Excitation energy in solution at EOM-CCSD level, a state specific approach within the polarizable continuum model

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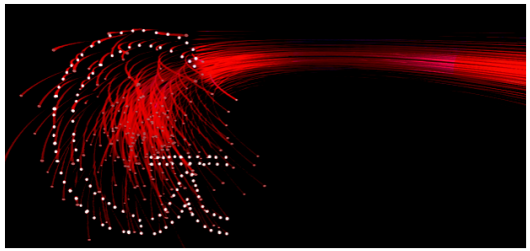
Gaussian, Inc.
Wallingford, CT



EOM-CCSD

High accuracy for one-electron transition energies of isolated molecules

Black box method (uniquely defined wavefunction)

Exact for two electron systems

Large computational effort ($O(N^6)$ iteratively)

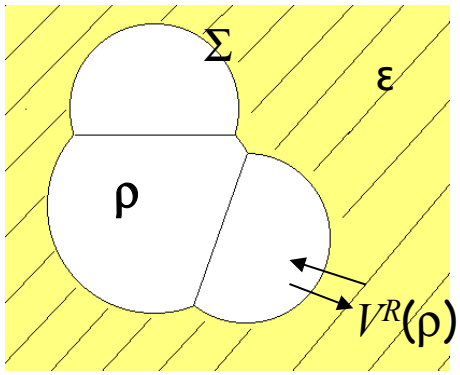
Many spectra are in solution – solvent effect is large

The Polarizable Continuum Model (PCM)

A charge density ρ in a cavity of general shape within a continuum medium with permittivity ε:

$$\begin{cases} -\mathrm{div}\left[\varepsilon(x)\nabla V(x)\right] = 4\pi\rho(x) \\ \\ + \text{ boundary conditions} \end{cases}$$

Electrostatic equations



The system is solved by introducing a **potential** V^R representing the solvent reaction:

$$\begin{cases} V(x) = V^0(x) + V^R(x) \\ V^R(x;\rho) = \int_\Sigma \dfrac{\sigma(y;\rho)}{|x-y|}\,dy \end{cases}$$

Free energy:

$$G = \int \rho(x)V^0(x)dx + \frac{1}{2}\int \rho(x)V^R(x)dx$$

Apparent surface charge

electrostatic response of the dielectric

IEF-PCM is the most general dielectric solvent model (uniform, anisotropic and ionic media)

$$\left[\left(\frac{\varepsilon-1}{\varepsilon+1}\right)\hat{I} - \frac{1}{2\pi}\hat{D}\right]\hat{S}\sigma^{PCM}(\mathbf{s}) = -\left(\hat{I} - \frac{1}{2\pi}\hat{D}\right)V(\mathbf{s})$$

J. Tomasi, B. Mennucci, R. Cammi Chem. Rev. 105 (2005) 2999

Continuous Surface Charge (CSC) scheme

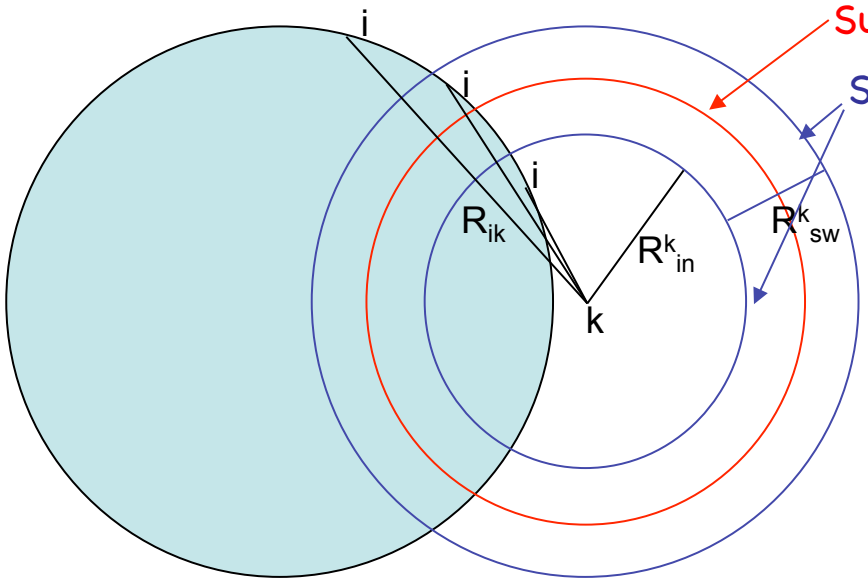
This scheme allows a smooth and continuous variation of the electrostatic interaction at the region of intersection between two (or more) cavity spheres. It greatly reduces numerical problems at intersection regions.

Normalized spherical Gaussian functions are used to represent the electrostatic potential and the interaction matrices

$$\phi_i(s) = \left(\frac{\xi_i^2}{\pi}\right)^{\frac{3}{2}} e^{\xi_i^2 |s - s_i|^2}$$

$$V_i = \int \frac{\rho(\mathbf{s}) \left(\frac{\xi_i^2}{\pi}\right)^{\frac{3}{2}} e^{\xi_i^2 |\mathbf{s} - \mathbf{s}_i|^2}}{|\mathbf{s} - \mathbf{s}_i|} d\mathbf{s}$$

Switching region



D. M. York, M. Karplus,
J. Phys. Chem. A, 103 (1999) 11060-79
G. Scalmani, M. J. Frisch,
J. Chem. Phys., 132 (2010) 114110

Solvent effect on post-SCF methods

Isolated system → Solvated system

$H^0 \rightarrow H$

$\Psi^0 \rightarrow \Psi$

Effective Hamiltonian

Polarized wavefunction

For SCF methods (HF or DFT) it is easy to define a variational formulation of the energy in the presence of the solvent, through an interaction potential which goes into the Hamiltonian

Mutual polarization of solute and solvent charge distributions

For post-SCF methods, the coupling of the solvent reaction field with the solute total density makes the calculation of the energy more difficult

For LR methods (CIS, TDHF and TDDFT) the solvent effect is introduced separately on the reference function (i.e. orbitals) and on the CIS/TD amplitudes.

cLR M. Caricato, B. Mennucci, J. Tomasi, F. Ingrosso, R. Cammi, S. Corni, G. Scalmani, JCP, 124, 124520 (2006)

For CC it is less clear which is the best strategy

O. Christiansen, K. V. Mikkelsen, JCP, 110, 1365 (1999)

Self-consistent PCM approach

- External iteration until self-consistency
- Computationally expensive
- Very expensive energy derivatives

State specific approach:

$$\Delta E = E^{exc} - E^{gs}$$

Excited state 1 particle density

T- MO-relaxed

$$\rho_1 = \rho_1^{SCF} + \left\langle \Phi_0 \middle| L_k e^{-T} p^+ q e^T R_k \middle| \Phi_0 \right\rangle + \left\langle \Phi_0 \middle| Z_k e^{-T} p^+ q e^T \middle| \Phi_0 \right\rangle + \text{M.O. terms}$$

i,j and a,b blocks

i,a block

$$\rho_2 = \left\langle \Phi_0 \middle| L_k e^{-T} p^+ q^+ r s e^T R_k \middle| \Phi_0 \right\rangle + \left\langle \Phi_0 \middle| Z_k e^{-T} p^+ q^+ r s e^T \middle| \Phi_0 \right\rangle, \text{ CPHF}$$

T-relaxed MO-unrelaxed

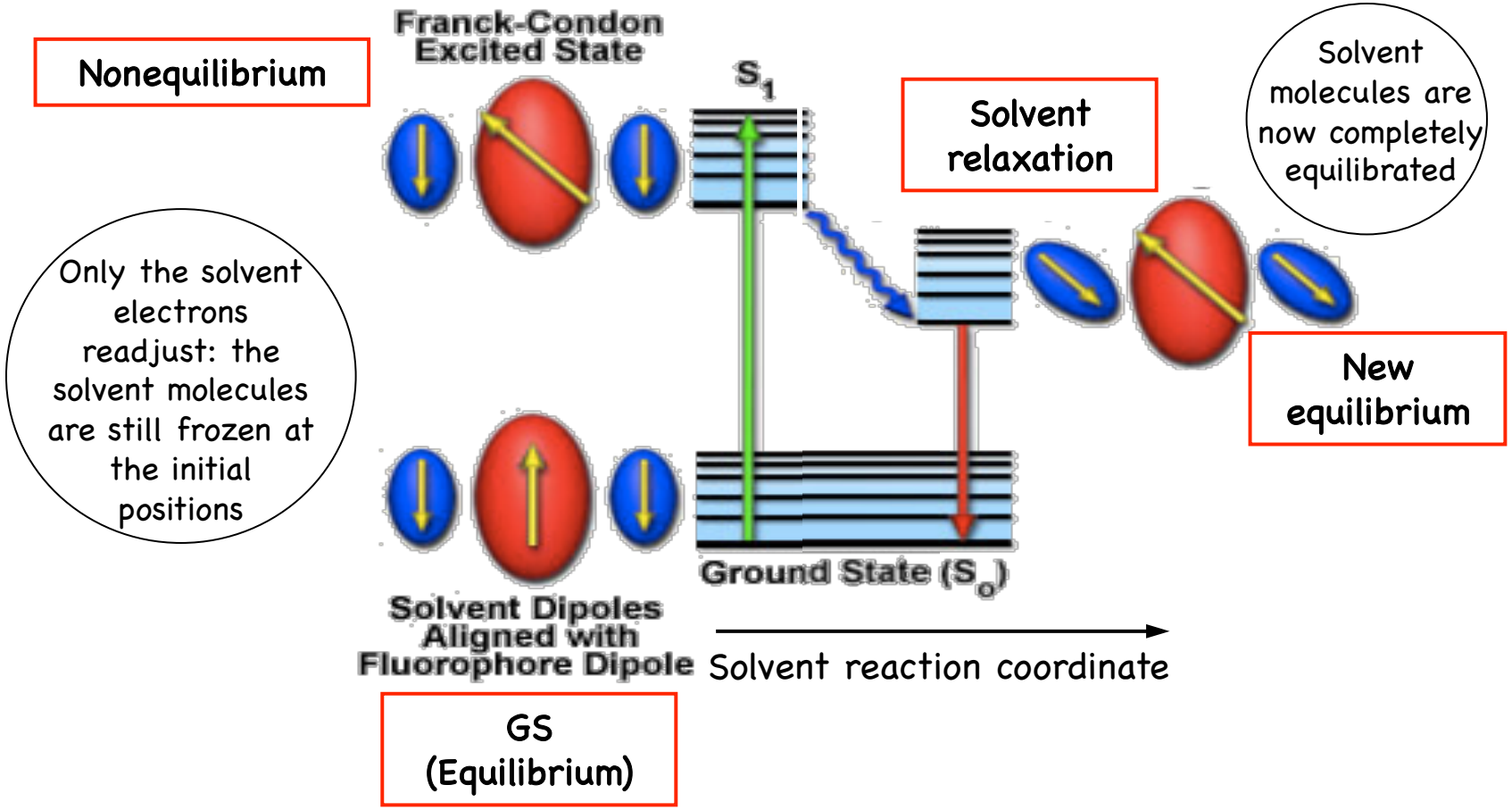
$$\rho_1 = \rho_1^{SCF} + \left\langle \Phi_0 \middle| L_k e^{-T} p^+ q e^T R_k \middle| \Phi_0 \right\rangle + \left\langle \Phi_0 \middle| Z_k e^{-T} p^+ q e^T \middle| \Phi_0 \right\rangle$$

T- MO-unrelaxed

$$\rho_1 = \rho_1^{SCF} + \left\langle \Phi_0 \middle| L_k e^{-T} p^+ q e^T R_k \middle| \Phi_0 \right\rangle$$

Contribution of the various terms to the final energy

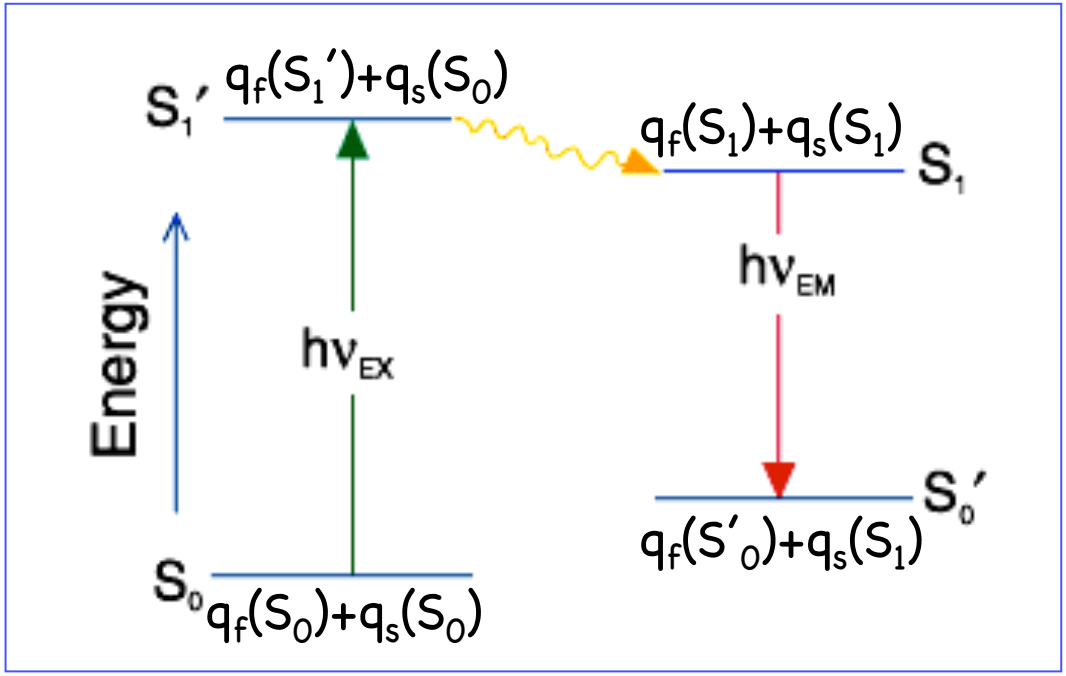
Electronic transitions in a polar solvent



PCM nonequilibrium approach in solute electronic transitions

The solvent response is divided into two contributions:

- Fast or dynamical, due to the electronic motions
- Slow or inertial, due to molecular and nuclear motions

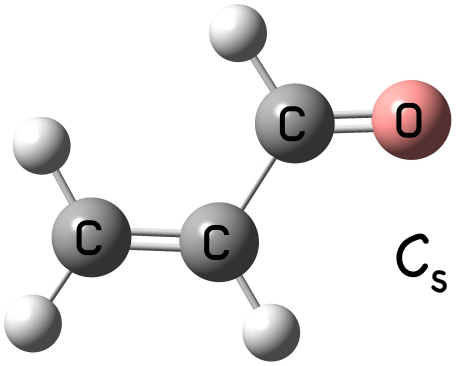


The PCM surface apparent charges are also divided into two contributions: the first one is related to the optical dielectric constant ε_∞, the second one to the static dielectric constant ε

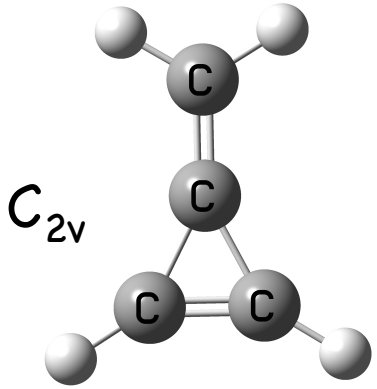
$$q(\rho^{fin}) = q_f(\rho^{fin}) + q_s(\rho^{ini})$$

B. Mennucci, R. Cammi and J. Tomasi, J. Chem. Phys., 109, 2798, 1998.

Acrolein



Methylenecyclopropene (MCP)



The first two transitions have opposite solvatochromic shift (polar ➔ apolar solvent)

Ground state geometry optimizations:
B3LYP and B3LYP/PCM with aug-cc-pVTZ basis set

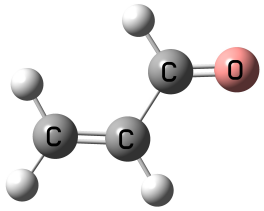
Excited state energies:
EOM-CCSD with 6-31+G* and aug-cc-pVDZ basis sets

Ground state energies:
CCSD with fully relaxed density

Solvents:

- Water and cyclohexane for acrolein
- Methanol and n-pentane for MCP

M.C., B. Mennucci, G. Scalmani, G. W. Trucks, M. J. Frisch, JCP, 132, 084102 (2010)



Acrolein

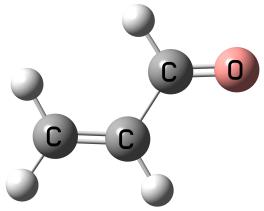
Non-equilibrium

First transition n➔π* A″

Transition energy (eV)	Gas phase		Water ε=78.4 ε_∞=1.8		Cyclohexane ε=2.0 ε_∞=2.0		Solvent shift (polar-apolar)	
Exp	3.71		3.94		3.71		+0.23	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	3.98	3.94	4.20	4.16	3.96	3.92	+0.23	+0.24
MO-unrelax			4.19	4.15	3.97	3.93	+0.22	+0.22
relaxed			4.18	4.14	3.98	3.93	+0.20	+0.21

Second transition π➔π* A′

Transition energy (eV)	Gas phase		Water ε=78.4 ε_∞=1.8		Cyclohexane ε=2.0 ε_∞=2.0		Solvent shift (polar-apolar)	
Exp	6.41		5.90		6.11		-0.21	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	7.08	6.89	6.58	6.52	6.84	6.75	-0.26	-0.23
MO-unrelax			6.59	6.53	6.84	6.76	-0.25	-0.23
relaxed			6.60	6.54	6.85	6.76	-0.25	-0.22



Acrolein

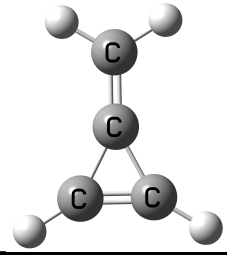
Equilibrium

First transition n➔π* A″

Transition energy (eV)	Gas phase		Water ε=78.4		Cyclohexane ε=2.0		Solvent shift (polar-apolar)	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	3.98	3.94	3.92	3.86	3.96	3.92	-0.04	-0.06
MO-unrelax			3.95	3.89	3.97	3.93	-0.02	-0.04
Relaxed			3.96	3.91	3.98	3.94	-0.02	-0.03

Second transition π➔π* A′

Transition energy (eV)	Gas phase		Water ε=78.4		Cyclohexane ε=2.0		Solvent shift (polar-apolar)	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	7.08	6.89	6.14	6.14	6.84	6.75	-0.70	-0.61
MO-unrelax			6.17	6.17	6.84	6.76	-0.67	-0.59
Relaxed			6.20	6.20	6.85	6.76	-0.65	-0.56



MCP

Non-equilibrium

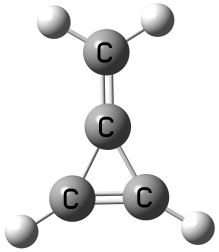
First transition $\pi \rightarrow \pi^*$ B_2

Transition energy (eV)	Gas phase		Methanol ε=32.6 ε_∞=1.8		N-pentane ε=1.8 ε_∞=1.8		Solvent shift (polar-apolar)	
Exp			4.49		4.01		+0.48	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	4.68	4.61	4.81	4.76	4.48	4.41	+0.33	+0.35
MO-unrelax			4.82	4.78	4.50	4.43	+0.32	+0.35
Relaxed			4.84	4.79	4.53	4.46	+0.31	+0.33

Second transition $\pi \rightarrow \pi^*$ A_1

Transition energy (eV)	Gas phase		Methanol ε=32.6 ε=1.8		N-pentane ε=1.8 ε_∞=1.8		Solvent shift (polar-apolar)	
Exp			5.90		6.02		-0.12	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	6.25	6.19	6.15	6.11	6.17	6.11	-0.02	0
MO-unrelax			6.15	6.10	6.17	6.11	-0.02	-0.01
Relaxed			6.13	6.09	6.17	6.11	-0.04	-0.02

+0.20 CIS, R. Cammi, S. Corni, B. Mennucci, J. Tomasi, JCP, 122, 104513 (2005)
+0.18 CASSCF, R. Cammi, L. Frediani, B. Mennucci, J. Tomasi, K. Ruud, K. V. Mikkelsen, JCP, 117, 13 (2002)



MCP

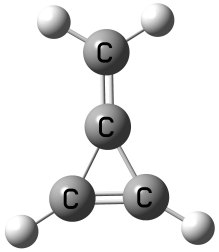
Equilibrium

First transition $\pi \rightarrow \pi^*$ B_2

Transition energy (eV)	Gas phase		Methanol ε=32.6		N-pentane ε=1.8		Solvent shift (polar-apolar)	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	4.68	4.61	4.14	4.06	4.48	4.41	-0.34	-0.35
MO-unrelax			4.21	4.13	4.50	4.43	-0.29	-0.30
Relaxed			4.29	4.21	4.53	4.46	-0.24	-0.25

Second transition $\pi \rightarrow \pi^*$ A_1

Transition energy (eV)	Gas phase		Methanol ε=32.6		N-pentane ε=1.8		Solvent shift (polar-apolar)	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	6.25	6.19	6.05	5.99	6.17	6.11	-0.12	-0.12
MO-unrelax			6.04	5.98	6.17	6.11	-0.13	-0.13
Relaxed			6.02	5.97	6.17	6.11	-0.15	-0.14



MCP

Equilibrium

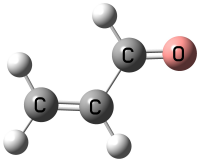
First transition $\pi \rightarrow \pi^*$ B_2

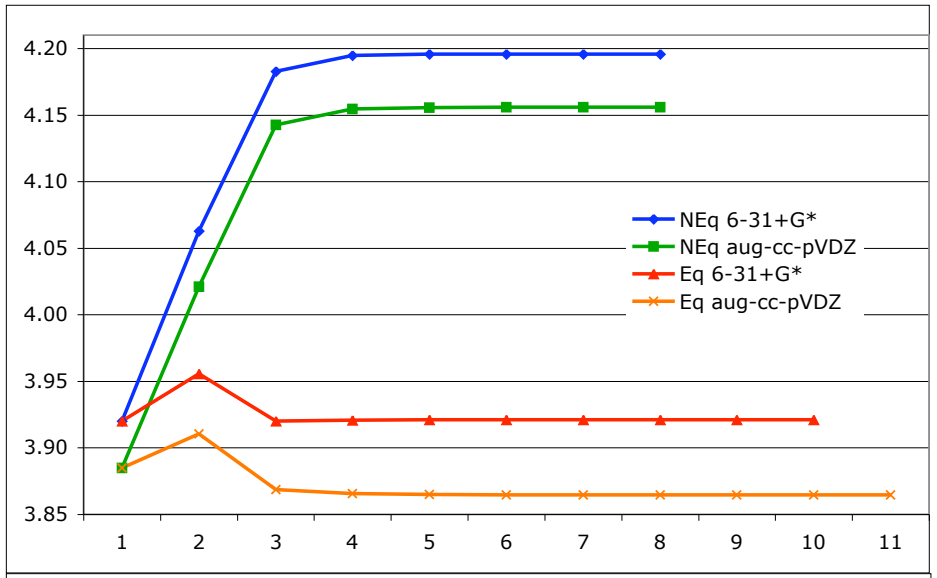
Transition energy (eV)	Gas phase		Methanol ε=32.6		N-pentane ε=1.8		Solvent shift (polar-apolar)	
	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ	6-31+G*	aug-cc-pVDZ
T- MO-unrel	4.68	4.61	4.14	4.06	4.48	4.41	-0.34	-0.35
MO-unrelax			4.21	4.13	4.50	4.43	-0.29	-0.30
Relaxed			4.29	4.21	4.53	4.46	-0.24	-0.25

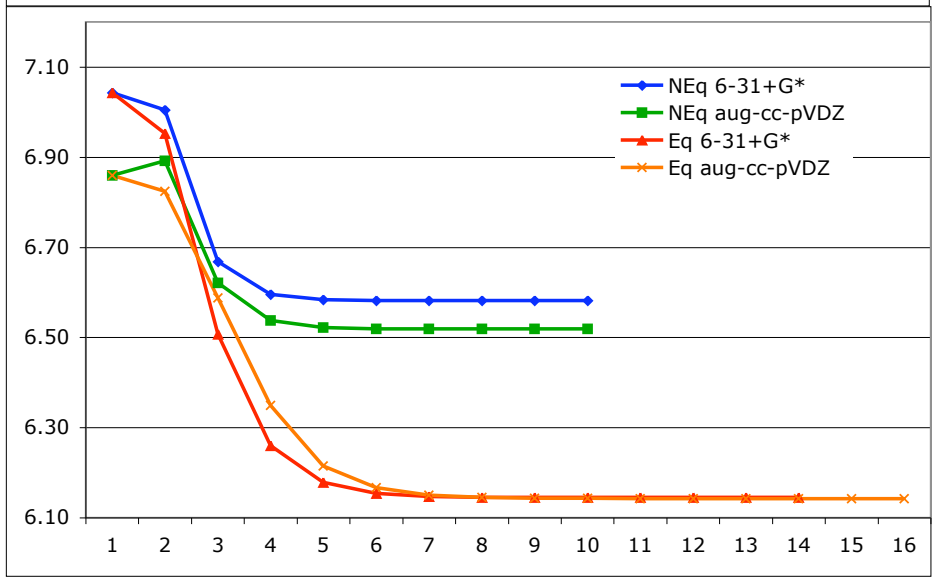
Dipole moment (D)	Methanol ε=32.6	
	6-31+G*	aug-cc-pVDZ
Ground state	-2.65	-2.76
T- MO-unrel	3.85	3.91
MO-unrelax	3.37	3.39
Relaxed	2.79	2.77

Acrolein in water

T- MO-unrelaxed density







First point is in vacuo
It is not state specific, but the linear response transition energy
Second point is the PCM correction with the vacuum density
This is state specific
The first two points are step 1

First transition n➔π* A″

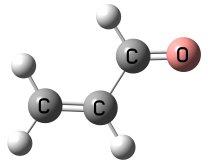
At convergence after 4 iterations.
Already close at 2nd iteration
Large change for NEq calculations

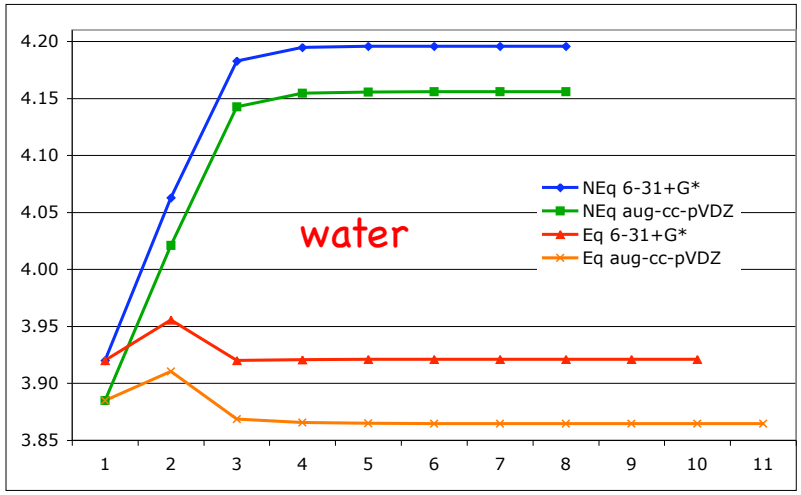
Second transition π➔π* A′

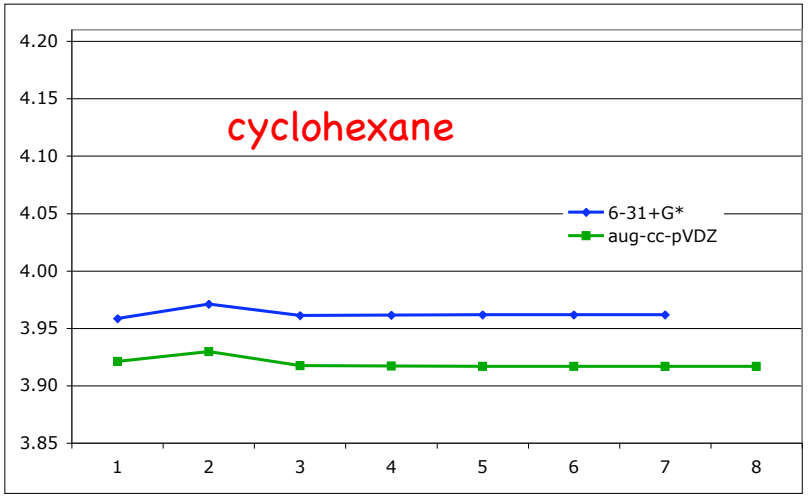
At convergence after 5 iterations for NEq and after 7 for Eq.
Large change for both schemes, especially for Eq.

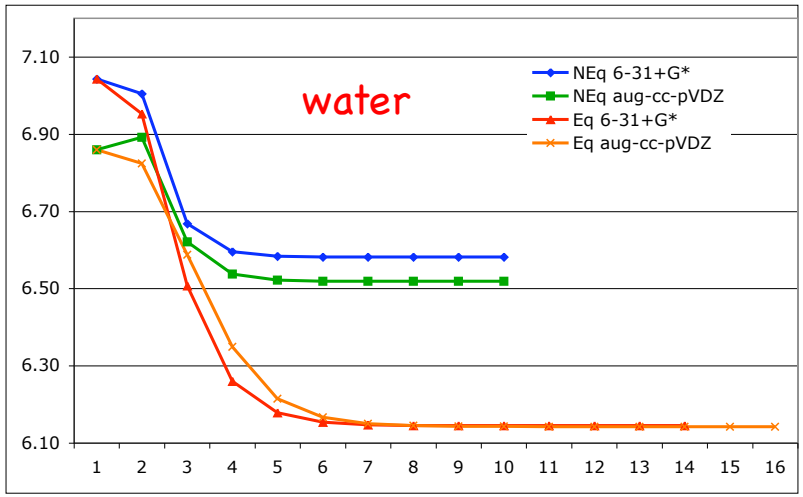
Acrolein

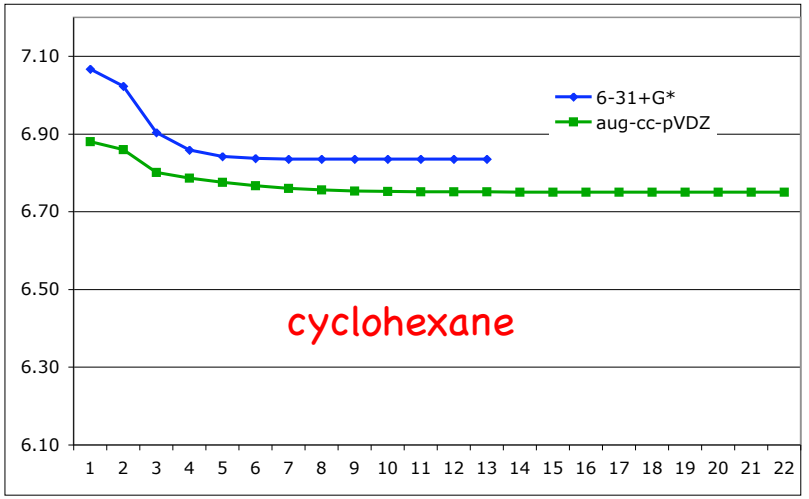
T- MO-unrelaxed density





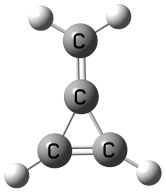


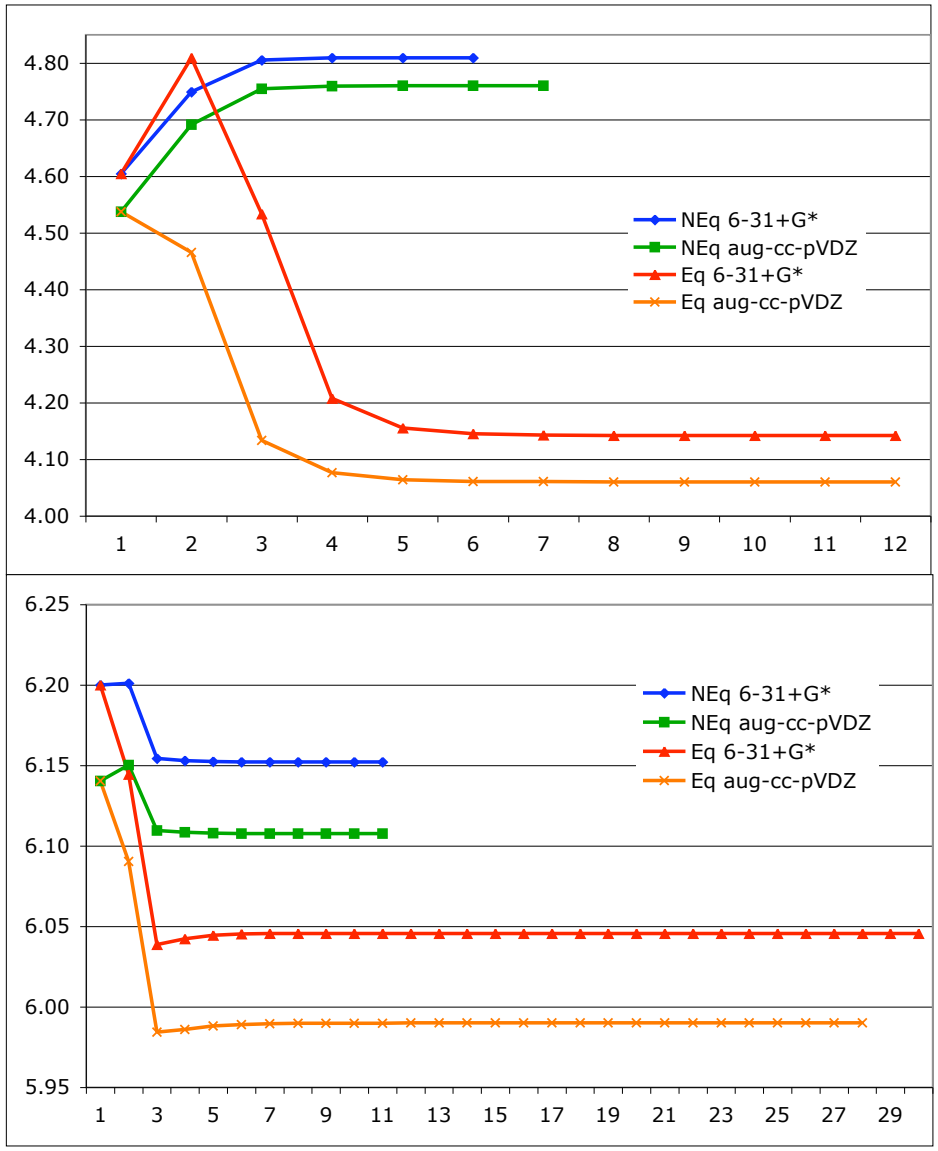




MCP in methanol

T- MO-unrelaxed density





First point is in vacuo
It is not state specific, but the linear response transition energy
Second point is the PCM correction with the vacuum density
This is state specific
The first two points are step 1

First transition $\pi \rightarrow \pi^*$ B_2

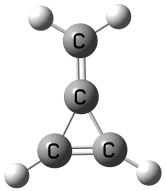
At convergence after 3 iterations for NEq and after 5 for Eq.
NEq already close at 2nd iteration
Large change for both schemes

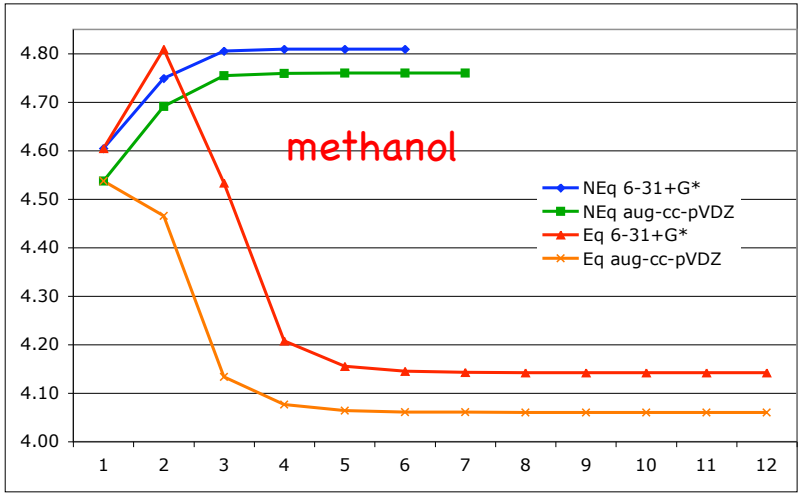
Second transition $\pi \rightarrow \pi^*$ A_1

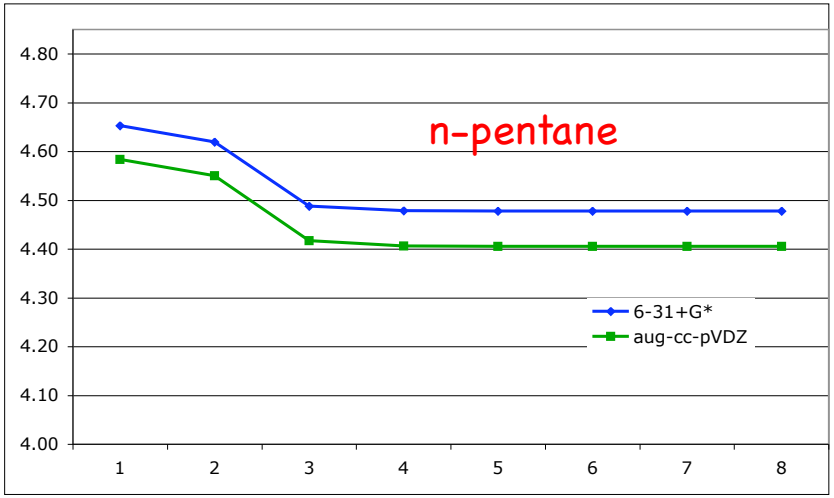
At convergence after a few iterations for both schemes, but large changes with respect to the vacuum

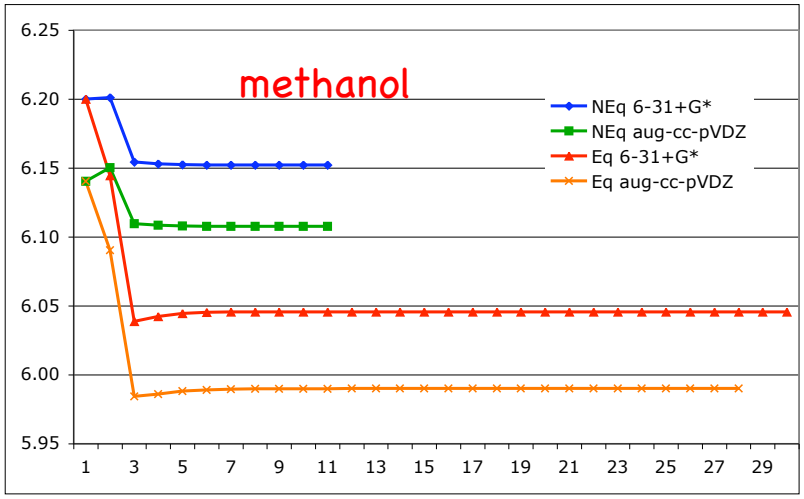
MCP

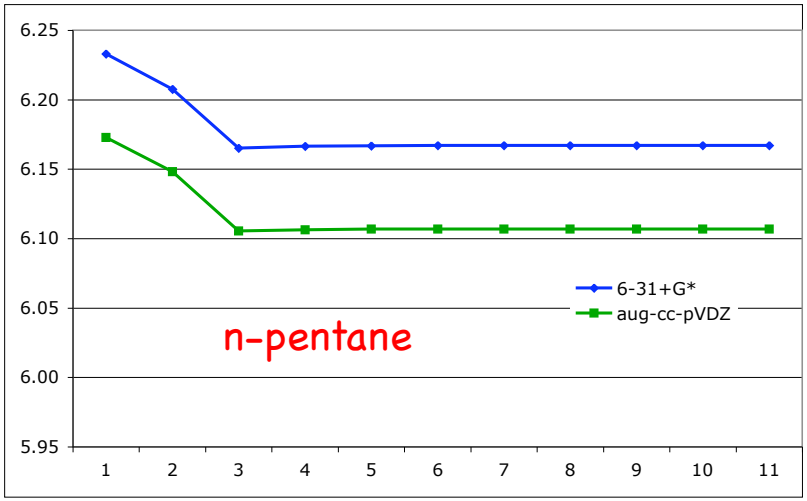
T- MO-unrelaxed density











Summary

- EOM-CCSD with PCM gives reliable estimates of electronic transition energies in solution
- The error introduced by PCM seems to be smaller than the error in gas phase
- The T- and MO-unrelaxed one particle density approximation introduces very small errors for non-equilibrium calculations. For equilibrium calculations the errors can be larger
- Very few iterations are necessary to reach convergence. And the EOM-CCSD calculations become cheaper close to convergence since the old amplitudes can be used as guess

Perspective

- Larger molecules and larger basis sets are under test
- Further approximations can be introduced, for instance introducing the solvent effect only at the SCF level
- The T- and MO-unrelaxed approximation seems a reasonable strategy to develop an efficient "integrated" EOM-CC/PCM model for vertical transition energies
- For equilibrium properties more data are needed

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Coupled cluster theory

$$\Psi_{CC} = e^{T}\Phi_0$$

$$= (1 + T + \frac{1}{2}T^2 + \frac{1}{3!}T^3 + \cdots)\Phi_0$$

$$T = T_1 + T_2 + T_3 + \cdots T_n$$

$$T_n = (n!)^{-2} \sum_{\substack{i,j,\ldots \\ a,b,\ldots}} t_{ij\ldots}^{ab\ldots} a_a^+ a_b^+ \cdots a_j a_i$$

Equation of motion-CCSD

Excited state Schrödinger equation:

$$H\Psi_k = E_k \Psi_k$$

$$\Psi_k = R_k \Psi_{CCSD}$$

$$= R_k e^{(T_1 + T_2)}\Phi_0$$

$$HR_k e^{(T_1+T_2)}\Phi_0 = E_k R_k e^{(T_1+T_2)}\Phi_0$$

$$\Downarrow$$

$$\left(\overline{H}R_k\right)_C \left|\Phi_0\right\rangle = \omega_k R_k \left|\Phi_0\right\rangle$$

$$R_k = R_0(k) + R_1(k) + R_2(k)$$

Similarity transformed Hamiltonian is not hermitian: different left eigenvectors

$$\left\langle\Phi_0\right| L_k \overline{H} = \left\langle\Phi_0\right| L_k \omega_k$$

J. F. Stanton, R. J. Bartlett, JCP, 98, 7029 (1993)