

POLARIZABLE CONTINUUM MODEL WITH TDDFT

Excited states with PCM: Linear response or state specific?

- The molecule in its ground state in equilibrium with the solvent is excited to the i th state in the presence of solvent polarization for ground state \rightarrow Excitation energy is ω_{0i}^0
- The dynamic component of the solvent polarization rearranges to equilibrate with the excited state charge density of the solute, changing the excitation energy.

Linear response is computed from the transition density P_{0i}^T

$$\omega_{0i}^{LR} = \omega_{0i}^0 + \langle i^0 | \hat{V} | 0 \rangle \langle 0 | \hat{Q} | i^0 \rangle$$

\hat{V} is the molecular electrostatic potential operator

State specific based on the difference in ground and excited state density P_{0i}^Δ

$$\omega_{0i}^{SS} = \omega_{0i}^0 + \frac{1}{2} [\langle i^0 | \hat{V} | i^0 \rangle - \langle 0 | \hat{V} | 0 \rangle] [\langle i^0 | \hat{Q} | i^0 \rangle - \langle 0 | \hat{Q} | 0 \rangle]$$

\hat{Q} is the dynamical apparent charge operator

Cammi, Corni, Mennucci, Tomasi
J. Chem. Phys. 2005, 122, 104513,
DOI: 10.1063/1.1867373

[Guido](#), [Jacquemin](#), [Adamo](#), and [Mennucci](#)
J. Chem. Theory Comput., 2015, 11, 5782
DOI: 10.1021/acs.jctc.5b00679

POLARIZABLE CONTINUUM MODEL WITH TDDFT

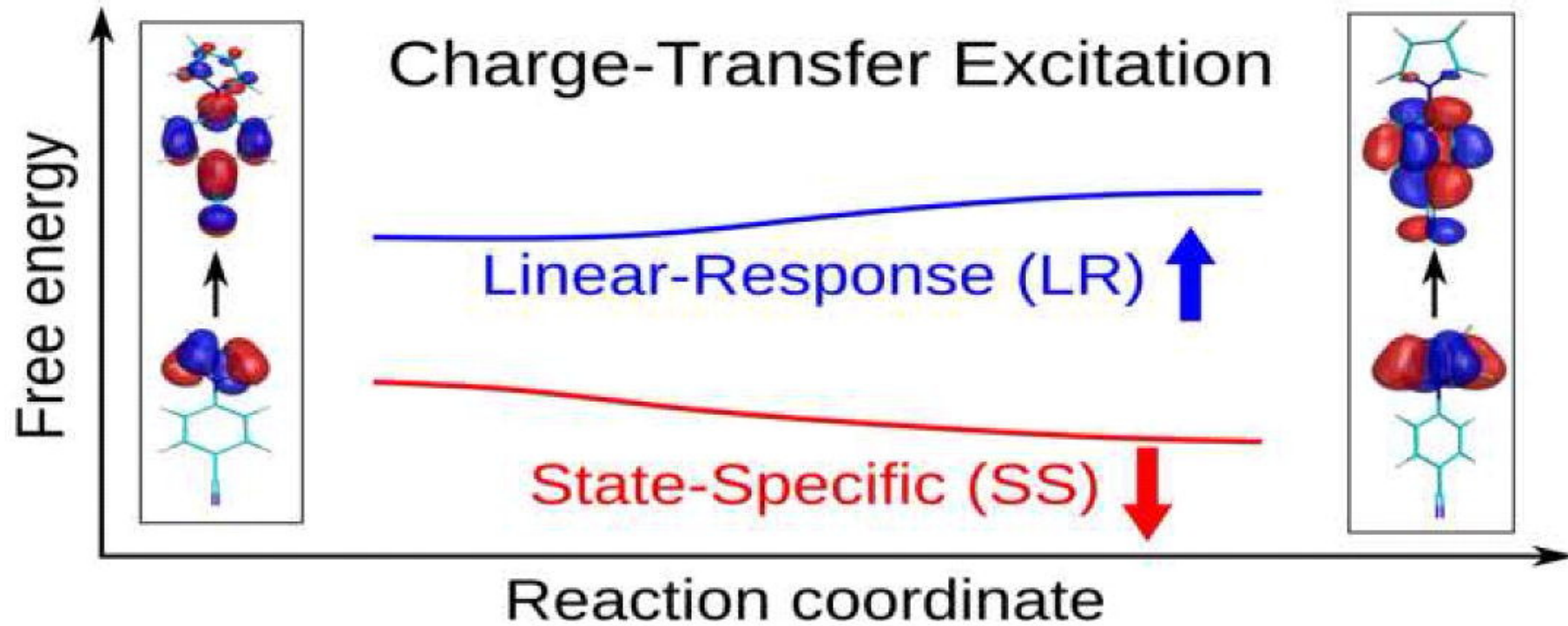
Linear response, based on the transition density P_{0i}^T

- Good for small changes in the density upon excitation
- Only non-equilibrium solvation is used

State specific, based on the difference in ground and excited state density P_{0i}^Δ

- Good if there are large changes in the electron density (ex. charge-transfer transitions)
- Equilibrium or non-equilibrium PCM is available, based on the time scale of interest.
 - Equilibrium state specific necessary for excited state geometry optimizations.

POLARIZABLE CONTINUUM MODEL WITH TDDFT

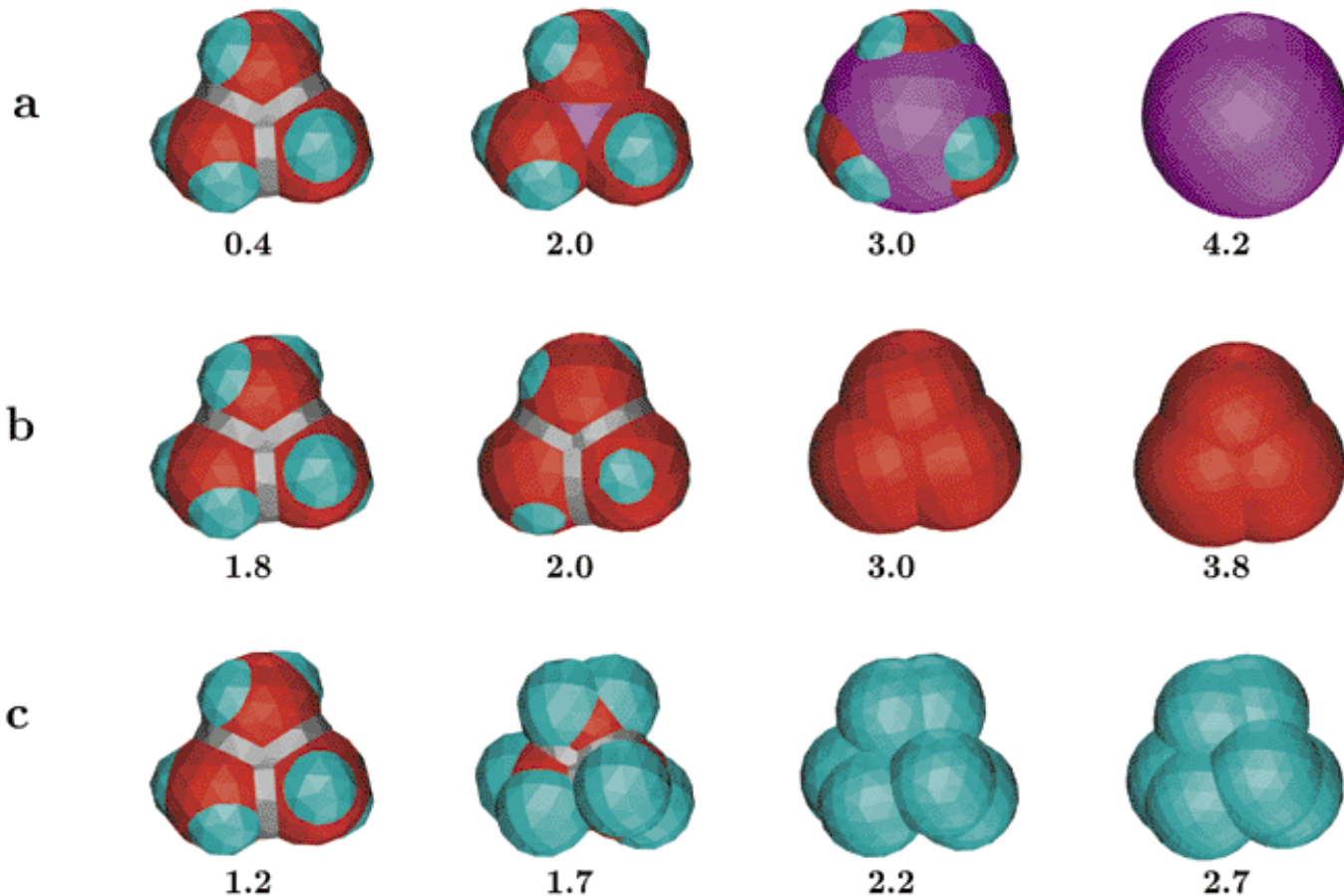


[Minezawa](#)

[Chemical Physics Letters](#) 608, 140, 2014

<https://doi.org/10.1016/j.cplett.2014.05.104>

Polarizable Continuum Model (PCM): which shape should be used for the cavity?



Influence of the atomic radii in the cavity shape for the Be^{2+} tetrahydrate.

(a) Radius of Be is changed from 0.4 to 4.2 Å.

(b) Radius of O is changed from 1.8 to 3.8 Å.

(c) Radius of H is changed from 1.2 to 2.7 Å.

(Surface contributions from Be are displayed in magenta, O in red, and H in blue, non atomic ones are in gray.)

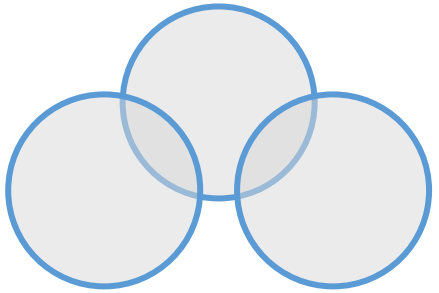
[Martínez](#), [Pappalardo](#), [Sánchez Marcos](#), [Mennucci](#), [Tomasi](#)

J. Phys. Chem. B, 2002, 106 (5), pp 1118–1123

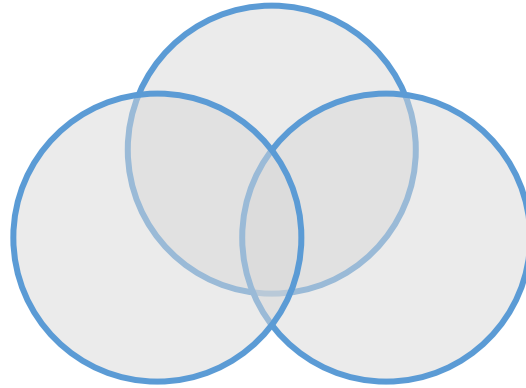
DOI: 10.1021/jp012404z

Polarizable Continuum Model (PCM) with TDDFT: Choice of Cavity

van der Waals
(VDW)

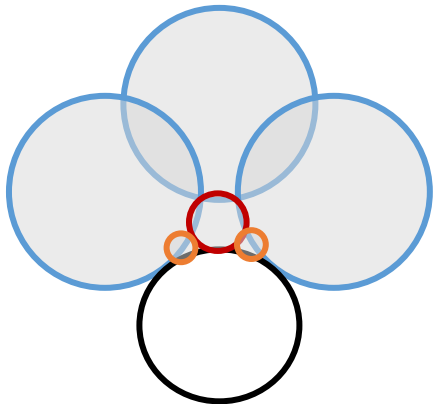


Scaled VDW

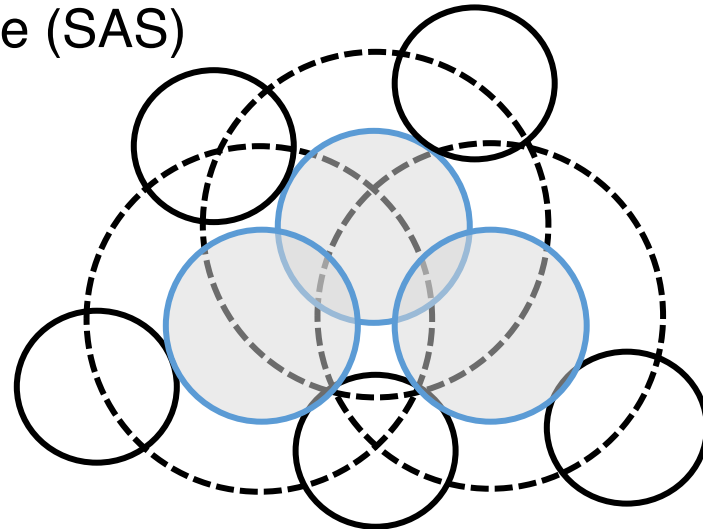


A set of radii (often parameterized to reproduce some solvation property) are often used to create the van der Waals surface (e.g. UFF or SMD radii)

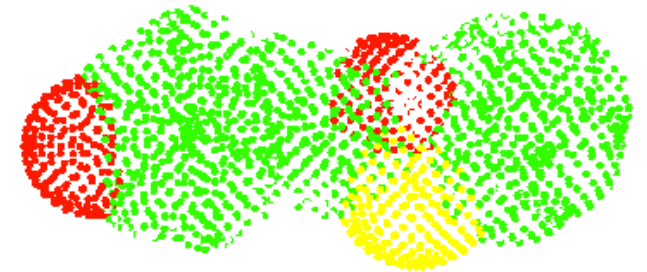
Solvent Excluded
Surface (SES)



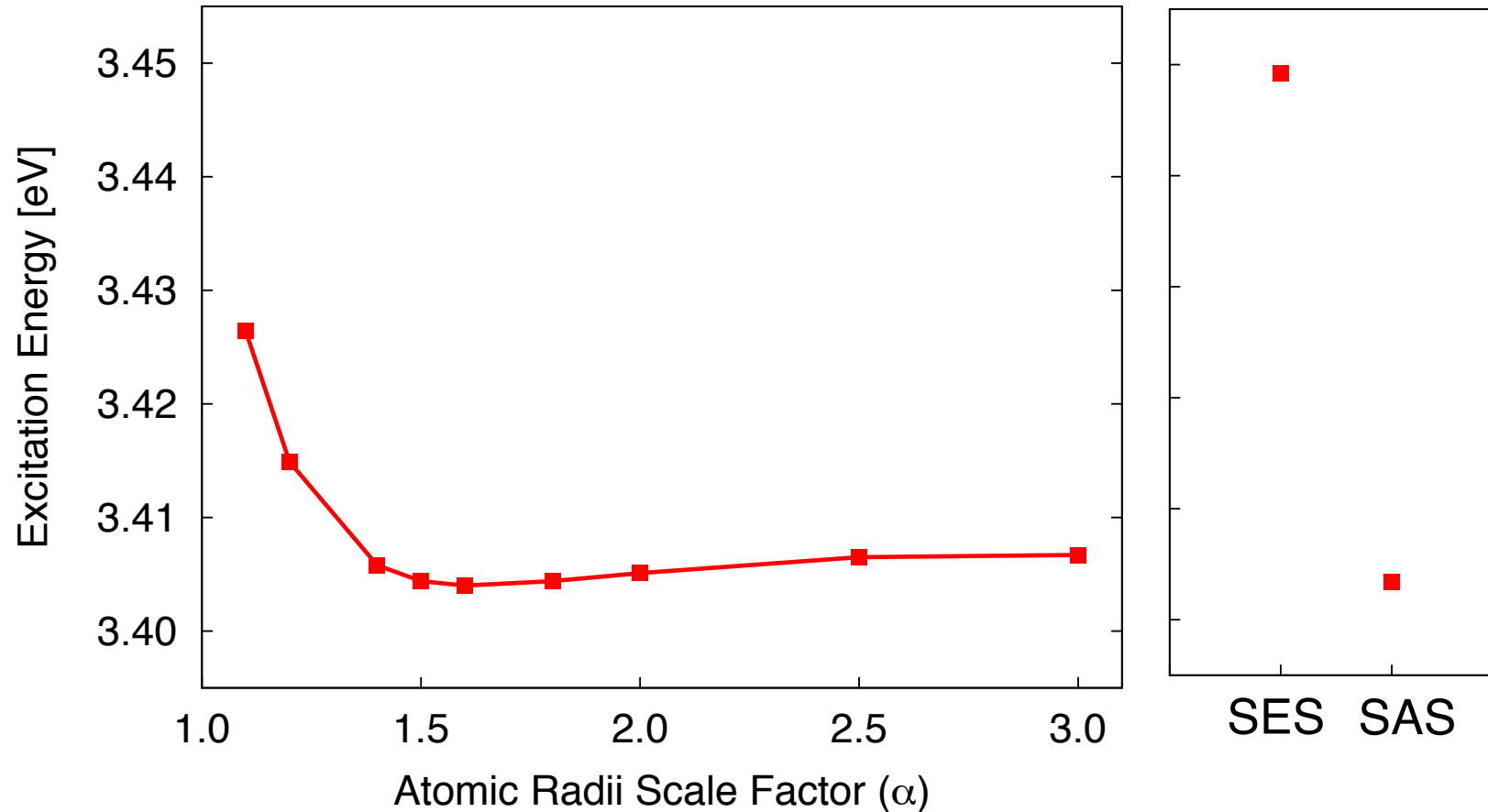
Solvent Accessible
Surface (SAS)



The cavity surface is then divided into small tiles (tesserae). The reaction field is determined by apparent point charges assigned to each surface tesserae, adjusted until self-consistency is reached with the QM region.



How Does the PCM Cavity Affect the TDDFT Excitation Energy?



Q: For a smaller cavity, should the excitation energy increase or decrease?

A: It depends on the excited and ground state dipole moment difference

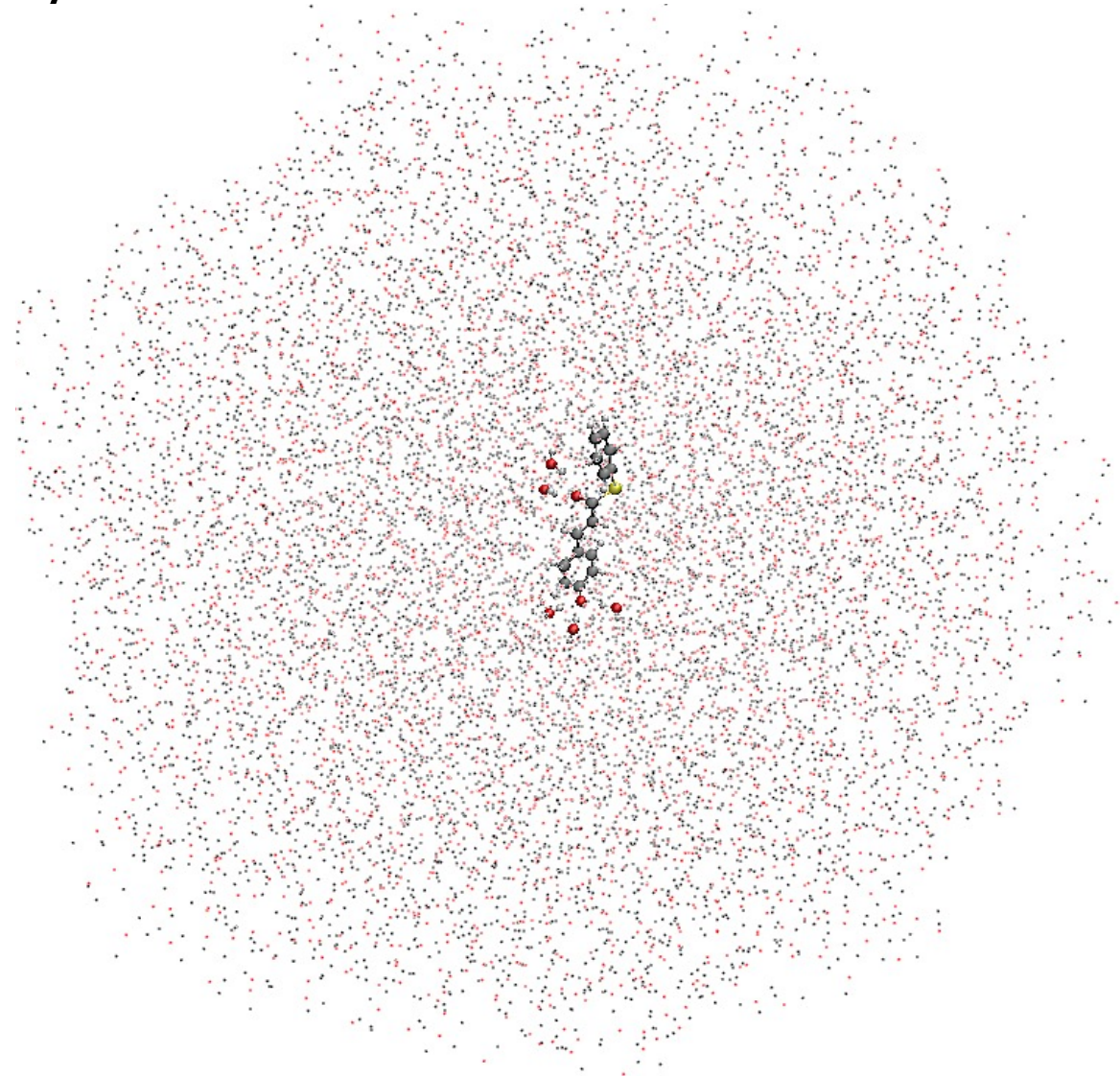
The choice of cavity can change the excitation energy by a nontrivial amount

MM solvent

Configurations often obtained from molecular dynamics

Computationally very affordable: fixed point charges included as one-electron terms in the QM Hamiltonian (similar to electron-nuclear attraction). Can easily add thousands of MM solvent molecules to a calculation.

The MM fixed charges do not explicitly appear in the TDDFT equations. They polarize the ground state density and will change the orbital energies.

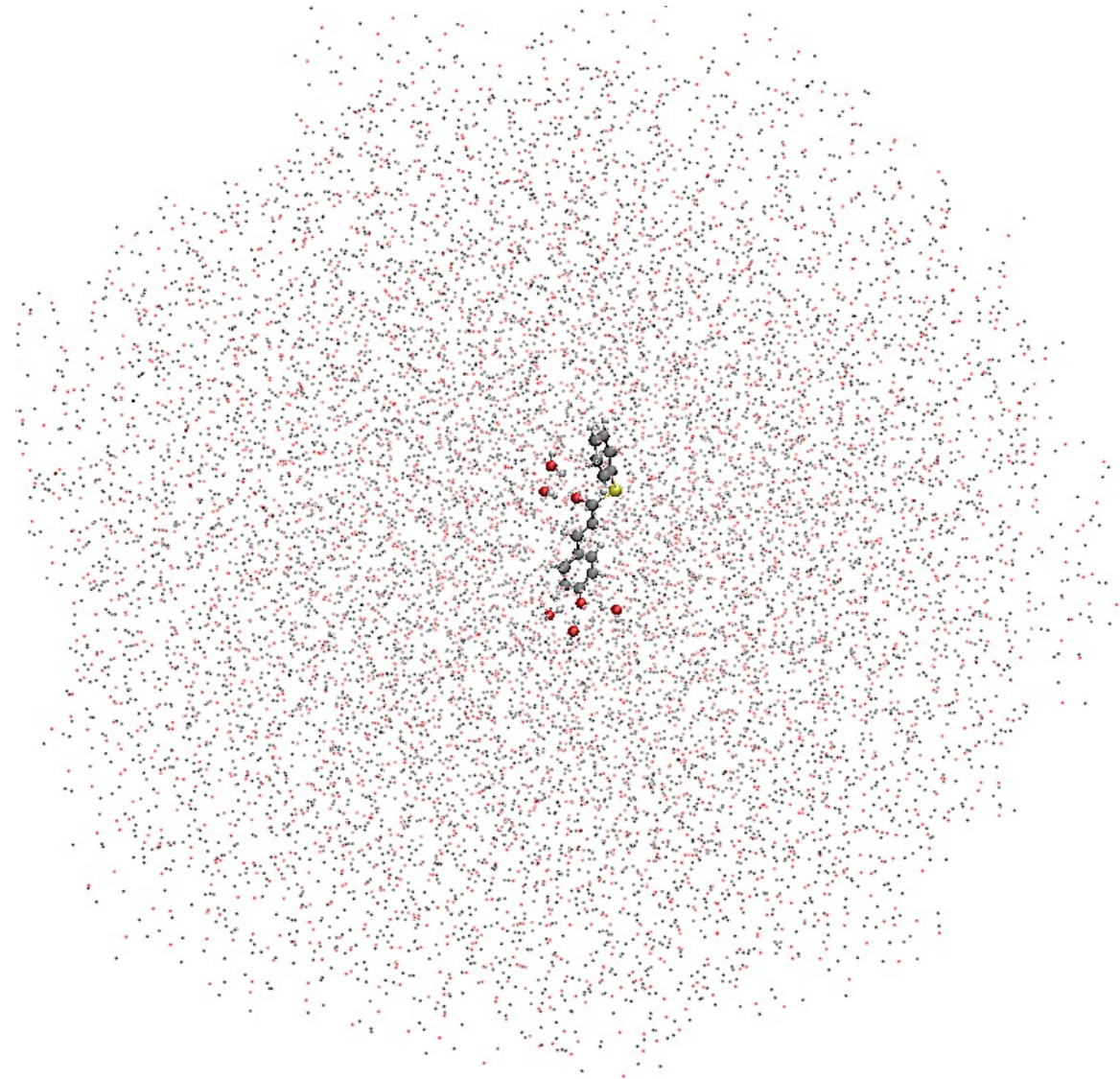


MM solvent

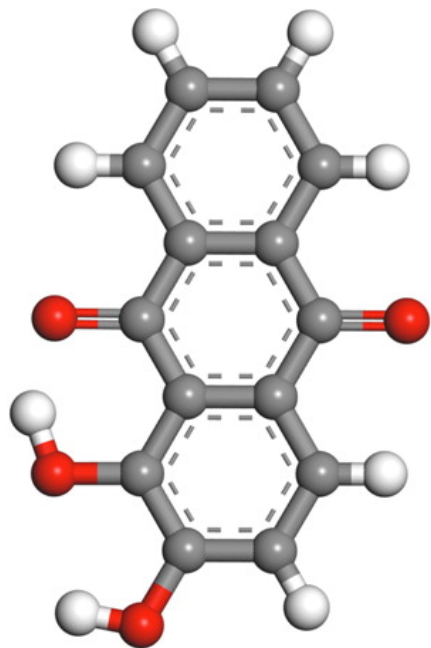
Be careful about:

- making sure you have a neutral MM environment (no solvent fragments)
- making sure you have enough MM solvent to converge the excitation energy

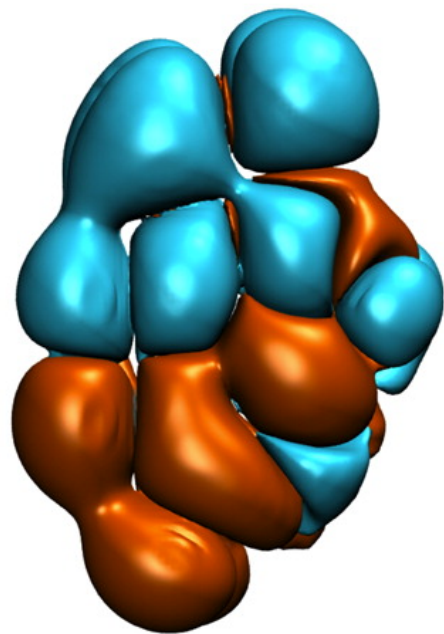
Also: polarizable MM solvent will have a term in the response equations



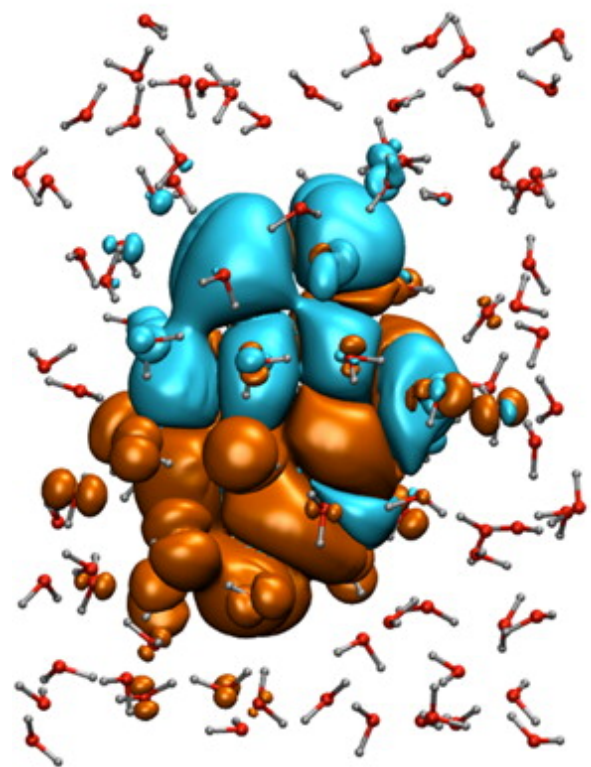
QM solvent: required for charge-transfer upon excitation...



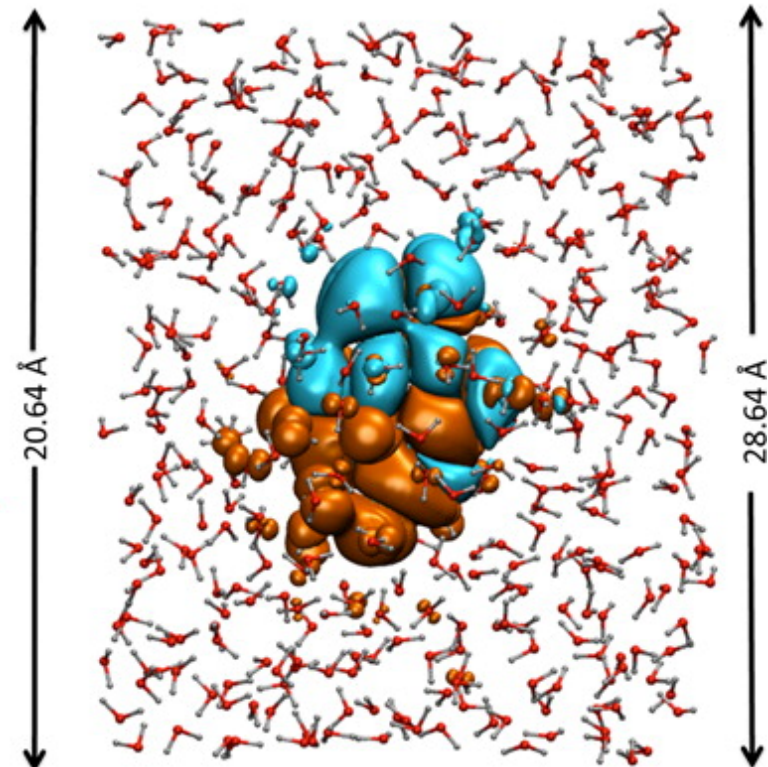
a) Alizarin structure



b) Implicit solvent

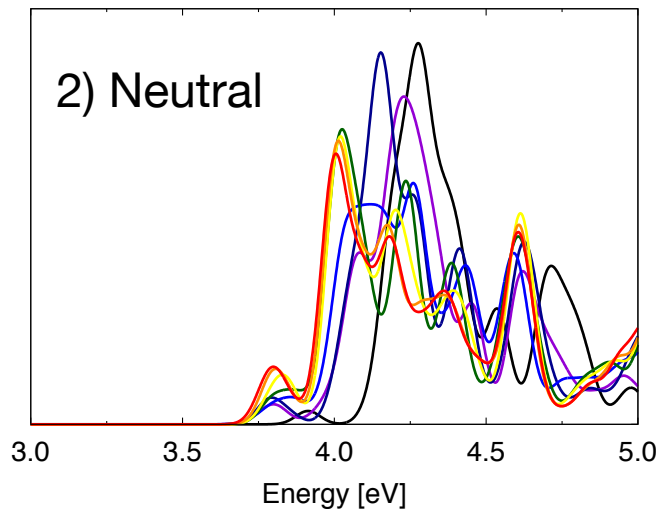
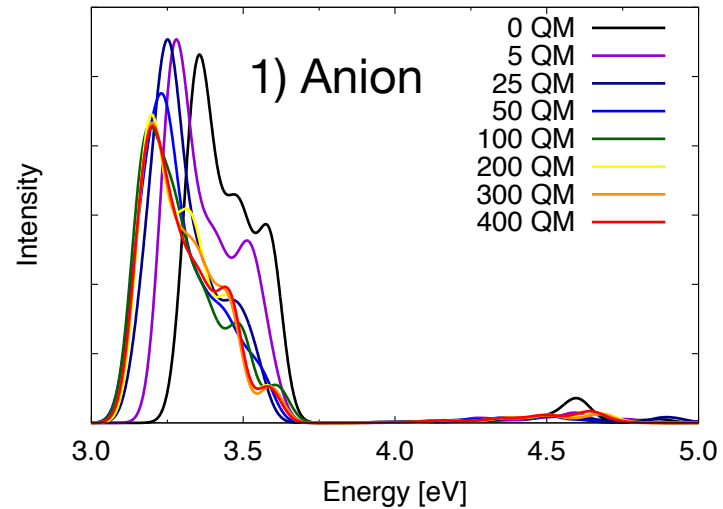
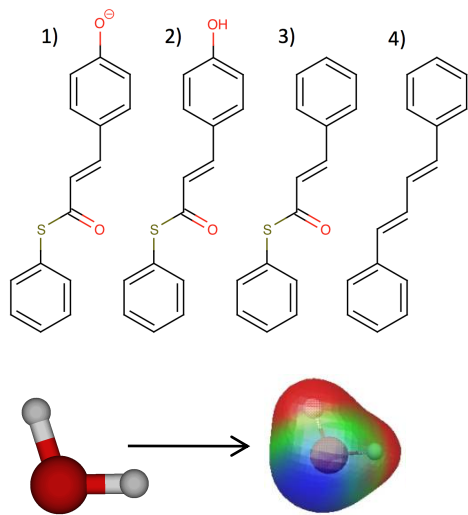


c) 6 Å water

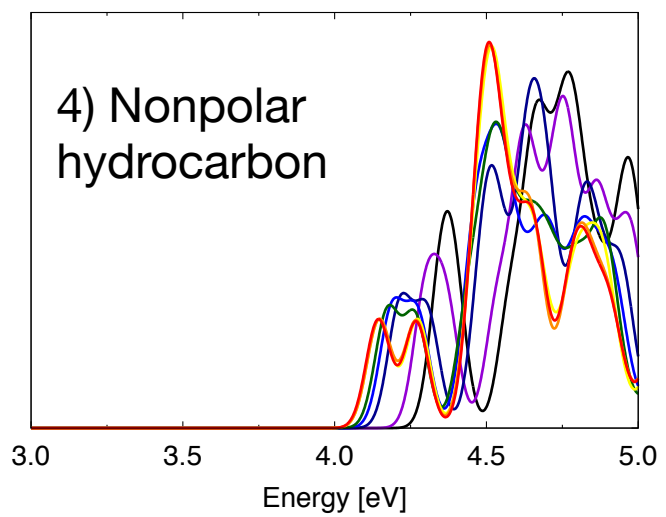
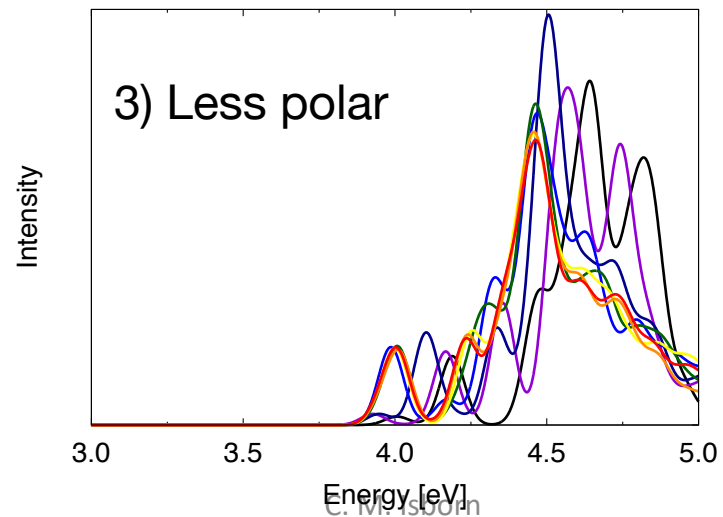


d) 10 Å water

QM solvent – how much to include for converged excitation energies?

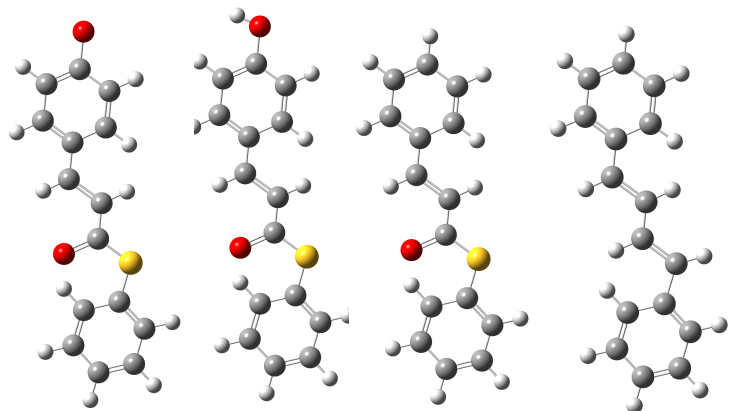


For all solutes, 100-200 QM solvent molecules are necessary to converge most spectral features

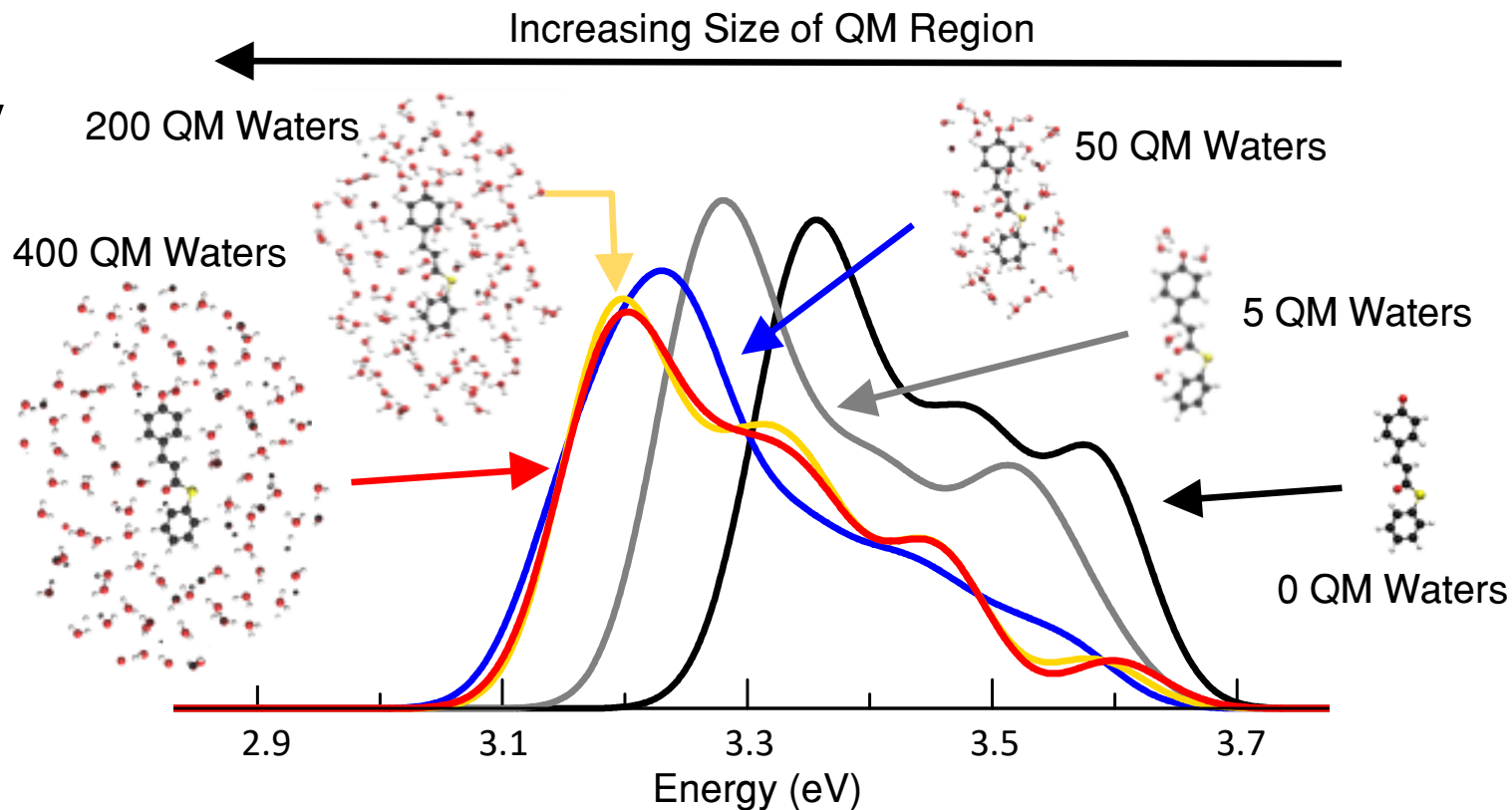


EFFECT OF QUANTUM MECHANICAL SOLVENT

Solutes of decreasing polarity

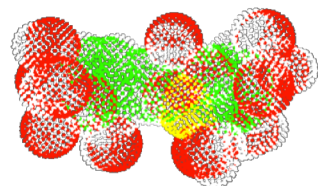
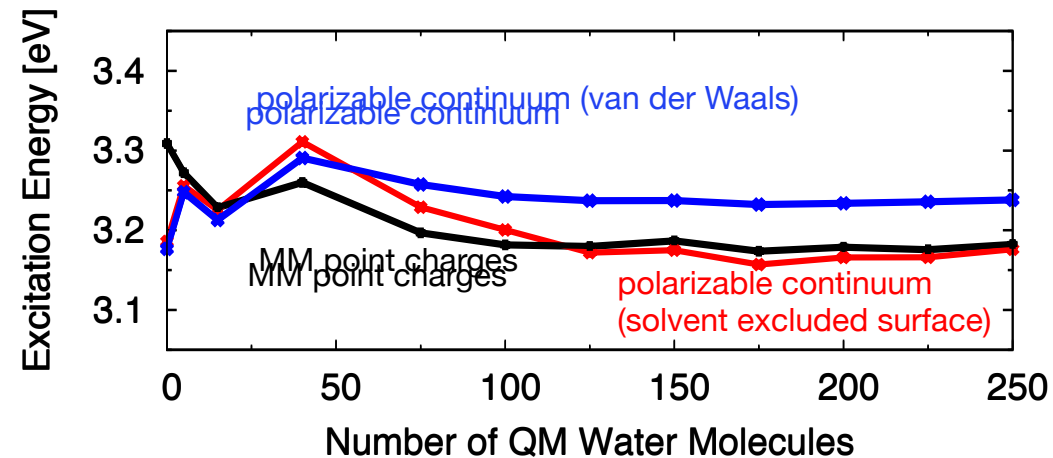
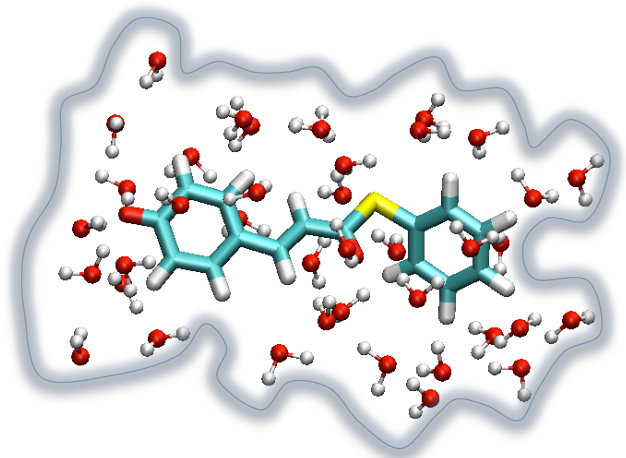


For all solutes, 100-200 QM solvent molecules are necessary to converge most spectral features

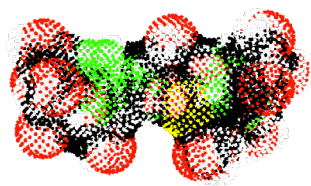
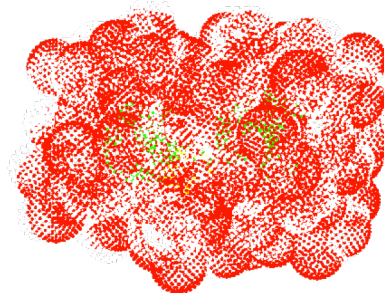


Milanese, Provorse, Alameda, Isborn
J. Chem. Theory Comput. 2017, 13, 2159–2171

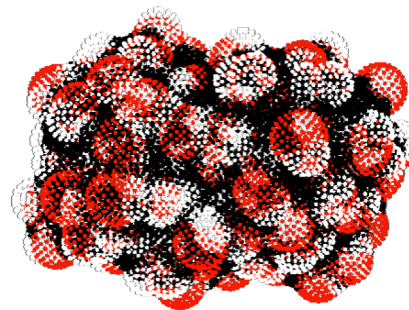
Combine QM solvent with PCM – now which cavity?



van der Waals cavity



Solvent excluded surface cavity



SUMMARY

A variety of solvation models can be combined with TDDFT calculations. Each with positives and negatives.

Continuum solvent: No sampling of solute-solvent specific interactions

Molecular mechanical solvent: very fast, some specific interactions, but no polarization

QM solvent: polarization and charge transfer, but computationally expensive

