Wave function embedding methods and excited states:

A guide to the perplexed

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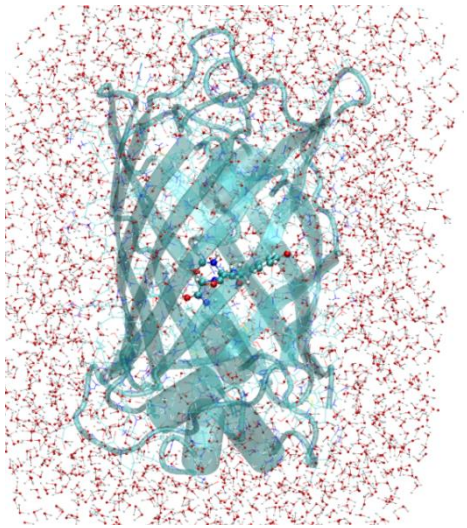
Vallico del Sotto, Tuscany, Italy, 27 July 2014

Excitations in complex environments

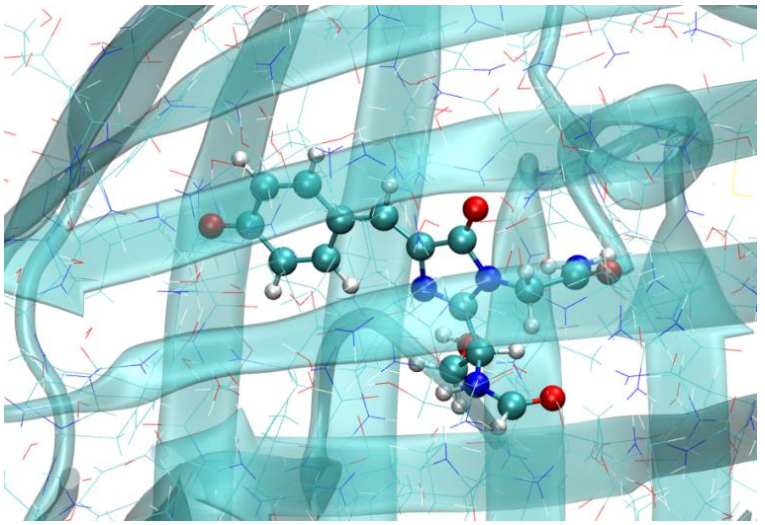
Goal: Describe excited states of photoactive biosystems as GFP, rhodopsin...

Full system



5000 atoms

Chromophore



50-100 atoms

Some choices are needed

- Quantum method to describe the photo-excited chromophore
- Embedding approach to describe the environment

Dramatis personæ

A zoo of methods for excited states

- Wavefunction-based approaches:

  CASSCF, CASPT2, CC2, CCSD, SAC-CI etc.

- What about QMC?

  It typically loses in speed to CC/PT2 for small systems

  but recovers for big systems, owing to favourable scaling (N^4 versus $>N^5$)

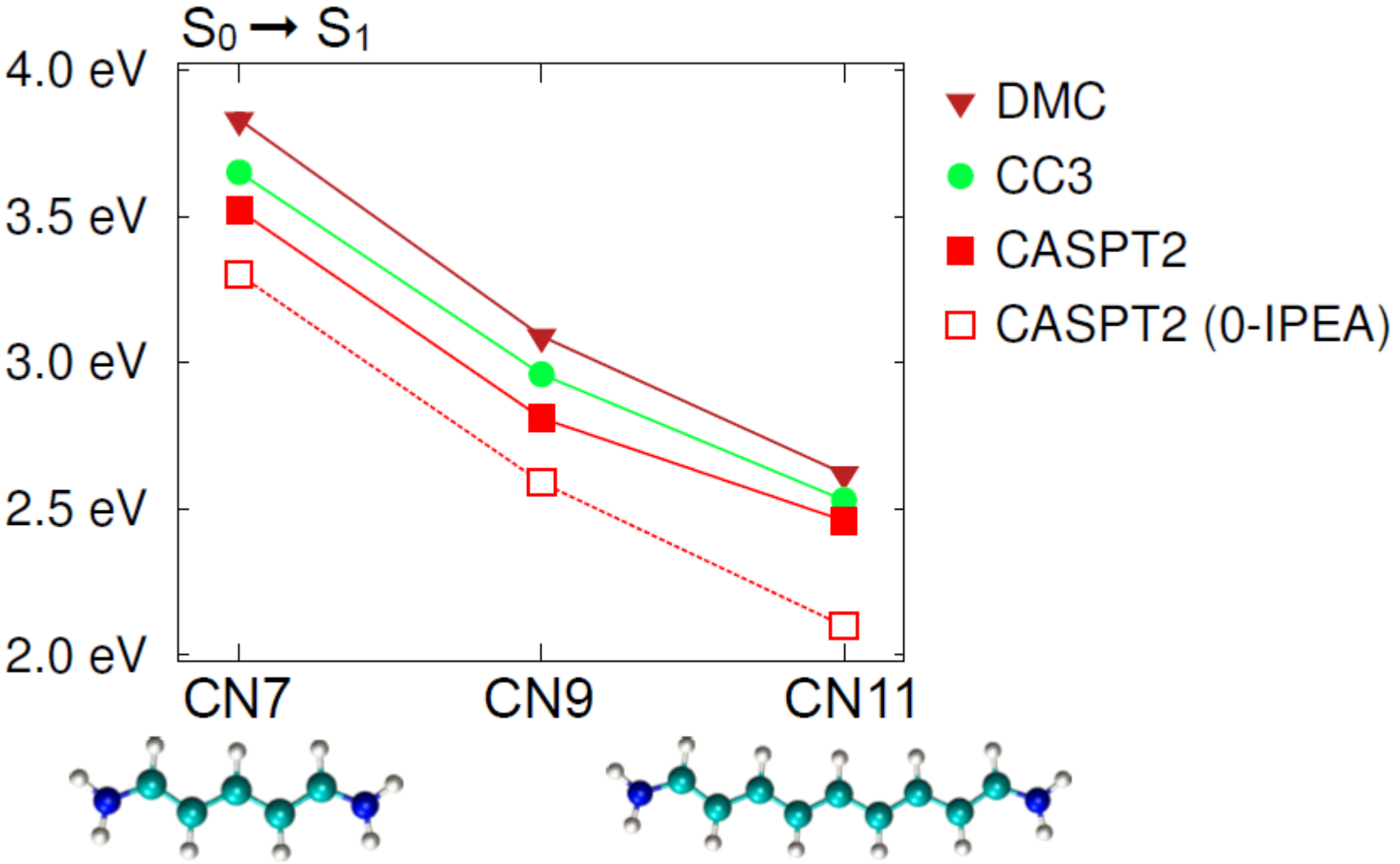
- TDDFT

  Popular due to low cost but can we really rely on it?

  Problems with charge transfer, multireference transitions

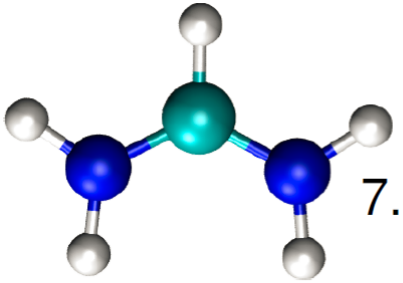
Prelude: Which WF method?

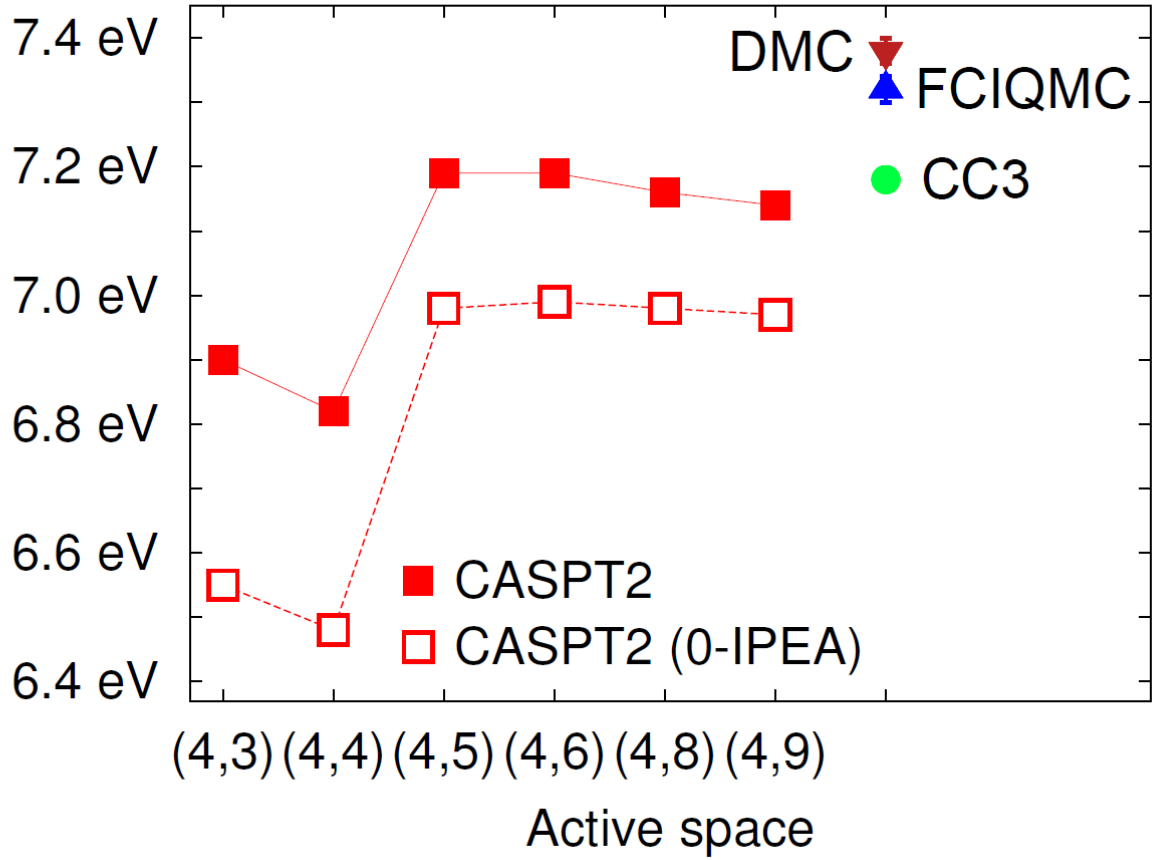
Typical example: Cyanine dyes



Send, Valsson, Filippi, JCTC 2011

Prelude: Which WF methods?

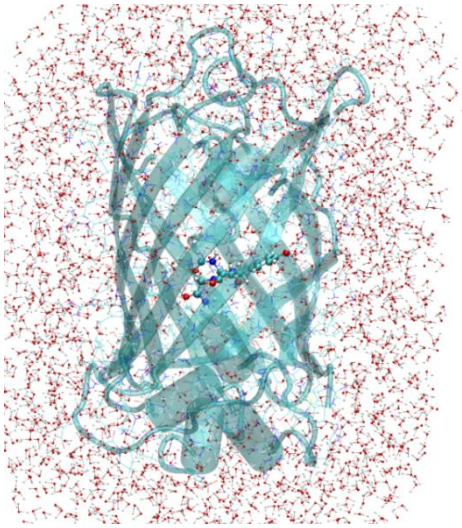


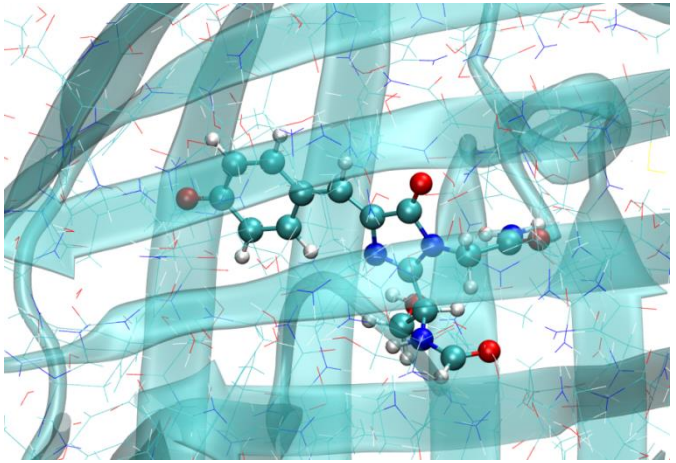


… perturbative approaches are dominant in photo-chemistry!

Send, Valsson, Filippi, JCTC 2011; Daday, Filippi, Alavi

Beyond the gas phase: Is QM/MM good enough?





Commonly used recipe for excited-state calculations

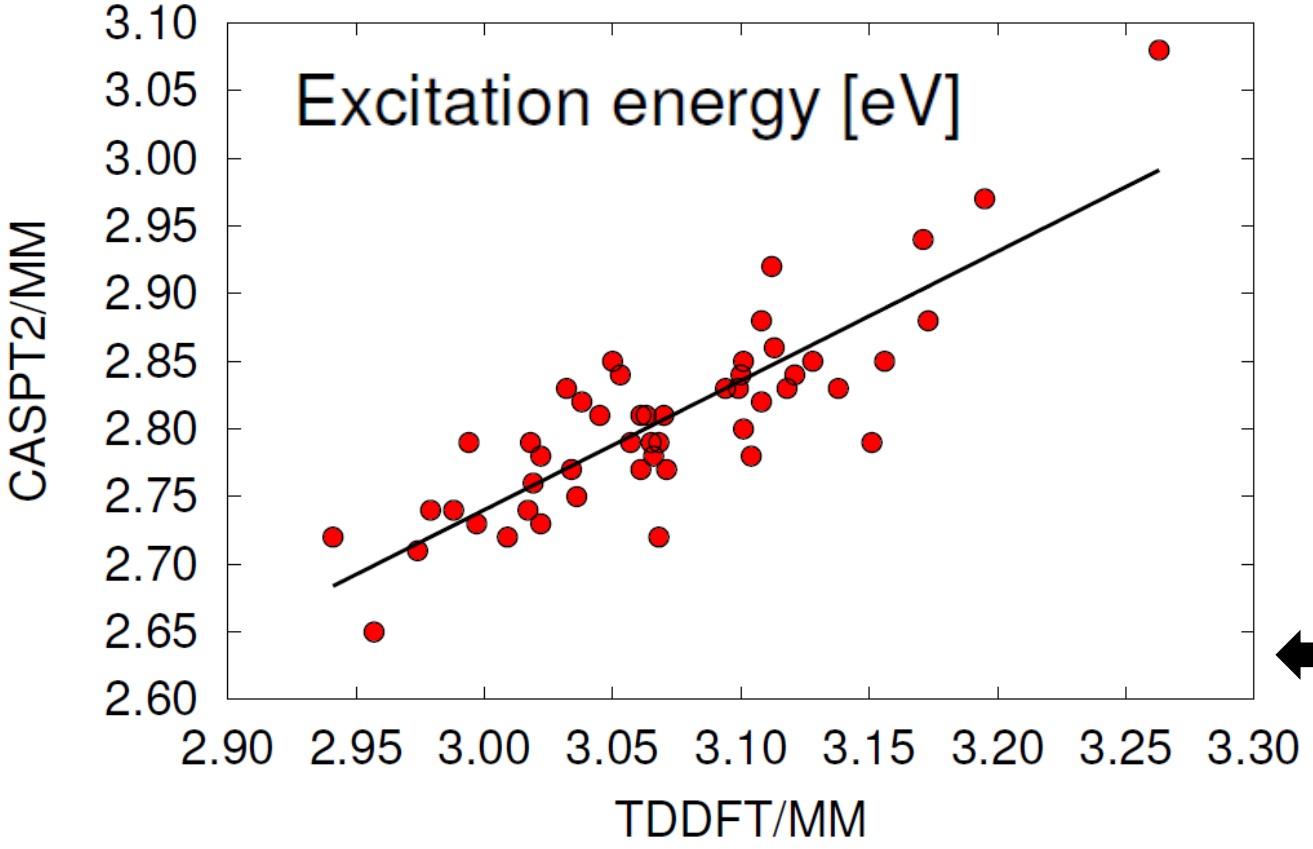
- Quantum chromophore in static classical point charges (QM/MM)
- Failures: 0.3-0.5 eV error for GFP, rhodopsin absorption (CAS/NEVPT2, QMC)

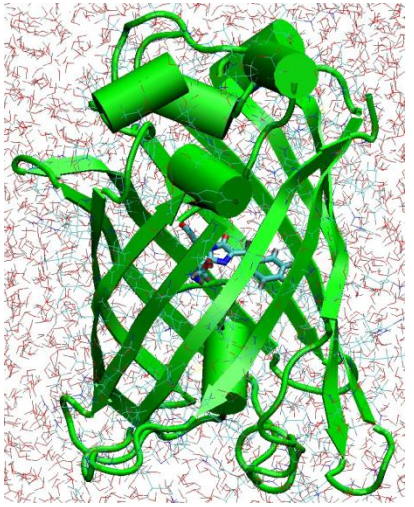
Filippi et al. JCTC 2012; Amat et al. JCTC 2013; Valsson et al. JCTC, 2013

GFP: How are we doing?

Our model: Extensive QM/MM PBE/Amber99 MD (about 20 ps)

Cluster analysis on trajectory ➡ representative snapshots





⬅ Expt.: 2.63 eV

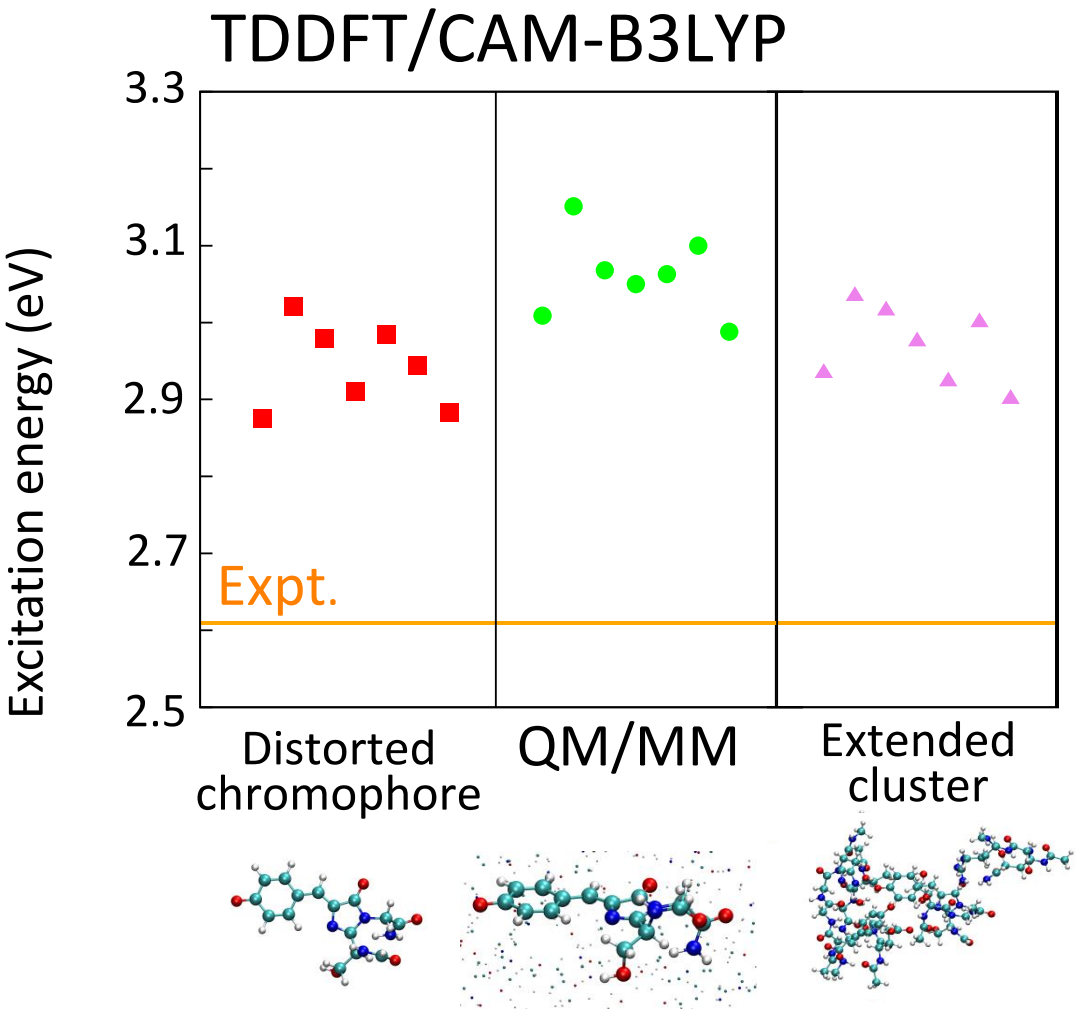
Good correlation between TDDFT/CAM-B3LYP/MM and CASPT2/MM

GFP: How are we doing?

TDDFT blue-shifted but applicable up to **300 atoms**

QM/MM ➡ cluster: Red-shift of about 0.1 eV

Correlated methods?



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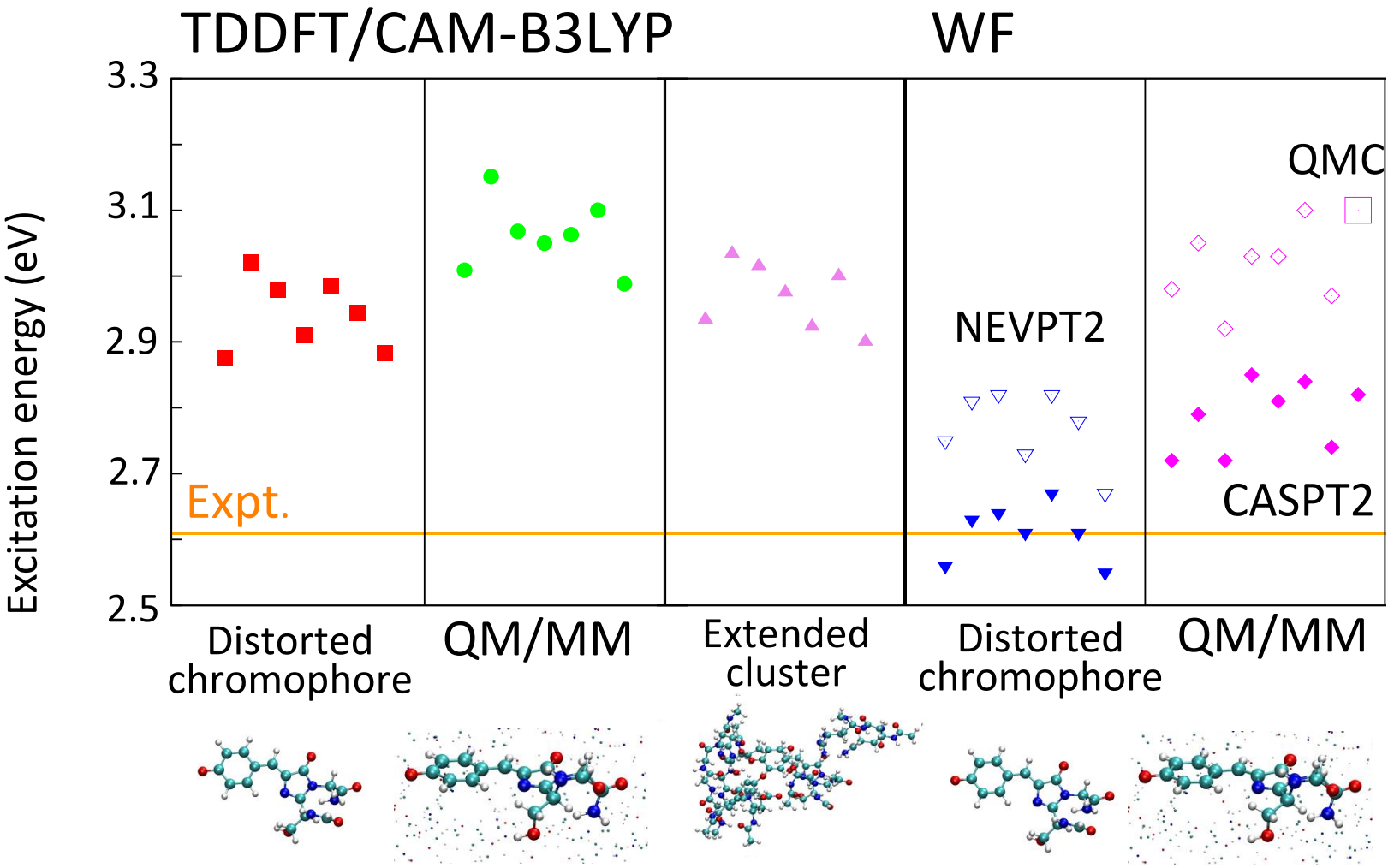
Correlated methods? Qualitatively similar but stronger response



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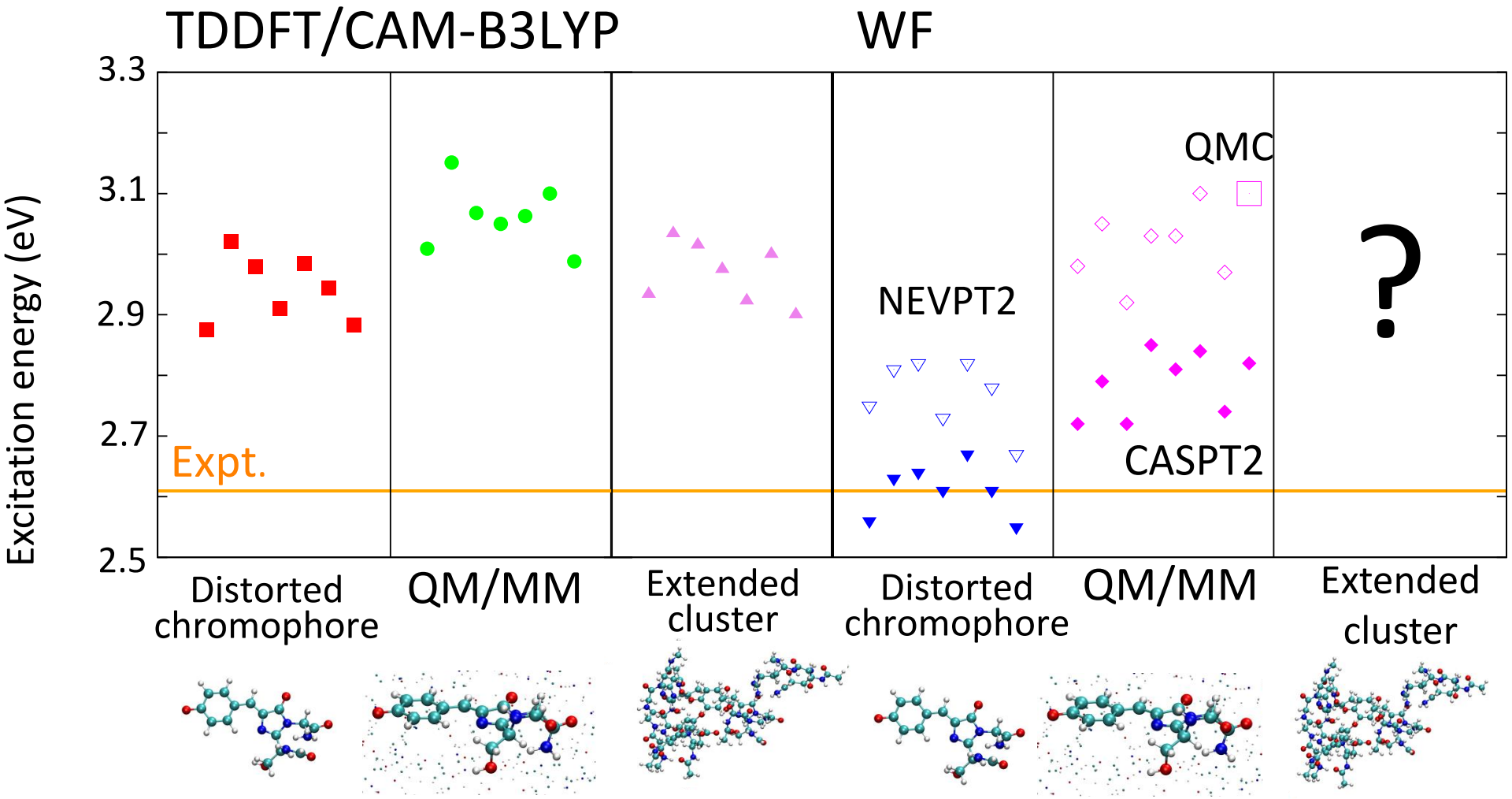


Beyond QM/MM

How to improve static MM environment?

- Description of the ground state

  Reparametrization, polarizable dipoles, or DFT embedding
- Improving excited-state description

  Allow a responsive environment (relaxing dipoles/density)

Pitfalls in classical route:

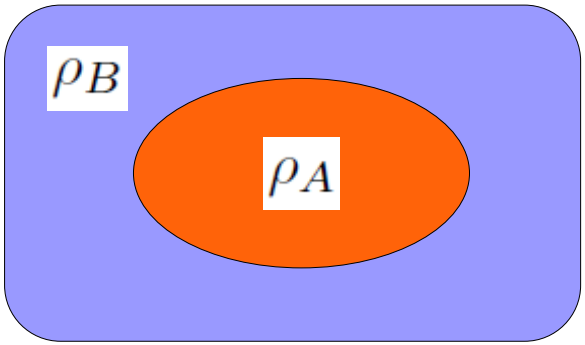
- Reparametrization: costly and not well-defined
- No Pauli repulsion

What about DFT embedding?

Subsystem DFT (quick reminder)

Partition system in two parts:

$$\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r});$$
$$N = N_A + N_B$$



The energy of the total system is written as

$$E_{(A+B)}[\rho_A + \rho_B] = E_A[\rho_A] + E_B[\rho_B] + \underbrace{\left(E_{(A+B)}[\rho_A + \rho_B] - E_A[\rho_A] - E_B[\rho_B]\right)}_{E_{\mathrm{int}}[\rho_A,\rho_B]}$$

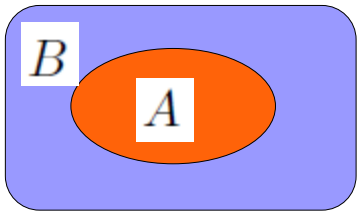
where $E_i[\rho_i] = T_{\mathrm{s}}[\rho_i] + J[\rho_i] + V_{\mathrm{nuc}i}[\rho_i] + E_{\mathrm{xc}}[\rho_i] \qquad i = A, B, A+B$

$$E_{\mathrm{int}}[\rho_A, \rho_B] = J[\rho_A, \rho_B] + V_{\mathrm{nucA}}[\rho_B] + V_{\mathrm{nucB}}[\rho_A] + T_{\mathrm{s}}^{\mathrm{nadd}}[\rho_A, \rho_B] + E_{\mathrm{xc}}^{\mathrm{nadd}}[\rho_A, \rho_B]$$

T. A. Wesolowski, A. Warshel *JPC,* **1993**, 97, 8050-8053.

Convergence: Freeze-and-thaw cycles

Freeze B



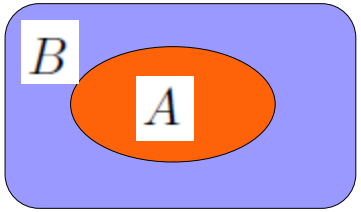
and minimize with respect to ρ_A

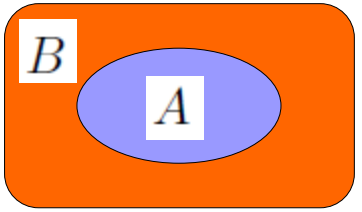
$$(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}[\rho_A](\mathbf{r}) + v^{\mathrm{emb}}[\rho_A,\rho_B](\mathbf{r}))\varphi_i^A(\mathbf{r}) = \varepsilon_i\varphi_i^A(\mathbf{r})$$

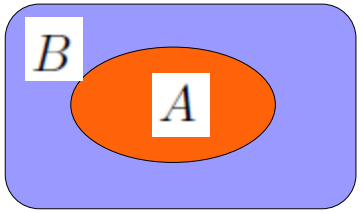
$$v_{\mathrm{KS}}[\rho_A](\mathbf{r}) = v_{\mathrm{nucA}}(\mathbf{r}) + \int \frac{\rho_A(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\mathrm{xc}}[\rho_A](\mathbf{r})$$

$$v_{\mathrm{emb}}[\rho_A,\rho_B](\mathbf{r}) = v_{\mathrm{nucB}}(\mathbf{r}) + \int \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\mathrm{xc}}^{\mathrm{nadd}}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})} + \frac{\delta T_{\mathrm{s}}^{\mathrm{nadd}}[\rho_A,\rho_B]}{\delta\rho_A(\mathbf{r})}$$

Alternate:







Treating the active part at WF level

Treat the active system with a wavefunction method (WF/DFT) and substitute

$$\boxed{E_A^{\mathrm{DFT}}[\rho_A] \rightarrow E_A^{\mathrm{WF}}[\Psi_A]}$$

$$E_A^{\mathrm{WF}}[\Psi_A] = \langle \Psi_A | \sum_i (-\frac{1}{2}\nabla_i^2 + v_{\mathrm{nucA}}(\mathbf{r}_i)) + \sum_{i<j} \frac{1}{r_{ij}} | \Psi_A \rangle$$

so that

$$E_{(\mathrm{A+B})}[\Psi_A, \rho_B] = \boxed{E_A^{\mathrm{WF}}[\Psi_A]} + E_B^{\mathrm{DFT}}[\rho_B] + E_{\mathrm{int}}[\rho_A^{\mathrm{WF}}, \rho_B]$$

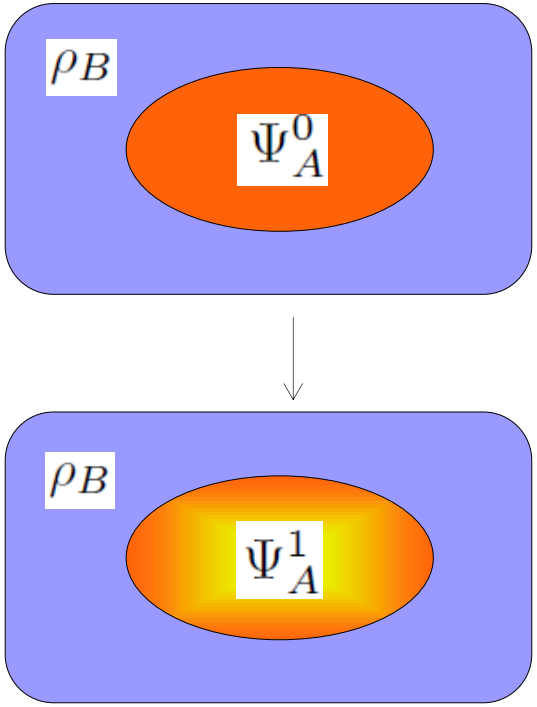
where E_{int} is as before

N. Govind, Y. A. Wang, A. J. R. Da Silva, E. Carter *J. Chem. Phys.* **1998**, 295, 129-134
T. A. Wesolowski *Phys. Rev. A*, **2008,** 77, 012504

Excited states in WF/DFT: Polarization

Minimization with respect to $\Psi_A \longrightarrow H^{\mathrm{emb}}\Psi_A = E_A^{\mathrm{emb}}\Psi_A$

$$H^{\mathrm{emb}} = \sum_i \left(-\frac{1}{2}\nabla_i^2 + v_{\mathrm{nucA}}(\mathbf{r}_i) + v_{\mathrm{emb}}(\mathbf{r}_i)\right) + \sum_{i<j}\frac{1}{r_{ij}}$$



Ground state Ψ_A^0 **and** excited states $\Psi_A^1, \Psi_A^2, \ldots$

$$E_{\mathrm{exc}} \approx \langle \Psi_A^1 | H^{\mathrm{emb}} | \Psi_A^1 \rangle - \langle \Psi_A^0 | H^{\mathrm{emb}} | \Psi_A^0 \rangle$$

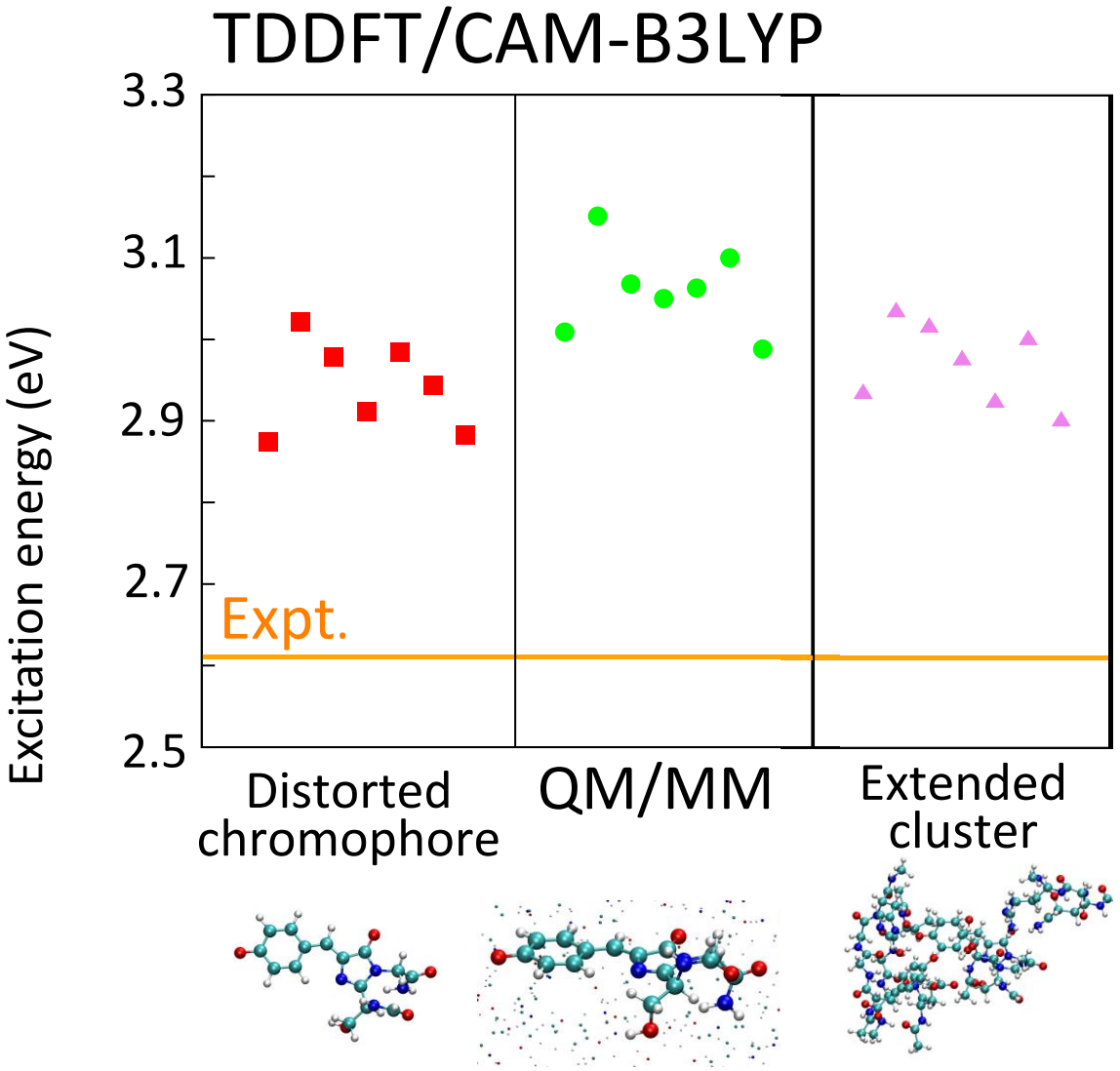
D.K. Kanan, S. Sharifzadeh, E. A. Carter, *Chem. Phys. Lett.* **2012**, 519-520, 18-24

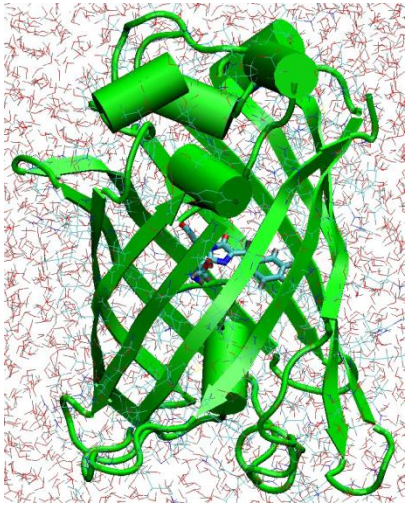
A. S. P. Gomes, C. R. Jacob, L. Visscher *Phys. Chem. Chem. Phys.* **2008**, 10, 5353-5362

GFP: How are we doing?

TDDFT/DFT embedding: 4-5 hours instead of 7 days!

But does it work?

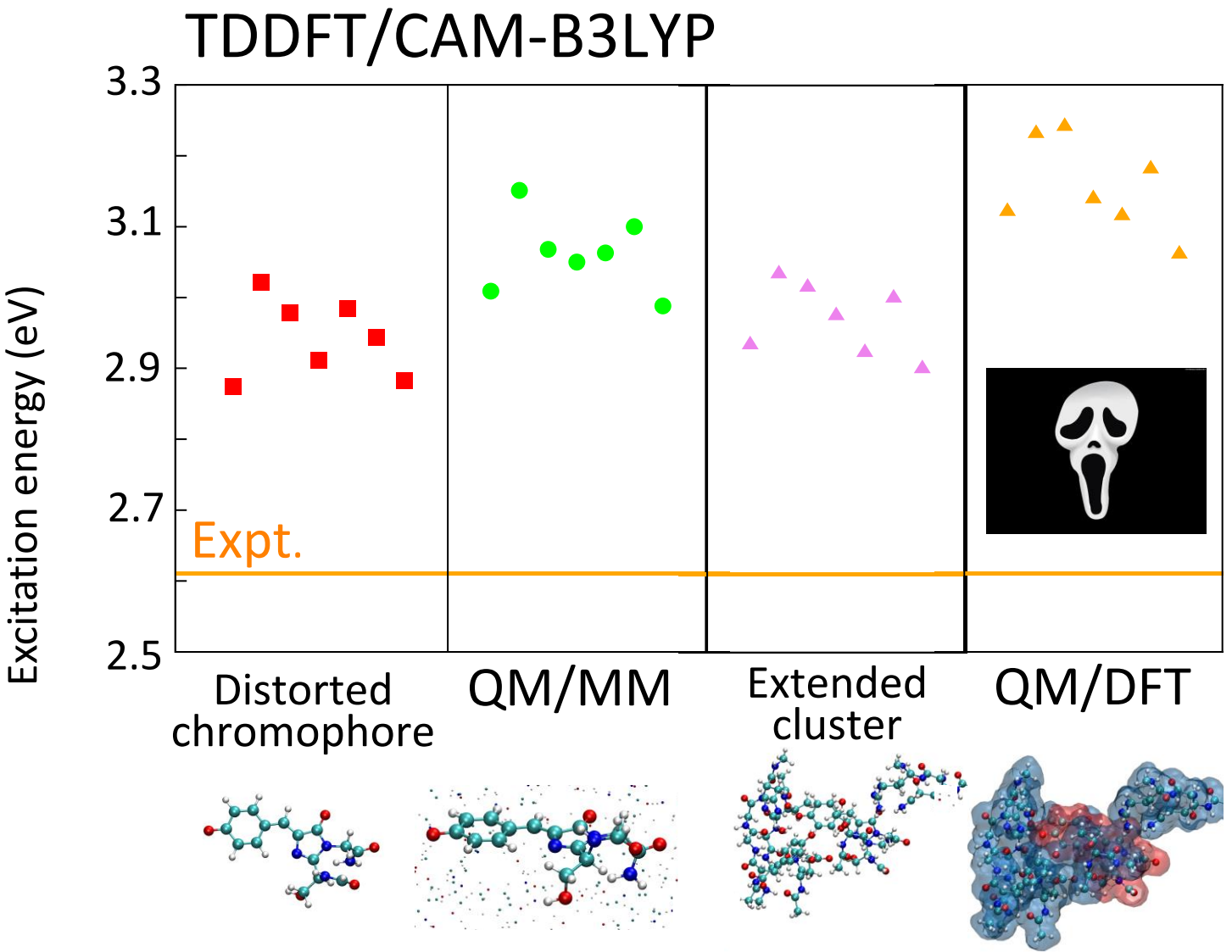


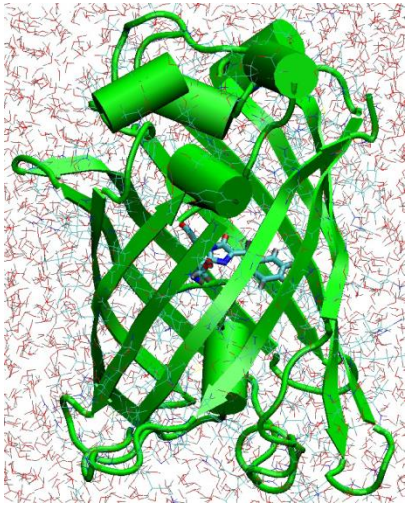


GFP: How are we doing?

TDDFT/DFT embedding: 4-5 hours instead of 7 days !

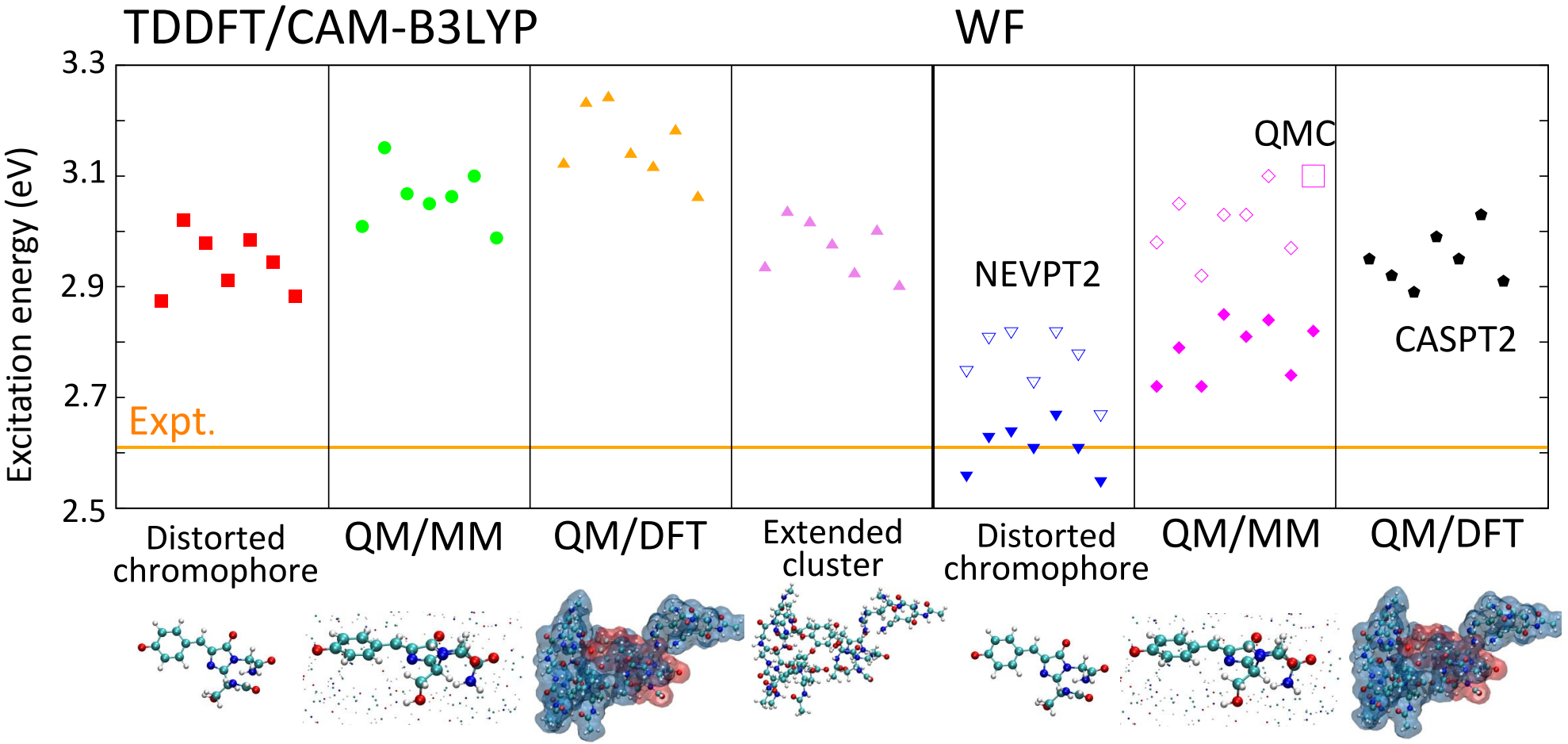
It does not work! What went wrong? Is it only an issue with TDDFT?





GFP: TDDFT vs correlated methods

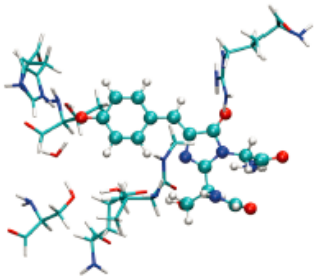
Embedding failure! What went wrong? Is it only an issue with TDDFT?



PT2/DFT behaves the same. What is missing from the embedding scheme?

GFP: DFT embedding and cluster size

CASPT2-in-DFT: What if we increase the environment?

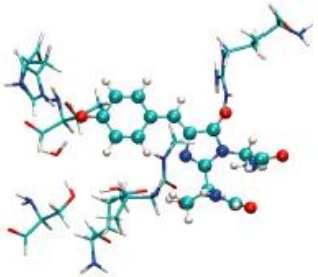


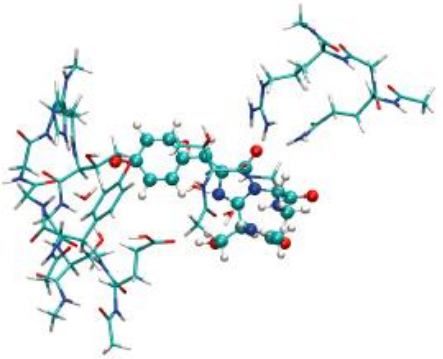
#atoms	168
QM/DFT	2.90 eV

Expt.: 2.63 eV

GFP: DFT embedding and cluster size

CASPT2-in-DFT: What if we increase the environment?



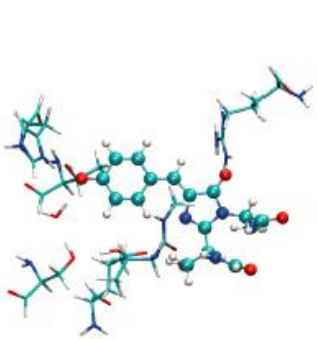


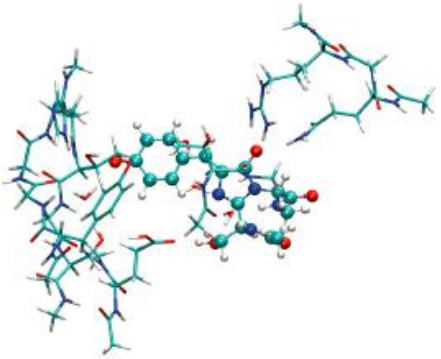
#atoms	168	279
QM/DFT	2.90 eV	3.02 eV

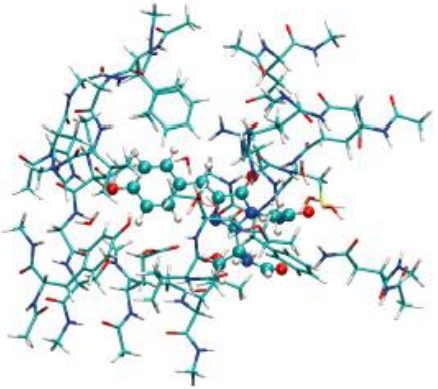
Expt.: 2.63 eV

GFP: DFT embedding and cluster size

CASPT2-in-DFT: What if we increase the environment?







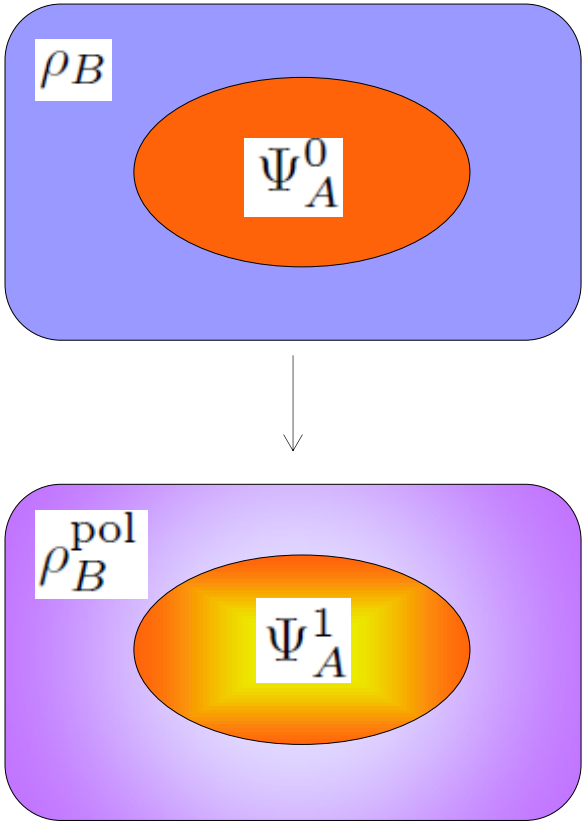
#atoms	168	279	528
QM/DFT	2.90 eV	3.02 eV	3.08 eV
Expt.: 2.63 eV			

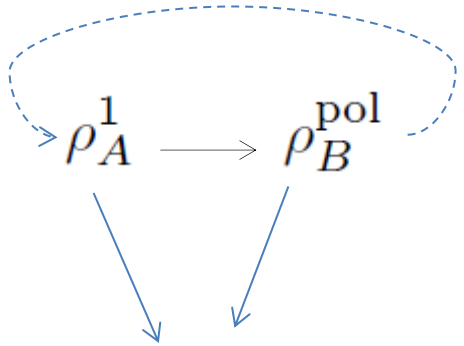
The bigger the cluster, the bigger the blue shift

Is a responsive environment the solution?

Let us try to include response from the environment in WF/DFT

1. Approximate excited-state DFT density of system A
2. Relax B in DFT ground state





State-specific embedding potential $v_{\mathrm{emb}}^1(\mathbf{r})$

One WF calculation for each state Ψ_A^1

Treating changes in environment

$$H^{\mathrm{emb},0} = \sum_i (-\frac{1}{2}\nabla_i^2 + v_{\mathrm{nucA}}(\mathbf{r}_i) + v^0_{\mathrm{emb}}(\mathbf{r}_i)) + \sum_{i<j} \frac{1}{r_{ij}}$$

$$H^{\mathrm{emb},1} = \sum_i (-\frac{1}{2}\nabla_i^2 + v_{\mathrm{nucA}}(\mathbf{r}_i) + v^1_{\mathrm{emb}}(\mathbf{r}_i)) + \sum_{i<j} \frac{1}{r_{ij}}$$

The best approximation for the excitation is:

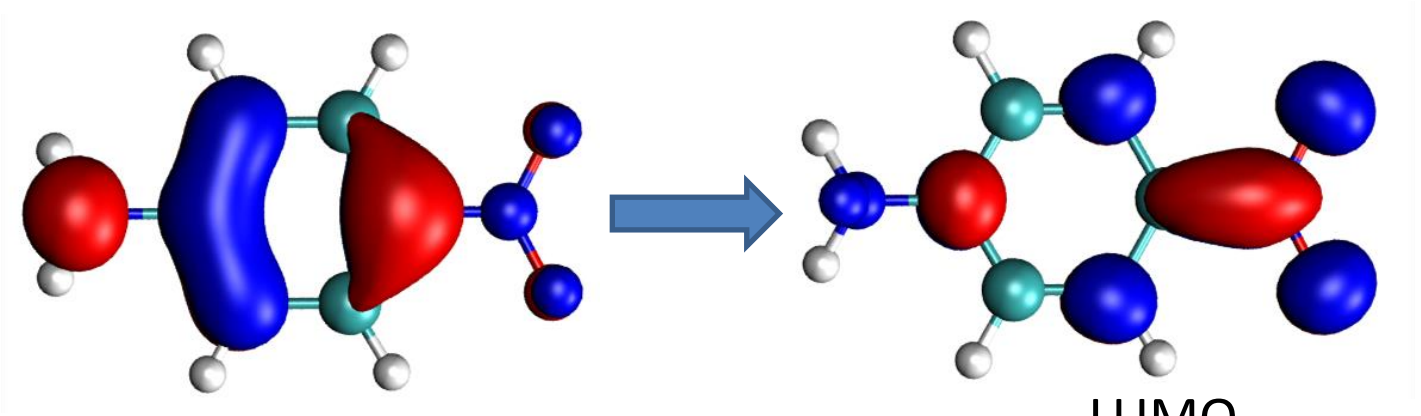
$$E_{\mathrm{exc}} \approx \langle \Psi^1_A | H^{\mathrm{emb},1} | \Psi^1_A \rangle - \langle \Psi^0_A | H^{\mathrm{emb},0} | \Psi^0_A \rangle + \underbrace{E_{\mathrm{DFT}}[\rho^{\mathrm{pol}}_B] - E_{\mathrm{DFT}}[\rho_B] + V_{\mathrm{nucA}}[\rho^{\mathrm{pol}}_B] - V_{\mathrm{nucA}}[\rho_B]}_{E_{\mathrm{cor}}}$$

E_{cor} includes changes in the energy which do not depend explicitly on Ψ_A

C. Daday, C. König, O. Valsson, J. Neugebauer, and C. Filippi *JCTC* **2013**, 9, 2355-2367

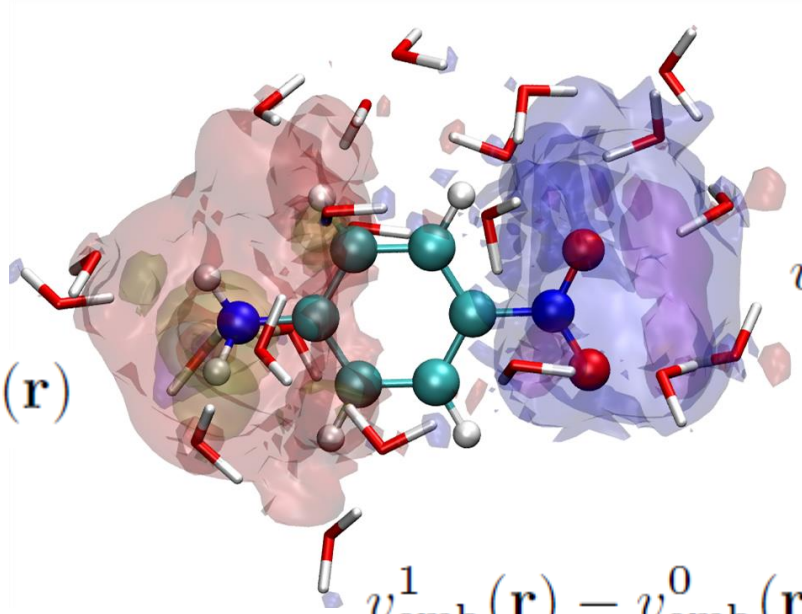
Smaller test first: PNA

p-nitroaniline as a test case



HOMO

LUMO



$v^1_{\mathrm{emb}}(\mathbf{r}) > v^0_{\mathrm{emb}}(\mathbf{r})$

$v^1_{\mathrm{emb}}(\mathbf{r}) < v^0_{\mathrm{emb}}(\mathbf{r})$

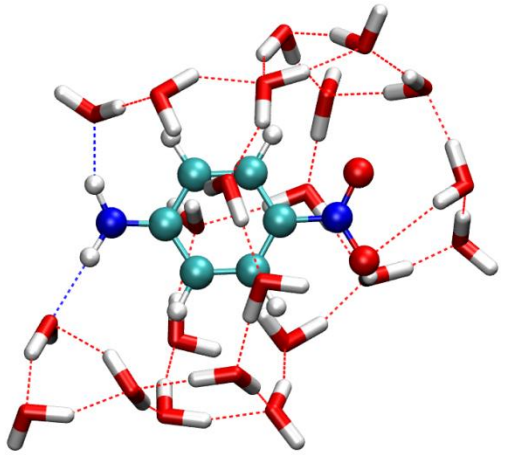
$v^1_{\mathrm{emb}}(\mathbf{r}) - v^0_{\mathrm{emb}}(\mathbf{r})$

Back-polarization: PNA

Back-polarization always improves on standard DFT embedding

E_{pol} → Polarization (ground-state DFT embedding)

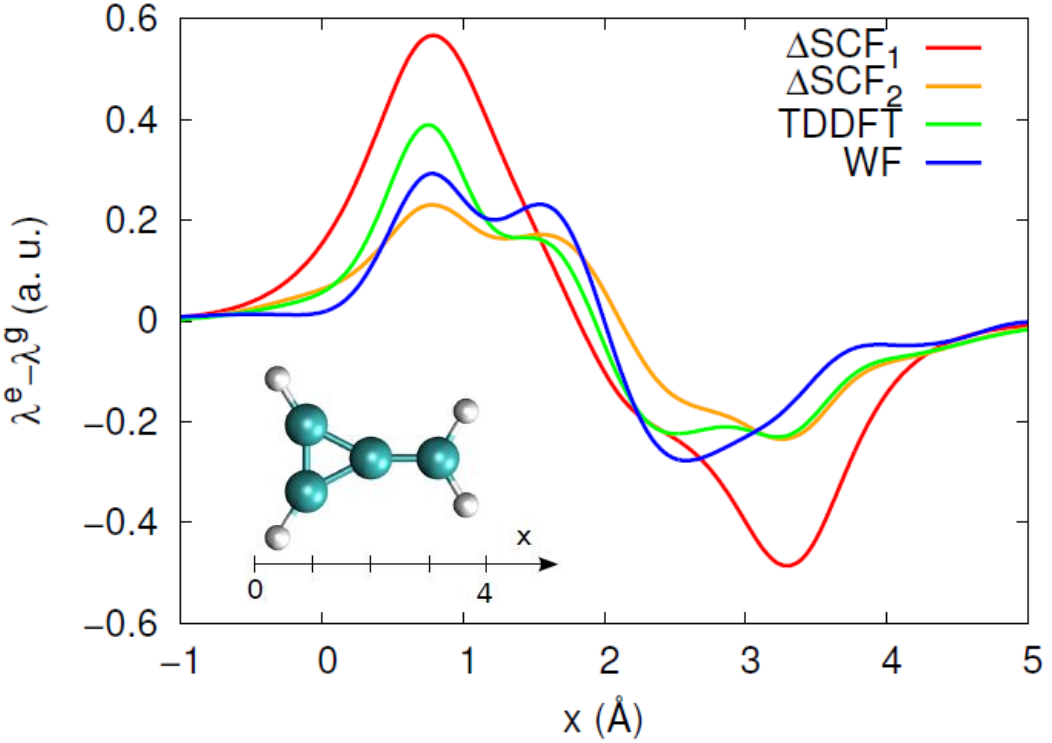
E_{back} → Back-polarization with correction



conf.	$E_{QM/MM}$	E_{pol}	E_{back}	E_{super}
1	3.81	3.70	3.48	3.46
2	3.67	3.54	3.48	3.34
3	3.61	3.46	3.47	3.27

Looks good! Does it always work?

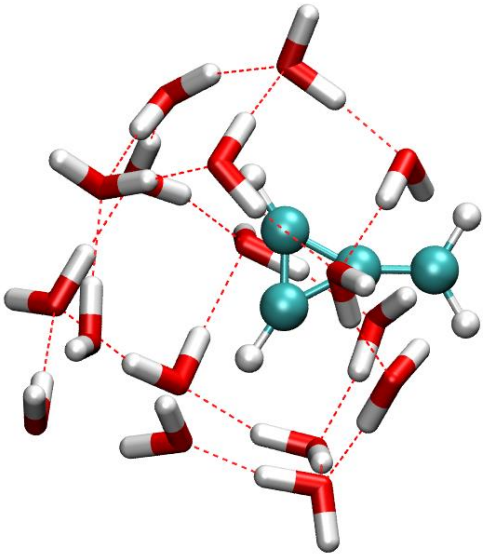
A more problematic case



Which excited-state density to use?

Several possibilities within KS DFT

$E_{QM/MM}$	E_{pol}	ρ_A^1	E_{back}	E_{super}
4.88	5.08	SCF_1	4.75	4.97
		SCF_2	4.87	
		WF	4.88	



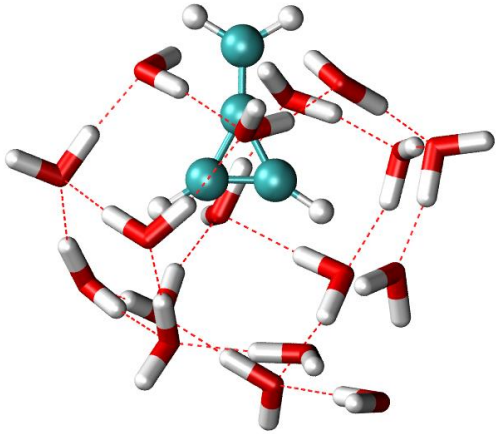
C. Daday, C. König, J. Neugebauer, and C. Filippi, CPC (submitted)

Cheaper alternative: TDDFT densities (work in progress)

Other WF methods?

Very consistent response to embedding potentials

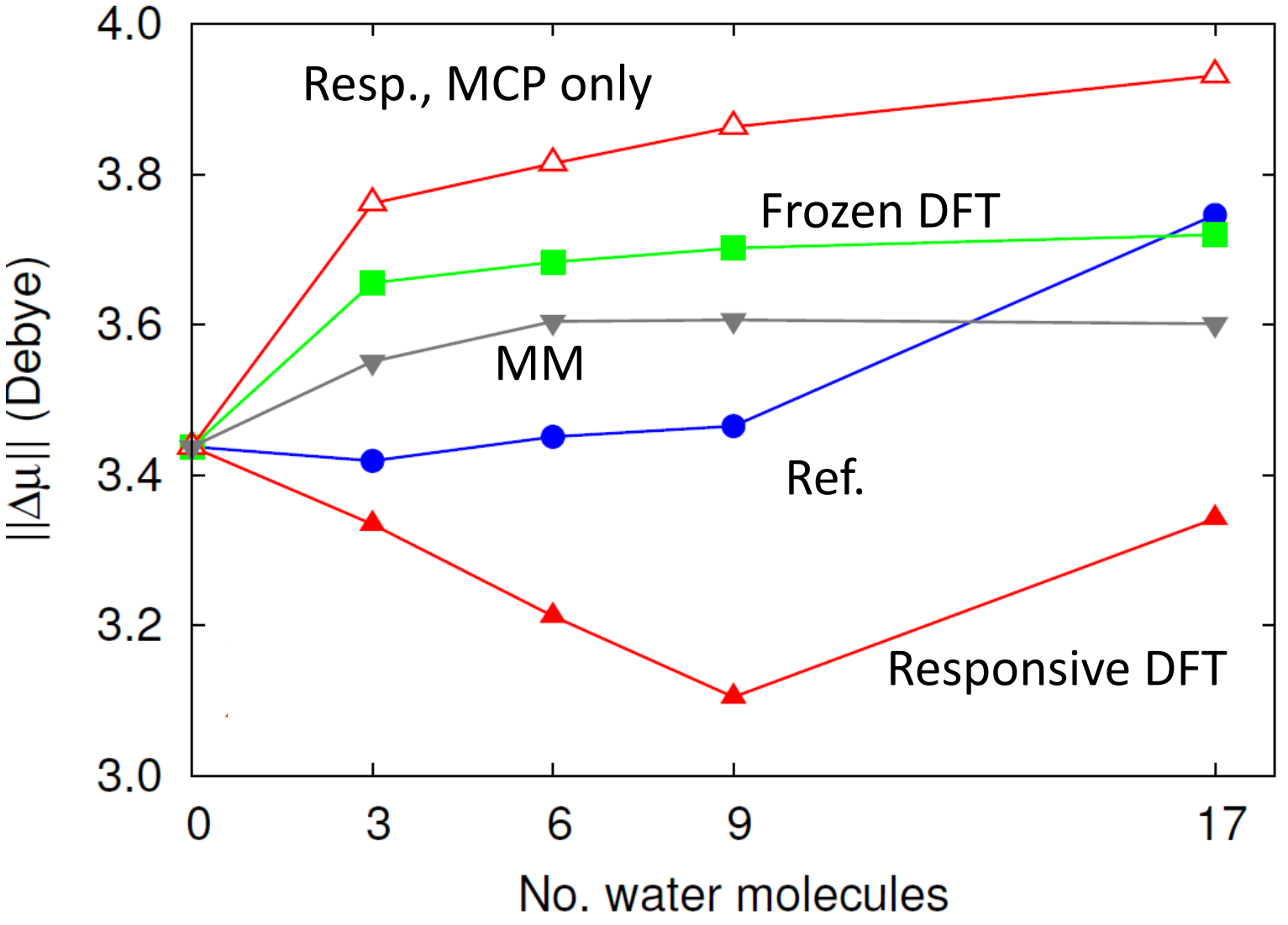
The choice of WF method is not the issue

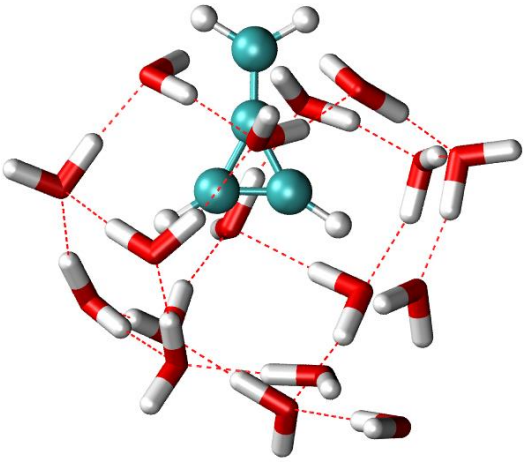


	WF/DFT		super
	frozen	responsive	
CASPT2	5.09	4.87	4.97
CCSDR(3)	5.12	4.90	-
DMC	5.18(1)	5.00(1)	5.07(4)

C. Daday, C. König, J. Neugebauer, and C. Filippi, CPC (submitted)

Looking deeper: Dipole moments

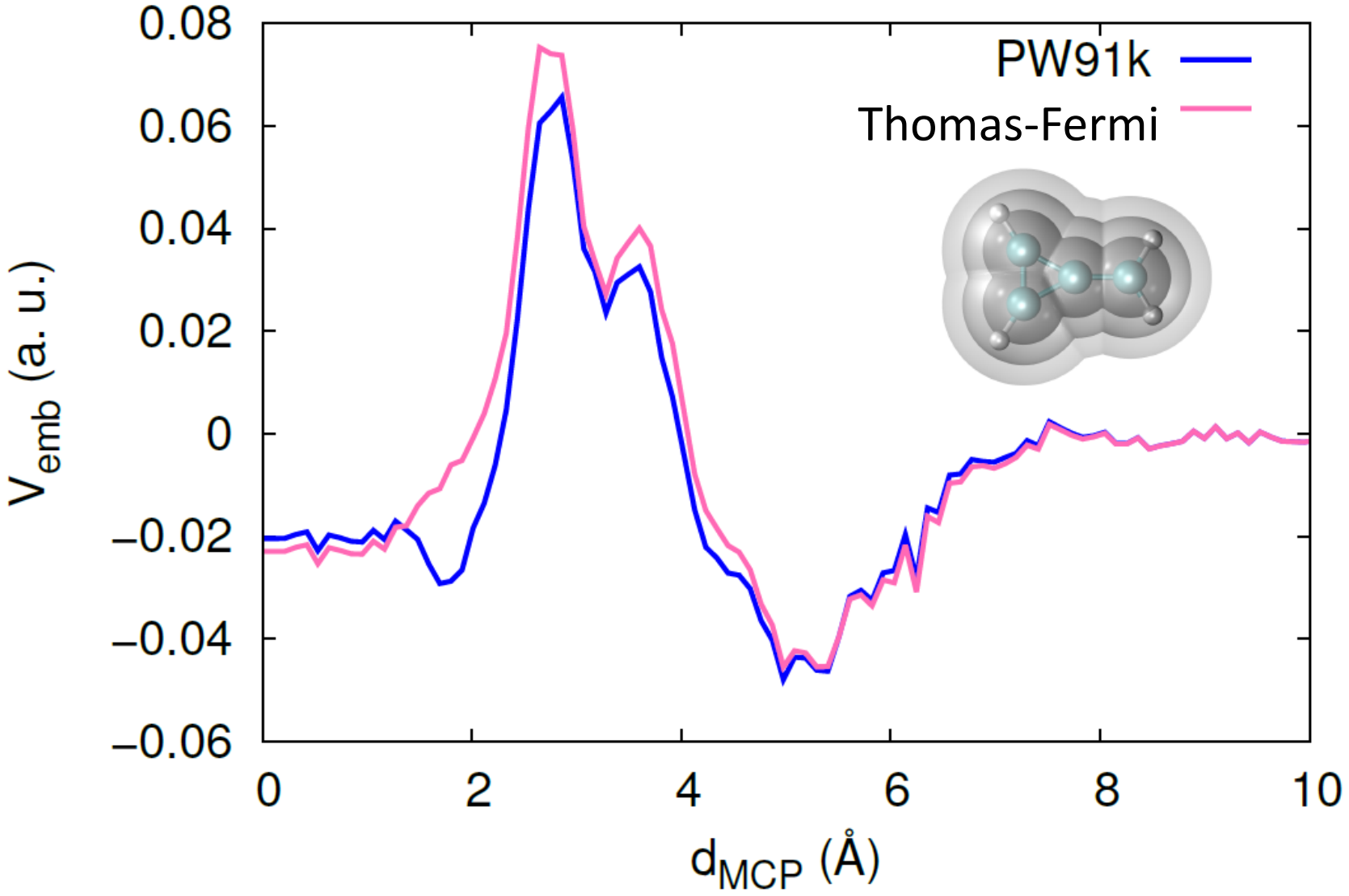




Our scheme **overpolarizes** the environment in excited state

C. Daday, C. König, J. Neugebauer, and C. Filippi, CPC (submitted)

Looking deeper: The barrier



The kinetic-energy functional creates a large barrier around the WF region

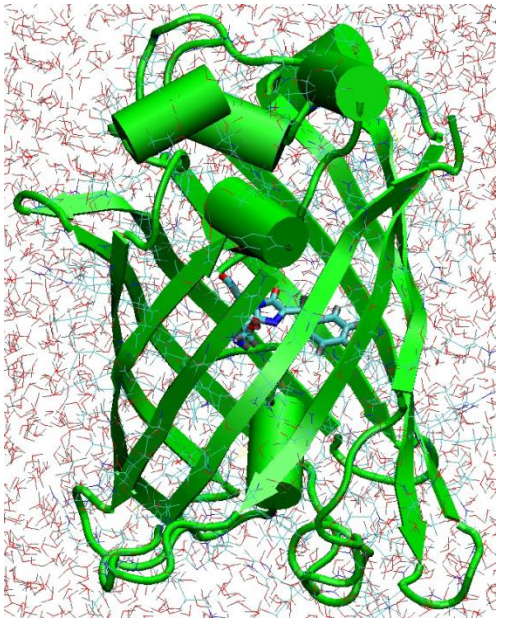
C. Daday, C. König, J. Neugebauer, and C. Filippi, CPC (submitted)

Back to GFP…

PT2/DFT with a frozen environment significantly worse than QM/MM …

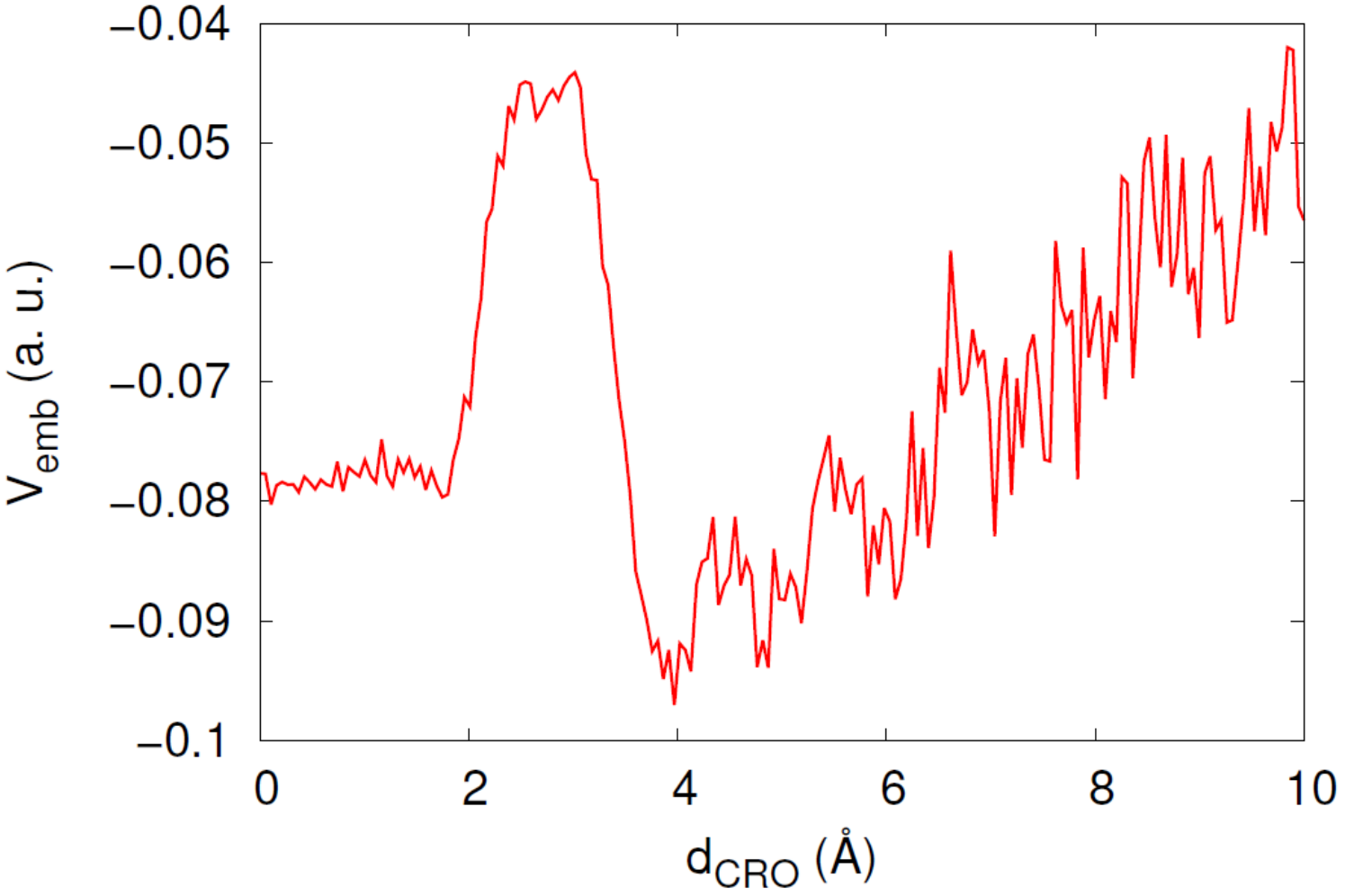
Responsive environment: No changes!

QM/MM	**CASPT2/DFT**		**Exp.**
	frozen	responsive	
2.72	2.95	2.95	2.63
2.82	3.07	3.06	



Suspect: Strong localization introduced by kinetic-energy potential

The barrier: Reprise



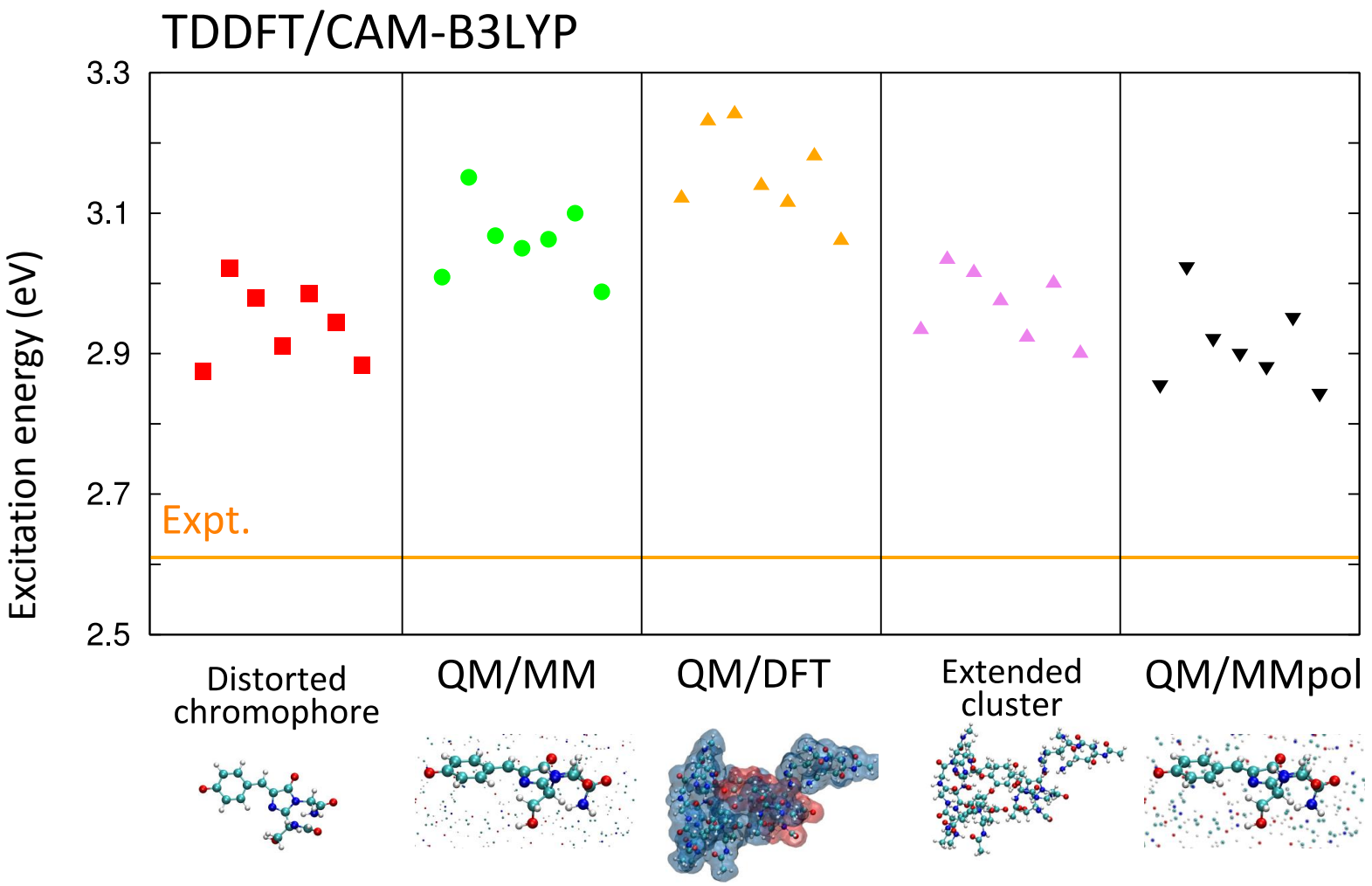
Possible reason for blue shift: The barrier is too steep/high

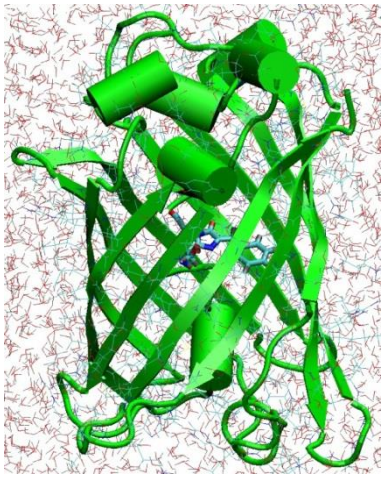
Other ways forward?

- Reconstructed embedding potential

$$\rho = \rho_A + \rho_B \longrightarrow v_s(\mathbf{r}) \text{ to yield ground-state } \rho_A$$

- Go back to polarizable dipoles? First tests on TDDFT are promising





Conclusions

"Good news for people who love bad news" (Modest Mouse)

- QM/MM description is inadequate for GFP, rhodopsin
- WF/DFT embedding: disappointing blue shift for excitations
  - Approximate kinetic-energy functionals are rather crude
  - Possible improvement: Reconstructed potentials
  - Environmental response: No improvement

Currently, QM/MMpol seems to be the more robust alternative

QMC/MMpol implemented in CHAMP and is coming soon for GFP …

The end

Thank you for your attention!

Questions/suggestions?

WF/DFT: Theoretical justification

The formal justification is tenuous:

- Khait and Hoffmann, JCP 133, 044107 (2010)

  The WF/DFT formalism is correct **if** the excited-state density is an extremum of the functional

- Perdew and Levy, PRB **31**, 6264 (1985)

  All extrema of the energy functional are stationary densities, but the vice versa is **not** true.