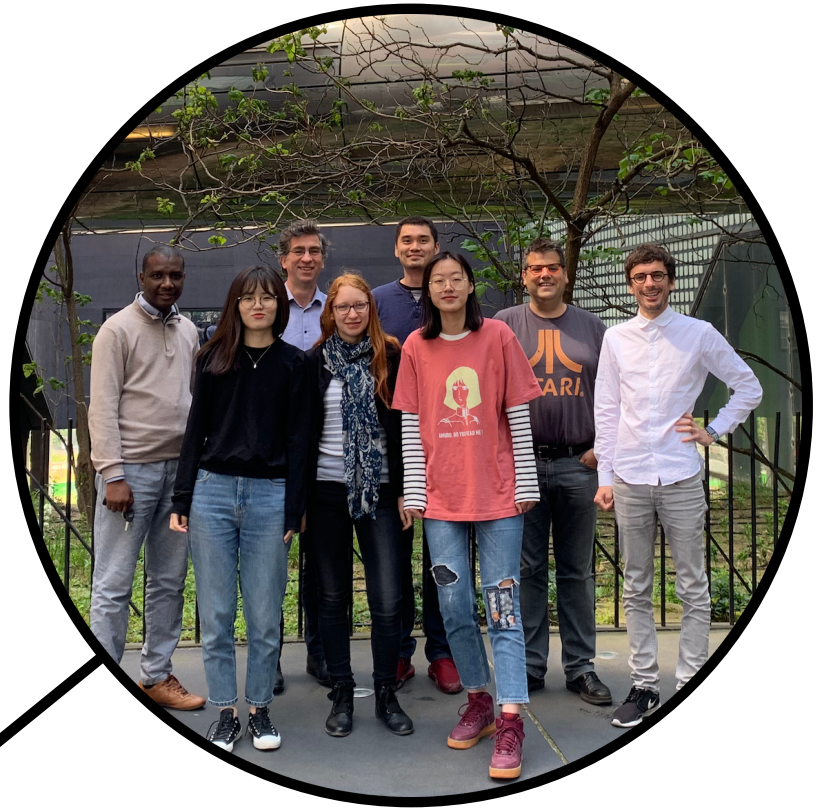


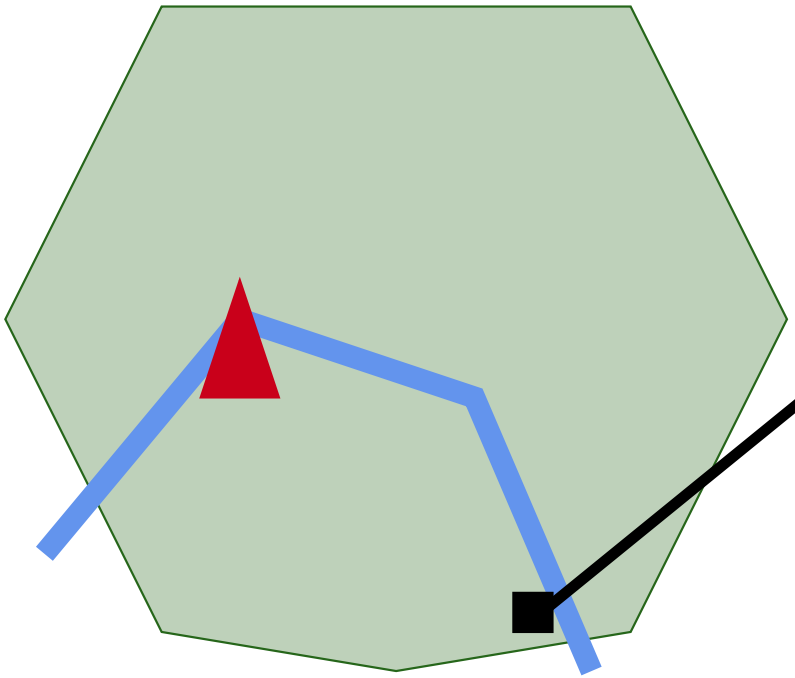


The Theoretical Chemistry & Modeling Team

Université de Paris

CTM @ ITODYS





Dr. Barbault **Mr. Nguyen**
Prof. Maurel **Dr. Seydou**

@ItodysC

Surface Enhanced UV/vis Spectroscopy

On the Road to the Modeling of Resonance UV/vis Spectroscopic Properties

Éric Brémond, Philippe Lainé, François Maurel

ITODYS UMR CNRS 7086, Université de Paris,
Paris, France

Lille, January 9, 2020