Dipartimento di Chimica e Chimica Industriale
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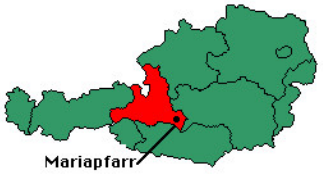
# The Modelling of Environment Effects in Quantum Chemistry

## QM/continuum models: from solvated systems to more complex environments

## (II)

Benedetta Mennucci

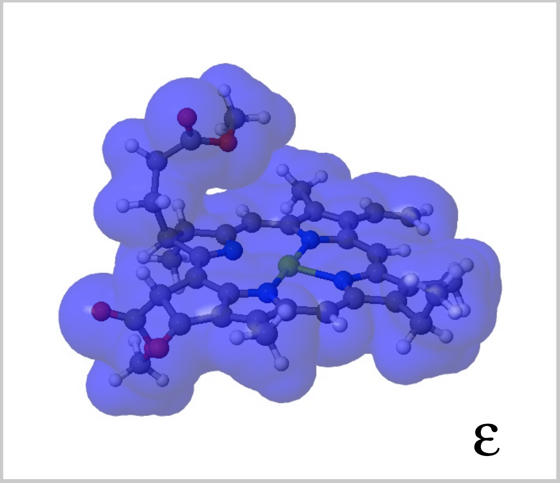


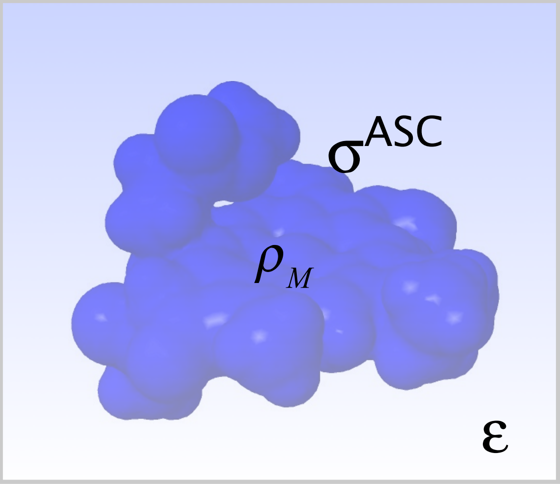
Mariapfarr, Salzburg, Österreich

MoLECoLAB PISA
MODELLING LIGHT AND ENVIRONMENT IN COMPLEX SYSTEMS

# QM/continuum: a step by step strategy

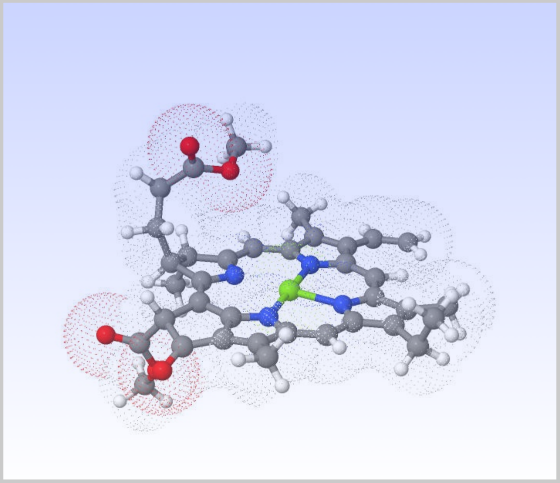
1) The definition of the boundary:
the molecular cavity made of interlocking spheres centered on atoms

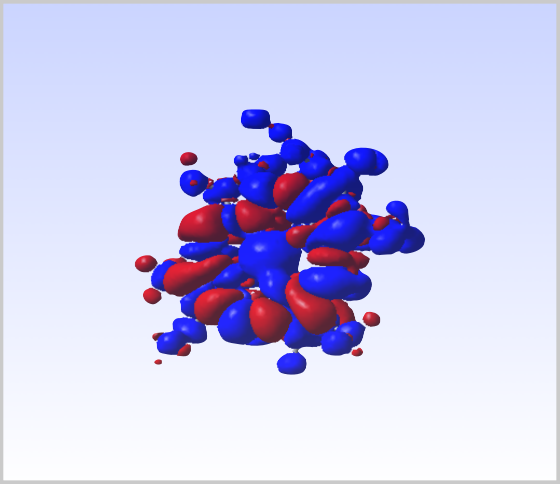




2) The electrostatic problem:
the Apparent Surface Charge approach

3) The numerical solution:
The introduction of a surface mesh and the discretization of the ASC density in point charges ($q^{ASC}$)





4) The coupling with a QM description

$$\hat{H}_{eff}\Psi = \left(\hat{H}_{QM} + \boxed{\hat{H}^{elec}_{QM/clas}}\right)\Psi = E\Psi$$

$$\boxed{\hat{V}_R = \sum_i q_i^{ASC}\hat{V}(\vec{s}_i)}$$

# Solvent effects on molecular properties & spectroscopies

# Solvent effects on molecular properties & spectroscopies: which modeling

## Physical issue:

the solvation model should include all the main physical interactions determining the solvent-induced change on the property/spectroscopic signal

## Quantum-Mechanical issue:

the QM model should be able to describe the effects of solvent on the solute charge density and on its response to perturbations

# Properties as derivatives of the energy

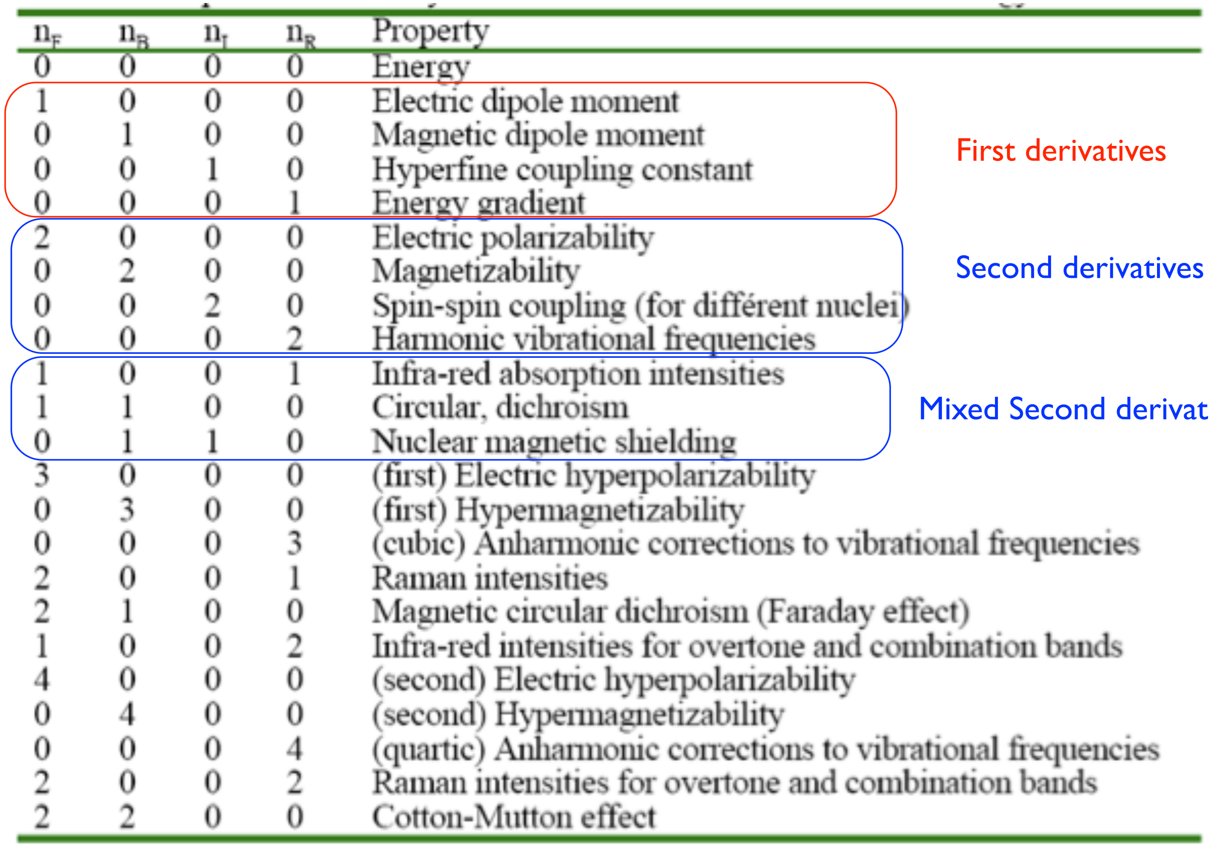
The energy is expanded in a Taylor series in the perturbation strength λ

$$E(\lambda) = E(0) + \frac{\partial E}{\partial \lambda}\lambda + \frac{1}{2}\frac{\partial^2 E}{\partial \lambda^2}\lambda^2 + \frac{1}{3!}\frac{\partial^3 E}{\partial \lambda^3}\lambda^3 + \ldots$$

The nth-order property is the nth-order derivative of the energy

For example,
by considering four types of
perturbations: external electric (F)
or magnetic field (B), nuclear
magnetic moment (nuclear spin, I)
and a change in the nuclear
geometry (R)

$$\text{Property} \propto \frac{\partial^{n_F+n_B+n_I+n_R} E}{\partial F^{n_F}\,\partial B^{n_B}\,\partial I^{n_I}\,\partial R^{n_R}}$$



| $n_F$ | $n_B$ | $n_I$ | $n_R$ | Property |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | Energy |
| 1 | 0 | 0 | 0 | Electric dipole moment |
| 0 | 1 | 0 | 0 | Magnetic dipole moment |
| 0 | 0 | 1 | 0 | Hyperfine coupling constant |
| 0 | 0 | 0 | 1 | Energy gradient |
| 2 | 0 | 0 | 0 | Electric polarizability |
| 0 | 2 | 0 | 0 | Magnetizability |
| 0 | 0 | 2 | 0 | Spin-spin coupling (for différent nuclei) |
| 0 | 0 | 0 | 2 | Harmonic vibrational frequencies |
| 1 | 0 | 0 | 1 | Infra-red absorption intensities |
| 1 | 1 | 0 | 0 | Circular, dichroism |
| 0 | 1 | 1 | 0 | Nuclear magnetic shielding |
| 3 | 0 | 0 | 0 | (first) Electric hyperpolarizability |
| 0 | 3 | 0 | 0 | (first) Hypermagnetizability |
| 0 | 0 | 0 | 3 | (cubic) Anharmonic corrections to vibrational frequencies |
| 2 | 0 | 0 | 1 | Raman intensities |
| 2 | 1 | 0 | 0 | Magnetic circular dichroism (Faraday effect) |
| 1 | 0 | 0 | 2 | Infra-red intensities for overtone and combination bands |
| 4 | 0 | 0 | 0 | (second) Electric hyperpolarizability |
| 0 | 4 | 0 | 0 | (second) Hypermagnetizability |
| 0 | 0 | 0 | 4 | (quartic) Anharmonic corrections to vibrational frequencies |
| 2 | 0 | 0 | 2 | Raman intensities for overtone and combination bands |
| 2 | 2 | 0 | 0 | Cotton-Mutton effect |

First derivatives

Second derivatives

Mixed Second derivatives

F. Jensen, Introduction to Computational Chemistry, Wiley

# First derivatives for variational methods: some notations

Expanding on an atomic basis set

In terms of the density matrix **D**:

$$E = tr\left(\mathbf{Dh}\right) + \frac{1}{2} tr\left(\mathbf{DG}(\mathbf{D})\right) + V_{NN}$$

$$\frac{\partial E}{\partial \lambda} = tr\left(\mathbf{Dh}^{(\lambda)}\right) + \frac{1}{2} tr\left(\mathbf{DG}^{[\lambda]}(\mathbf{D})\right) - tr\mathbf{S}^{(\lambda)}\mathbf{W} + V_{NN}^{(\lambda)}$$

$$W_{\alpha\beta} = 2\sum_i c_{\alpha i} c_{\beta i} \varepsilon_i$$

$$S_{\alpha\beta}^{(\lambda)} = \left\langle \chi_\alpha \mid \chi_\beta \right\rangle^{(\lambda)}$$

$$h_{\alpha\beta}^{(\lambda)} = \left\langle \chi_\alpha \mid h \mid \chi_\beta \right\rangle^{(\lambda)} = \left\langle \chi_\alpha \mid h^{(\lambda)} \mid \chi_\beta \right\rangle + \left\langle \chi_\alpha^{(\lambda)} \mid h \mid \chi_\beta \right\rangle + \left\langle \chi_\alpha \mid h \mid \chi_\beta^{(\lambda)} \right\rangle$$

$$G_{\alpha\beta}^{[\lambda]} = \sum_{\lambda\sigma} D_{\lambda\sigma}\left[\left\langle \chi_\alpha \chi_\sigma \middle| g \middle| \chi_\beta \chi_\lambda \right\rangle - \left\langle \chi_\alpha \chi_\sigma \middle| g \middle| \chi_\lambda \chi_\beta \right\rangle\right]^{(\lambda)}$$

No need to calculate the derivative of the density matrix

# For a solvated system

$$\frac{\partial G}{\partial \lambda} = \frac{\partial}{\partial \lambda}\left[\left\langle \Psi \middle| \hat{H}^0 \middle| \Psi \right\rangle + \frac{1}{2}\left\langle \Psi \middle| \hat{V}^R \middle| \Psi \right\rangle\right]$$

Direct differentiation
of the free energy of
the solvated system

$$= tr\left(\mathbf{D}\mathbf{h}^{(\lambda)}\right) + \frac{1}{2} tr\left(\mathbf{D}\mathbf{G}^{[\lambda]}(\mathbf{D})\right) - tr\left(\mathbf{S}^{(\lambda)}\mathbf{W}\right) + V_{NN}^{\lambda} + \frac{1}{2} tr\left(\mathbf{D}\mathbf{V}_R^{[\lambda]}(\mathbf{D})\right)$$

Within the ASC formulation of the continuum solvation model

$$\boxed{\hat{V}_R = \sum_k q_k^{ASC} \hat{V}(\vec{s}_k)}$$

$$tr\left(\mathbf{D}\mathbf{V}_R^{[\lambda]}(\mathbf{D})\right) = \sum_k \left[ q_k^{[\lambda]}(\mathbf{D}) V_k(\mathbf{D}) + q_k(\mathbf{D}) V_k^{[\lambda]}(\mathbf{D}) \right]$$

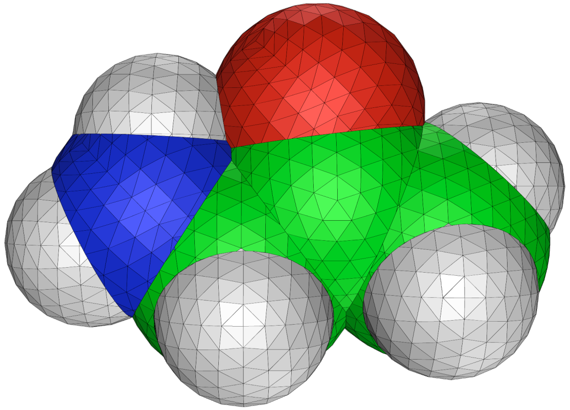
As a result the corresponding response properties will be changed by the presence of the environment

# Geometry optimization of a solvated system: the cavity specificity

Differentiation of the reaction term = derivatives of ASCs

$$tr\left(\mathbf{D}\mathbf{V}_R^{[\lambda]}(\mathbf{D})\right)=\sum_k\left[q_k^{[\lambda]}(\mathbf{D})V_k(\mathbf{D})+q_k(\mathbf{D})V_k^{[\lambda]}(\mathbf{D})\right]$$

As the geometry changes,
the cavity also changes.



Derivatives of the geometrical parameters which define the charges

$$\mathbf{T}(\varepsilon)\mathbf{q}^{\mathrm{ASC}}=-\mathbf{R}\mathbf{V}_{QM}$$

Derivatives of position and area of surface elements

More costly than in gas-phase and sometimes more difficult to converge

# Geometry optimization of a solvated system: the cavity specificity

A continuous surface charge (CSC) formalism has been developed to improve geometry optimizations within ASC.
The basic idea is to rewrite the surface charge in terms of an expansion of surface elements basis functions which are typically spherical Gaussian functions

$$\sigma(\mathbf{r}) = \sum_i \frac{q_i}{a_i} \phi_i(\mathbf{r}; \mathbf{s}_i, \zeta_i)$$

q are the ASC charges.

$$a_i = w_i R_A^2 F_{iA}$$

$w_i$ are the integration weights for the surface of the unit sphere and $R_A$ is the radius of the sphere chosen for atom A.
$F_{iA}$ is a switching function that varies smoothly from 0 to 1 so to assure that $a_i$ varies smoothly from the full value down to zero when the *ith* element falls inside an nearby sphere.

D. York and M. Karplus, J. Phys. Chem. A 103, 11060 (1999).

Scalmani G, Frisch MJ. *J. Chem. Phys.* 2010, 132:114110

# Properties which require second (or higher order) derivatives

$$\frac{\partial^2 E}{\partial\eta\partial\lambda} = tr\left(\mathbf{D}\mathbf{h}^{(\lambda,\eta)}\right) + \frac{1}{2} tr\left(\mathbf{D}\mathbf{G}^{[\lambda,\eta]}(\mathbf{D})\right) + V_{NN}^{(\lambda,\eta)} - tr\mathbf{S}^{(\lambda,\eta)}\mathbf{W}$$
$$+ tr\left(\mathbf{D}^{(\eta)}\mathbf{h}^{(\lambda)}\right) + tr\left(\mathbf{D}^{(\eta)}\mathbf{G}^{[\lambda]}(\mathbf{D})\right) - tr\mathbf{S}^{(\lambda)}\mathbf{W}^{(\eta)}$$

$$\mathbf{W}^{(\eta)} = \mathbf{D}^{(\eta)}\mathbf{F}\mathbf{D} + \mathbf{D}\mathbf{F}^{[\eta]}\mathbf{D} + \mathbf{D}\mathbf{G}(\mathbf{D}^{(\eta)})\mathbf{D} + \mathbf{D}\mathbf{F}\mathbf{D}^{(\eta)}$$

How can we obtain the derivatives of the density matrix?

# Coupled Perturbed Hartree-Fock

We expand each matrix (**F, C, S,** ε) in terms of the strength of the perturbation (e.g. $\mathbf{F} = \mathbf{F}^{(0)} + \lambda\mathbf{F}^{(1)} + \ldots$ ) ad we collect terms of the same order:

## First-order *Coupled Perturbed Hartree-Fock* (CPHF)

$$\boxed{\mathbf{F}^{(1)}\mathbf{C}^{(0)} + \mathbf{F}^{(0)}\mathbf{C}^{(1)} = \mathbf{S}^{(1)}\mathbf{C}^{(0)}\boldsymbol{\varepsilon}^{(0)} + \mathbf{S}^{(0)}\mathbf{C}^{(1)}\boldsymbol{\varepsilon}^{(0)} + \mathbf{S}^{(0)}\mathbf{C}^{(0)}\boldsymbol{\varepsilon}^{(1)}}$$

Orthonormality condition:
$$\left[\mathbf{C}^{(1)}\right]^{\dagger}\mathbf{S}^{(0)}\mathbf{C}^{(0)} + \left[\mathbf{C}^{(0)}\right]^{\dagger}\mathbf{S}^{(1)}\mathbf{C}^{(0)} + \left[\mathbf{C}^{(0)}\right]^{\dagger}\mathbf{S}^{(0)}\mathbf{C}^{(1)} = 0$$

First-order terms

$$\mathbf{F}^{(1)} = \mathbf{h}^{(1)} + \mathbf{G}^{(1)}(\mathbf{D}^{(0)}) + \mathbf{G}^{(0)}(\mathbf{D}^{(1)})$$

$$\mathbf{D}^{(1)} = 2\left\{\mathbf{C}^{(1)}\left[\mathbf{C}^{(0)}\right]^{\dagger} + \mathbf{C}^{(0)}\left[\mathbf{C}^{(1)}\right]^{\dagger}\right\}$$

# For a solvated system

Effective Fock :

$$\tilde{\mathbf{F}} = \mathbf{F}^{vac} + \mathbf{X}^{R}$$

ASC model:

$$\mathbf{X}^{R} = \sum_{k} q_{k}^{ASC}(\mathbf{D})\mathbf{V}_{k}$$

Coupled perturbed equations for a continuum model

$$\tilde{\mathbf{F}}^{(1)} = \mathbf{h}^{(1)} + \mathbf{G}^{(1)}(\mathbf{D}^{(0)}) + \mathbf{G}^{(0)}(\mathbf{D}^{(1)}) + \mathbf{X}^{R(1)}(\mathbf{D}^{(0)}) + \mathbf{X}^{R(0)}(\mathbf{D}^{(1)})$$

As a result the density matrix (and the corresponding response properties) will be changed by the presence of environment

# Molecular properties in solution:
# a schematization of solvent effects

## Indirect effects:

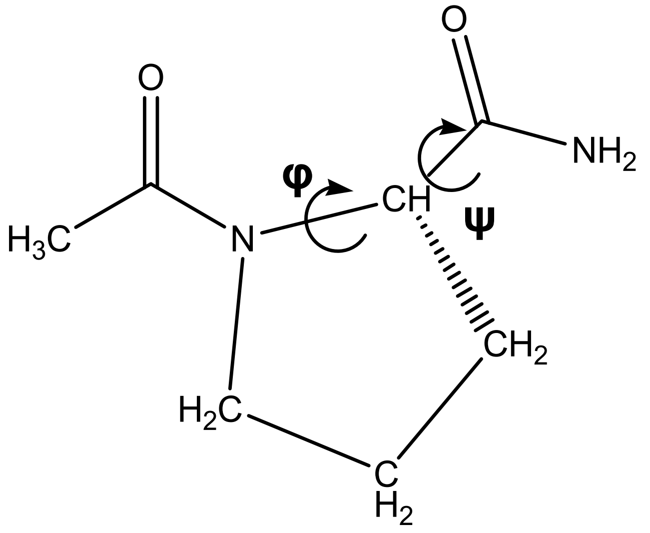
solvent induced changes in the solute geometry and/or in the relative energies of different conformers

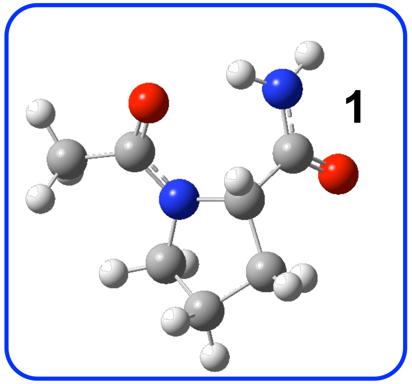
## Direct effects:

solvent induced changes in the solute electronic charge

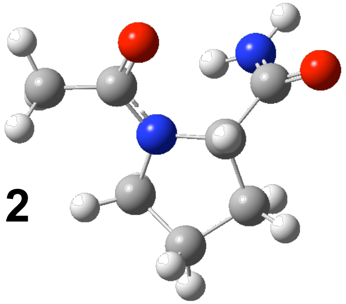
# Conformational analysis

N-Methyl Acetylproline Amide (NAP):
a simple model for peptides




1

In gas-phase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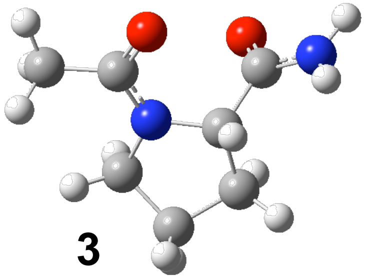

3

Boltzmann Populations (%)

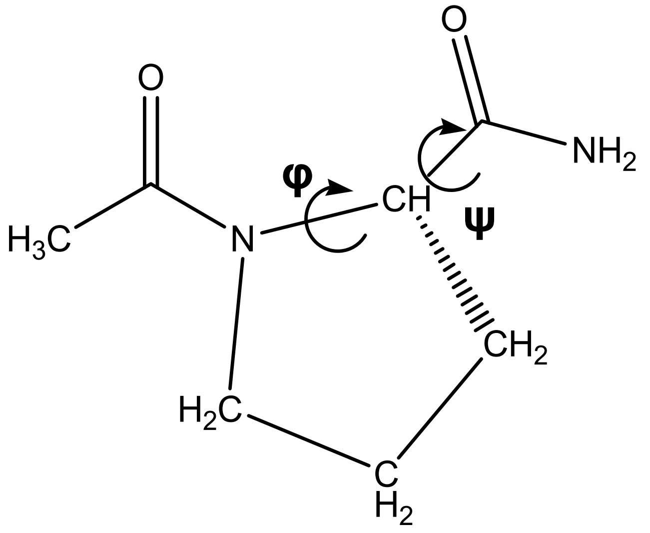
| | In gas-phase<br>B3LYP/6-311++G(d,p) |
|---|---|
| 1 | 99 |
| 2 | 1 |
| 3 | - |

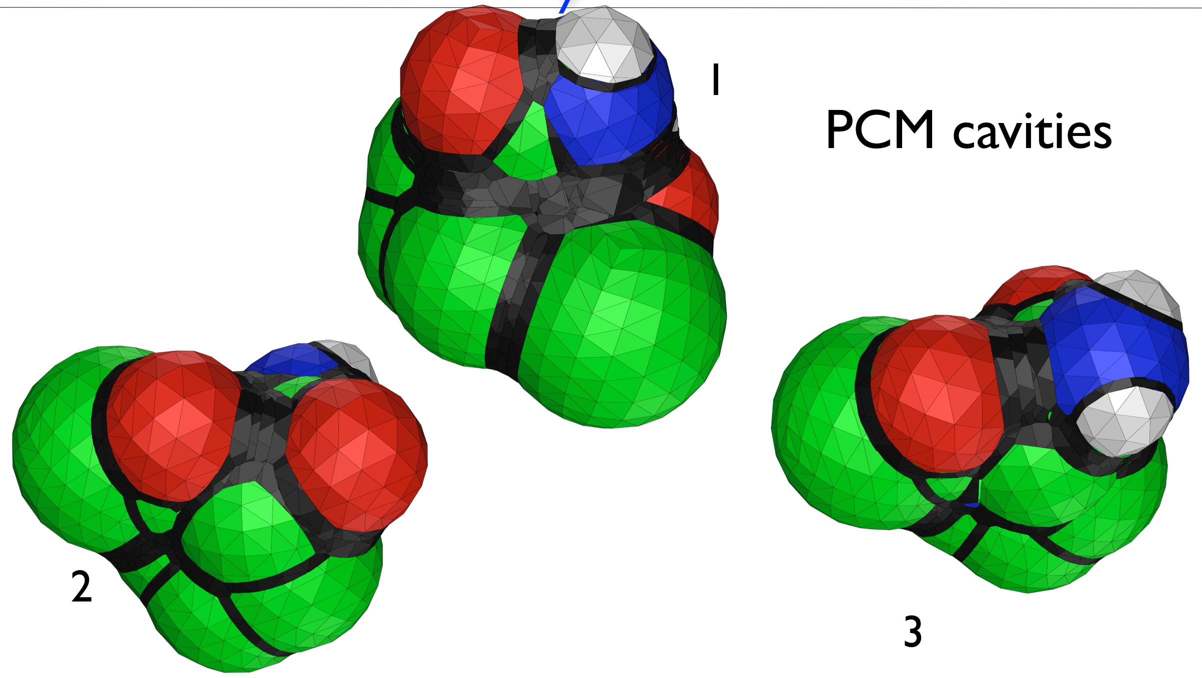
Conformer 1 dominates in **gas-phase** due to the presence of a stabilizing intra-molecular H-bond.

C. Cappelli and B. Mennucci J. Phys. Chem. B **2008**, 112, 3441

# Conformational analysis

N-Methyl Acetylproline Amide (NAP):
a simple model for peptides





PCM cavities

Boltzmann Populations (%)

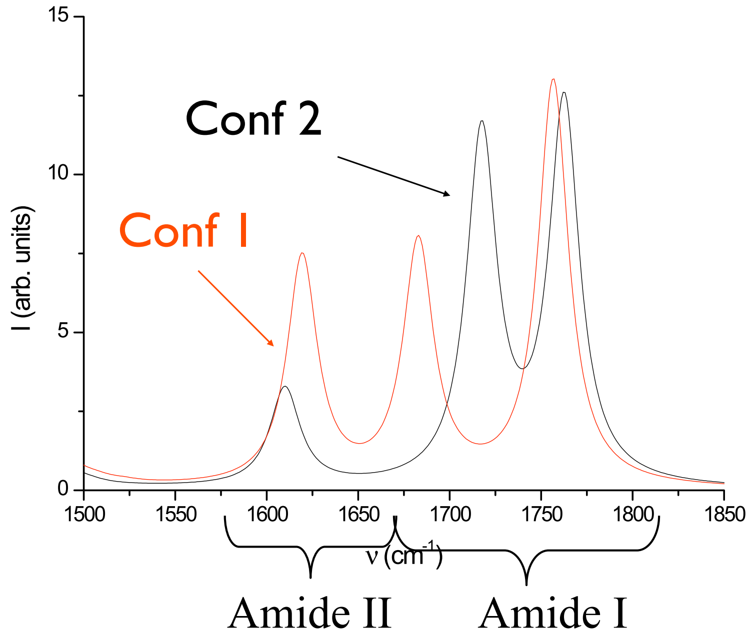
| | In gas-phase<br>B3LYP/6-311++G(d,p) | In water (PCM) |
|---|---|---|
| 1 | 99 | 4 |
| 2 | 1 | 28 |
| 3 | - | 68 |

In **water** the two other conformers become important: they present a better interaction with the solvent (polar groups are more exposed to the solvent)

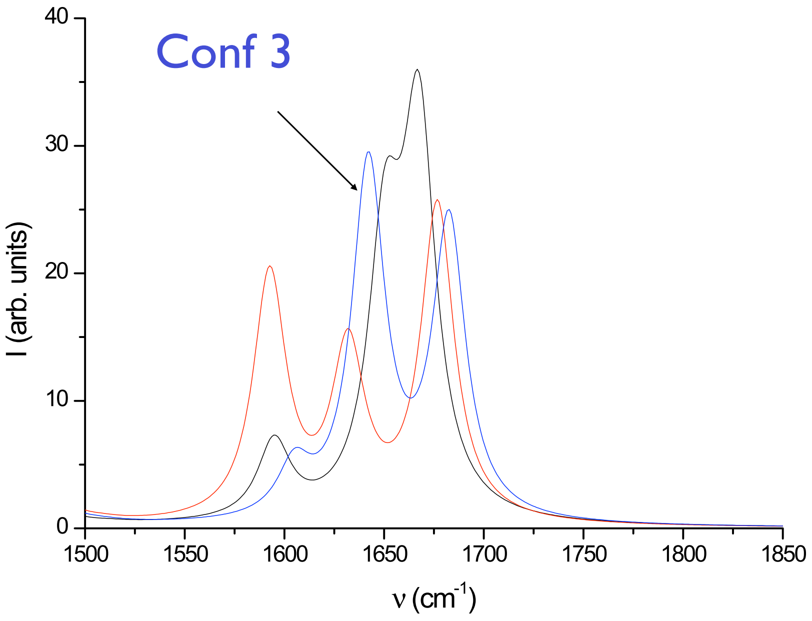
# Infrared spectra of single conformers: direct effects

**IR**

**In gas-phase**



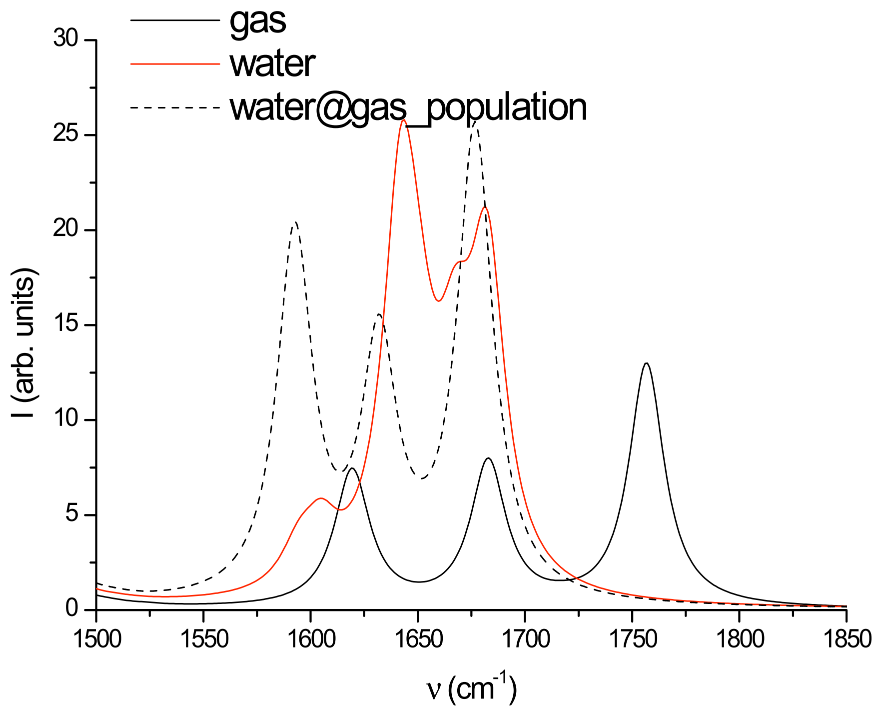
**In water**



B3LYP/6-311++G(d,p)

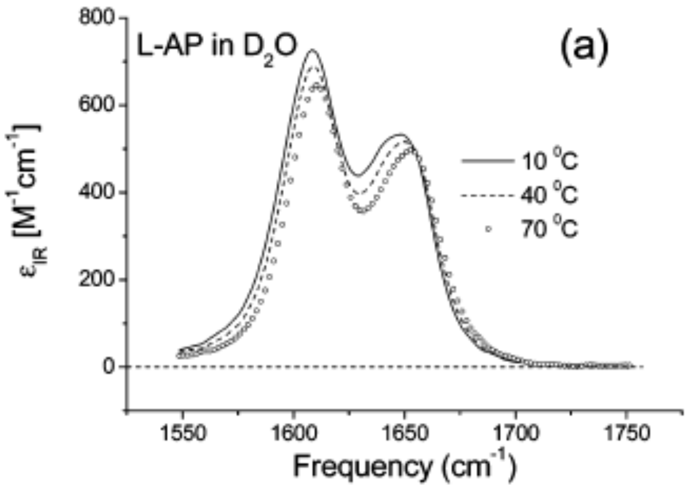
Both position and intensity of peaks
change passing from gas-phase to water

# Averaged Infrared spectra:
# direct vs indirect effects



B3LYP/6-311++G(d,p)

**EXP**



Exp taken from: Oh, K.-I.; Han, J.; Lee, K.-K.; Hahn, S.; Han, H.; Cho, M. J. Phys. Chem. B **2006**, 110, 13335–13365.

Only by combining direct and indirect (conformational) effects we can recover the full picture

# Molecular properties in solution: a schematization of solvent effects

## Indirect effects:

solvent induced changes in the solute geometry and/or in the relative energies of different conformers

## Direct effects:

solvent induced changes in the solute electronic charge

Bulk
versus
specific
effects

# Specific versus bulk solvation

Some questions need to be addressed:

- ✓ Does solvation at the solute surface differ from the bulk?
- ✓ Are there local rigid structures of solvent at the solute surface?

**If the answers are YES**

**Supermolecule**

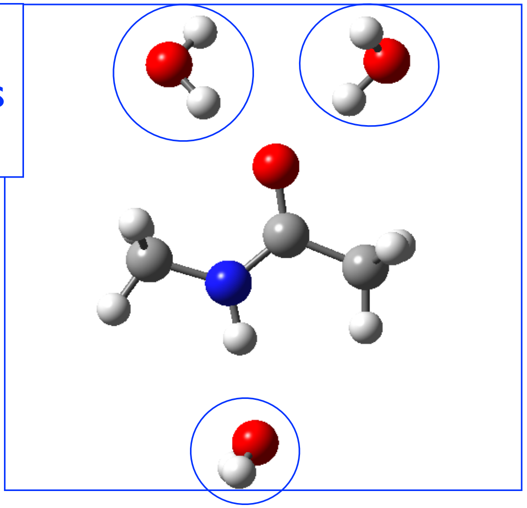
=

solute surrounded by some explicit solvent molecules

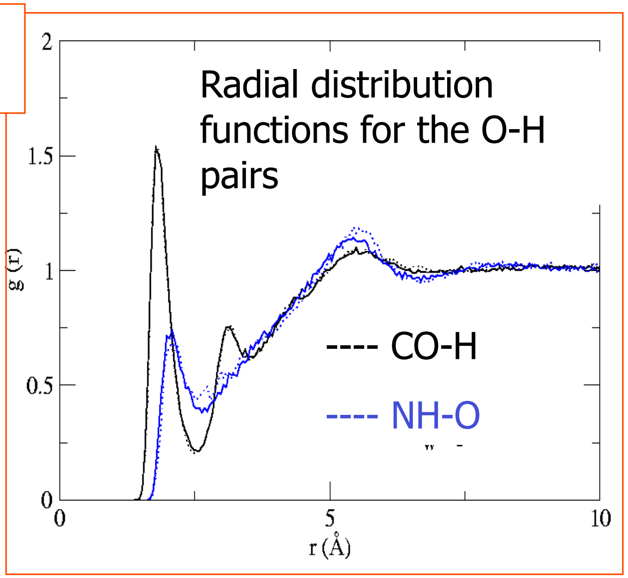
# The Supermolecule

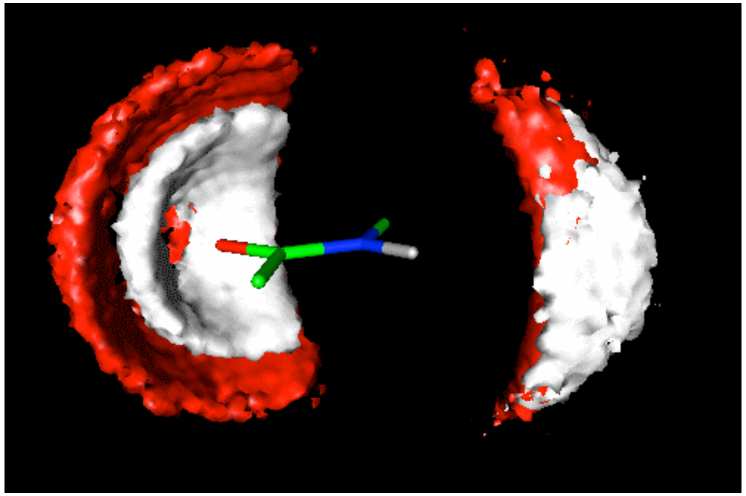
## How many explicit solvent molecules are needed?

From the chemical analysis of the system



From MD simulations





# The Supermolecule

## Which configuration?

- From QM geometry optimization: the most stable configuration

  Proper description for strongly interacting solute-solvent systems giving rise to stable clusters (example: strong H-bonded clusters)

- From MD simulations:

  More general than the QM optimization.

  Better for weaker solute-solvent interactions described by a more dynamic situation.

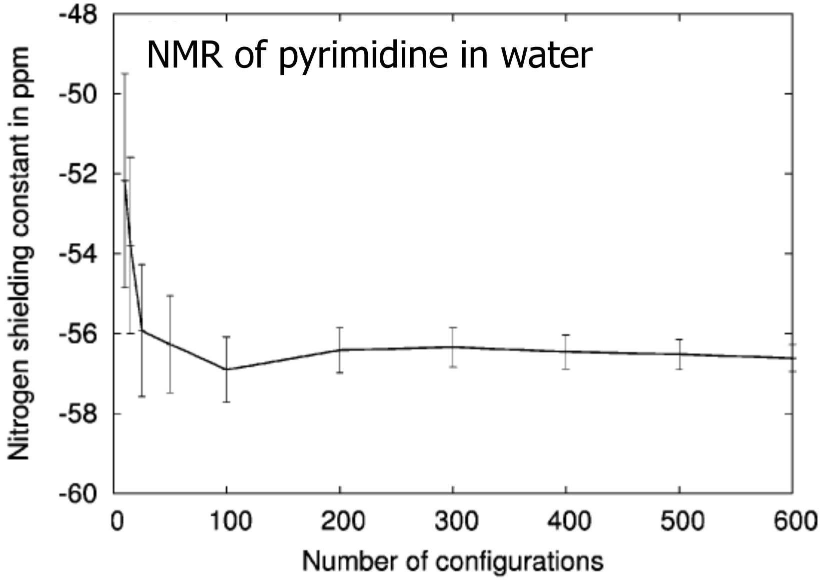
# Clusters from MD simulations

## Advantage

Proper description of weaker solute-solvent specific interactions which cannot be represented by a single configuration obtained from a QM geometry optimization

## Disadvantage

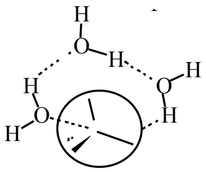
Calculations of the property of interest have to be repeated for many different clusters so to obtain statistically meaningful average value



# Long range effects

## How can we include long-range effects?

- **Enlarging the dimension of the supermolecule:**



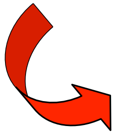
Problems:

1. By increasing the dimensions, the accuracy of the QM level has to be reduced (or a QM/MM model has to be introduced)
2. The issue of the statistical representativity becomes more problematic

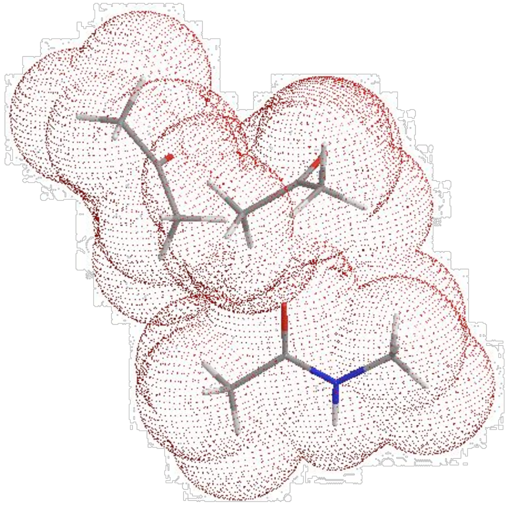
# Long range effects

## How can we include long-range effects?

- Adding an "external" continuum:



the solvated supermolecule



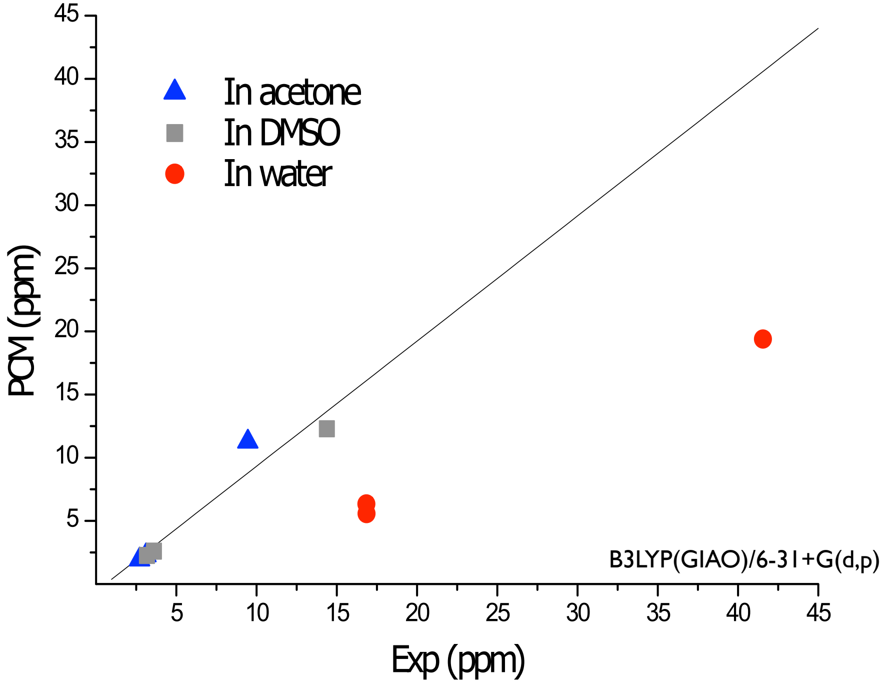
The two problems disappear:

1. The dimensions do not increase, we do not need to reduce the accuracy of the QM level, or to shift to an hybrid QM/MM method
2. The statistical representativity is automatically satisfied by using the continuum description in terms of the solvent bulk properties.

# Specific vs. Long range effects

## A simple but clear example: $^{15}N$ nuclear shieldings of diazines in solution

### A continuum-only approach



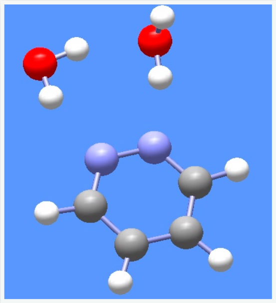
In **water** the calculated values are smaller than what observed:

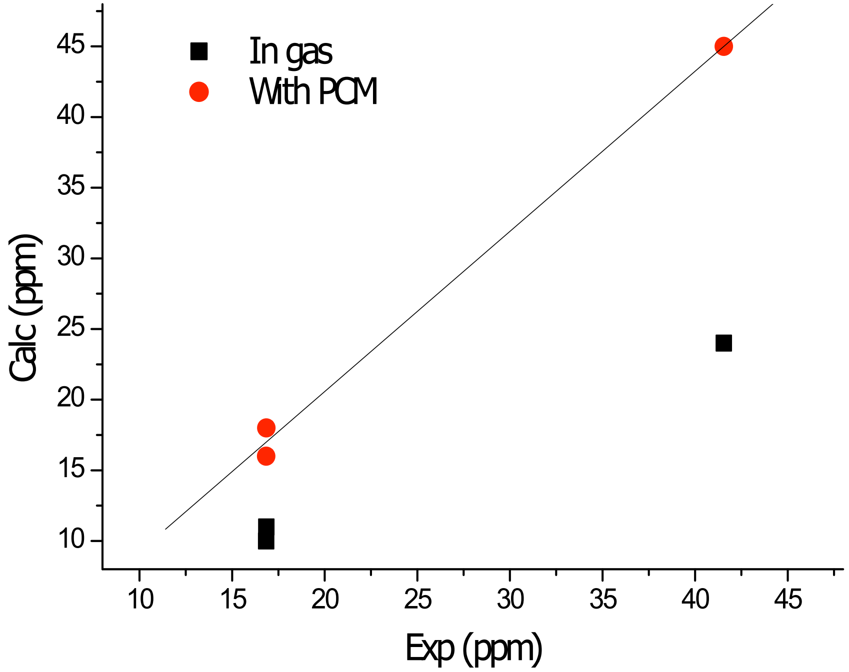
a part of the solvent effect is missing

Mennucci, B. J. Am. Chem. Soc. 2002, 124, 1506

In water:

QM optimized supermolecule





Specific effects are now correctly accounted for but only with inclusion of bulk effects (solvated supermolecule) the solvent effect is fully reproduced

# Solvent effects on molecular properties: “global” versus “local” sensitivity

Solvent effects are difficult to define:

they act differently on different quantities

✓ Solvation free energies are generally “globally” sensitive:

they are properly described by a continuum model even when specific effects are present

✓ Molecular response properties are generally “locally” sensitive:

they often require to move from a pure continuum to a mixed discrete/continuum model

# Beyond ground state

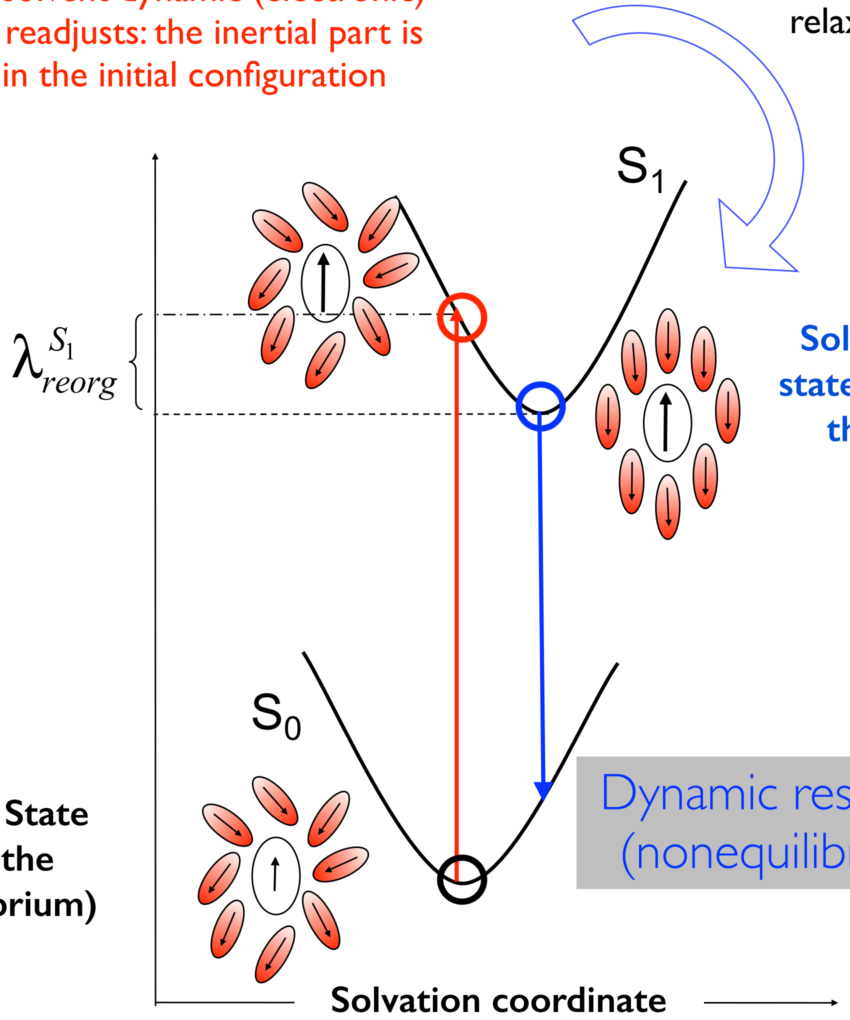
# Electronic transitions in solvated molecules

In a polar solvent

Dynamic response (nonequilibrium)

Only the solvent dynamic (electronic) response readjusts: the inertial part is frozen in the initial configuration

Orientational relaxation



Solvent reorganization energy

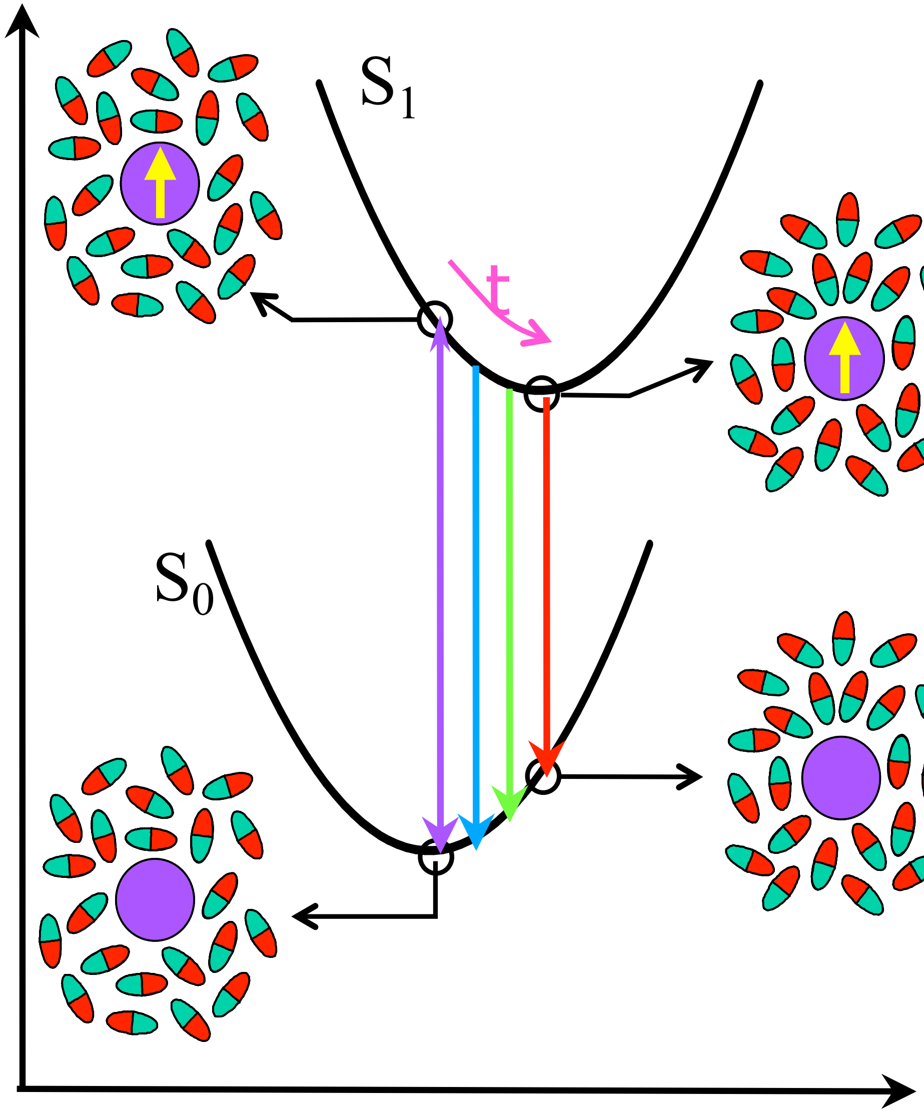
**Solute in its excited state equilibrated with the environment**

**Solute in its ground State equilibrated with the environment (equilibrium)**

Dynamic response (nonequilibrium)

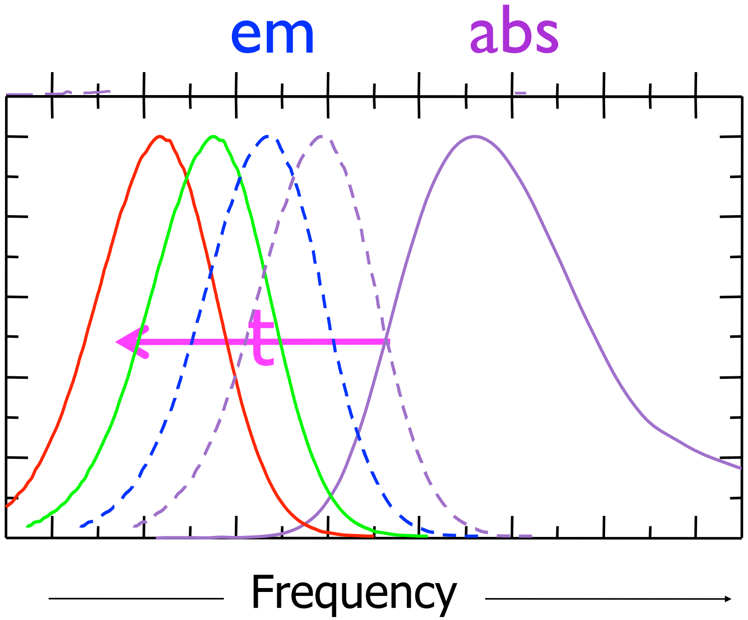
# Nonequilibrium & solvation dynamics

In a polar solvent



Solvation Coordinate

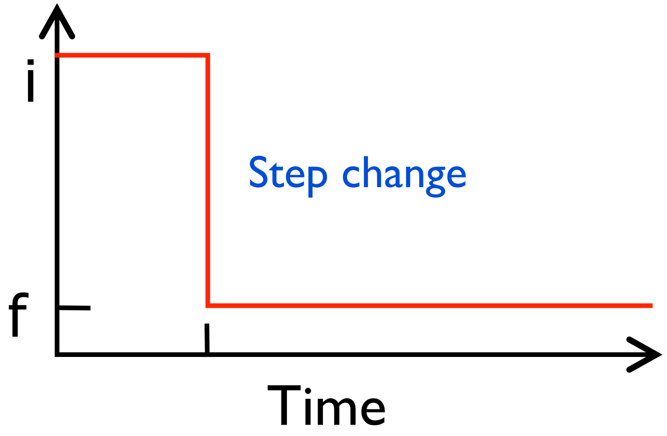
The experimental evidence:
time-dependent Stokes shift



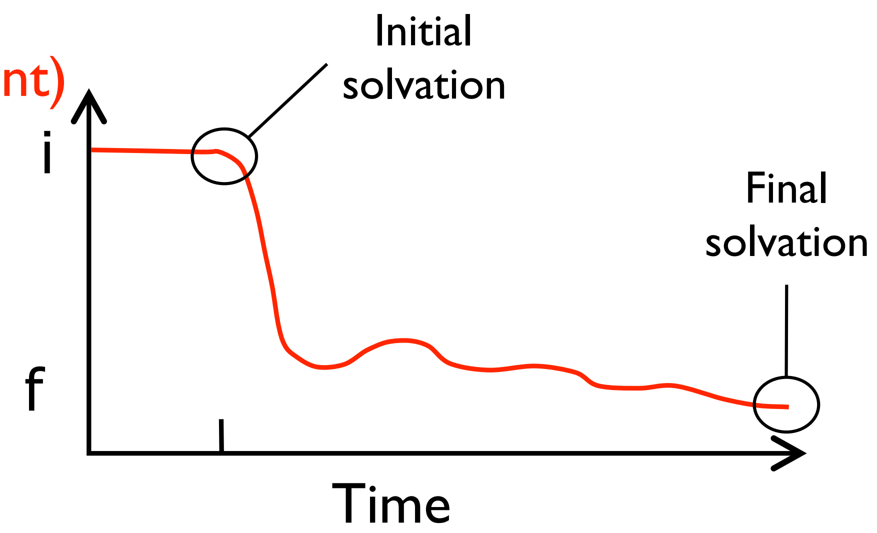
$$S(t)=\frac{\nu(t)-\nu(\infty)}{\nu(0)-\nu(\infty)}$$

# Solvation dynamics & polarization

Solute Perturbation



Solvation Response (polar solvent)



## Solvent Polarization

$$\vec{P}(t)=\int_{-\infty}^{t}\underbrace{\chi(t-t')}\vec{E}(t')\,dt' \xrightarrow{\text{Convolution}} \vec{P}(\omega)=\frac{\varepsilon(\omega)-1}{4\pi}\vec{E}(\omega)$$

Time-dependent dielectric response

Frequency-dependent permittivity

# Solvation dynamics: the Debye model

Dielectric relaxation response of an ideal, noninteracting population of dipoles to an alternating external electric field:

Polarisation decays exponentially with one relaxation time $\tau_D$

The resulting permittivity

$$\varepsilon(\omega) = \boxed{\varepsilon(\infty)} + \boxed{\frac{\varepsilon(0) - \varepsilon(\infty)}{1 + i\omega\tau_D}}$$

Fast
(electronic)
response

Relaxation
(orientations)

# Solvent polarization

**Deformation (induced) polarization**

Nuclei & electrons in the solvent molecules are displaced under the influence of external electric field.

**Orientation (dipole) polarization:**

If the solvent molecules have a permanent dipole moment, the electric field tends to orient such dipoles.

An effective modelization

$$\overrightarrow{P} \approx \overrightarrow{P}_{ele/dyn} + \overrightarrow{P}_{or/in}$$

Electronic/dynamic (deformation) polarization

Orientational/inertial polarization (only for **polar solvents**)

$$P_{dyn}(\varepsilon(\infty))$$

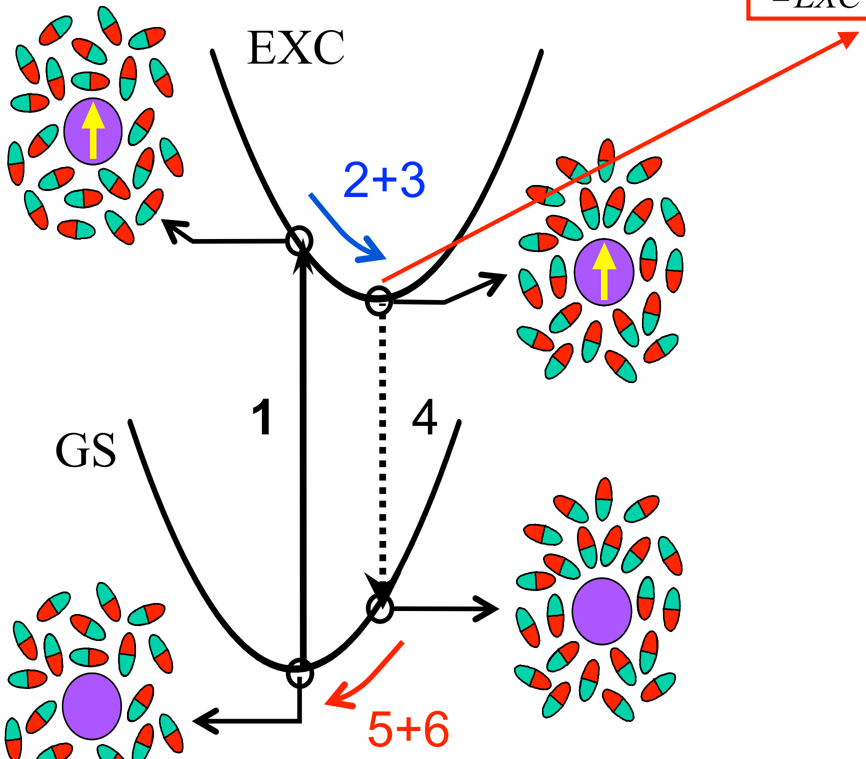
$$P(\varepsilon) - P_{dyn}(\varepsilon(\infty))$$

# Solvent polarization: the ASC formulation

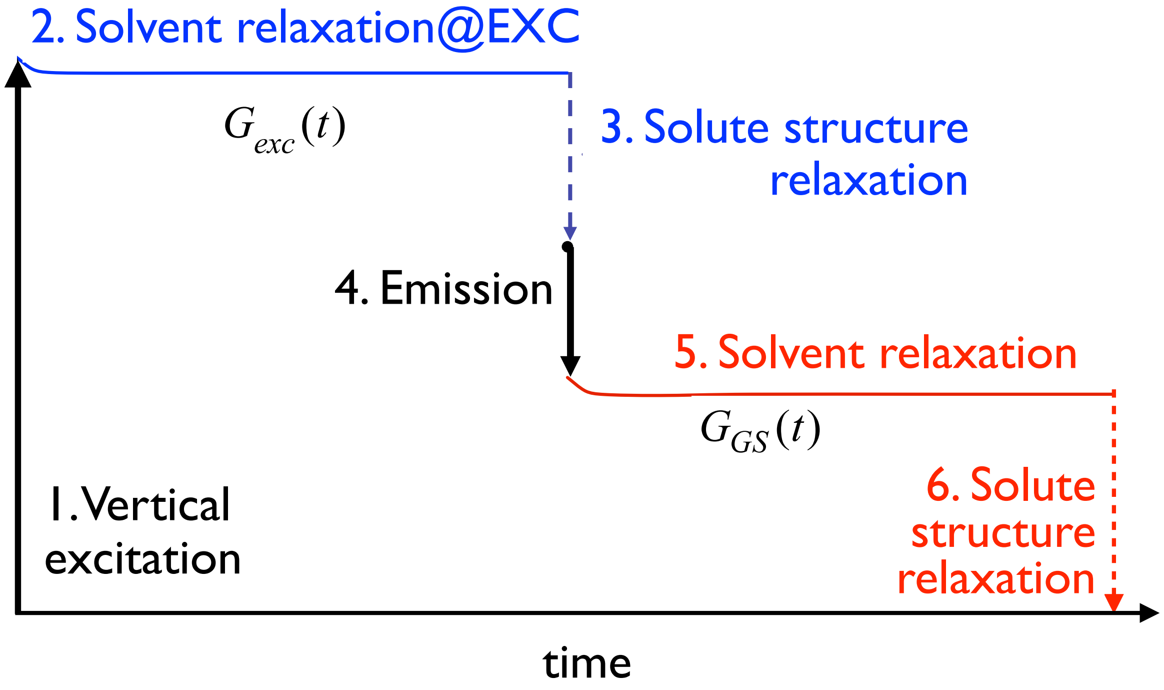
**Apparent surface charges for the vertical excited state**

$$\boxed{\begin{aligned}\mathbf{q}_{EXC}(t=0) &= \mathbf{q}^{neq}_{EXC} \\ &= \mathbf{q}^{in}_{GS} + \mathbf{q}^{dyn}_{EXC}\end{aligned}}$$

$$\boxed{\mathbf{q}_{EXC}(t\to\infty) = \mathbf{q}^{eq}_{EXC}}$$



$$\mathbf{q}^{eq}_{GS} = \mathbf{q}^{in}_{GS} + \mathbf{q}^{dyn}_{GS}$$



2. Solvent relaxation@EXC

$G_{exc}(t)$

3. Solute structure relaxation

4. Emission

5. Solvent relaxation

$G_{GS}(t)$

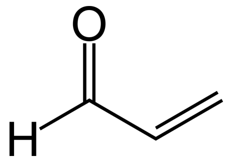
6. Solute structure relaxation

1.Vertical excitation

time

# Equilibrium vs Nonequilibrium

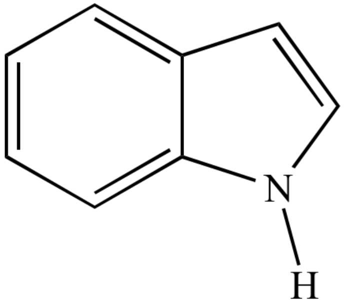
## Acrolein: solvatochromic shifts (acetonitrile-cyclohexane)



|  | n-π* | π- π* |
|---|---|---|
| Exp | +0.23 | -0.21 |
| neq | +0.21 | -0.22 |
| eq | -0.03 | -0.56 |

PCM EOM-CC/6-31+G(d)

## Indole: solvatochromic shifts (water-cyclohexane)



|  | $L_a$ | $L_b$ |
|---|---|---|
| Exp | -0.01 | -0.06 |
| neq | +0.02 | -0.07 |
| eq | 0 | -0.44 |

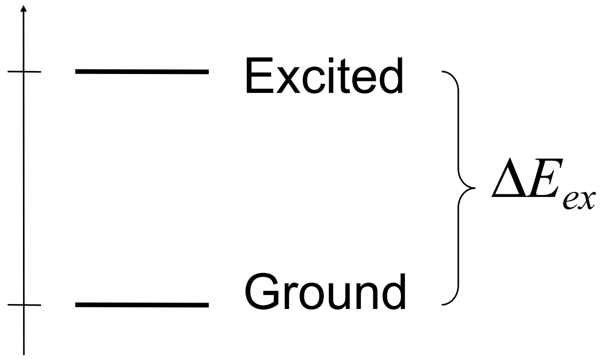
PCM EOM-CC/6-31+G(d)

Two nearly degenerate electronic states ($L_a$, $L_b$) with perpendicular transition moments

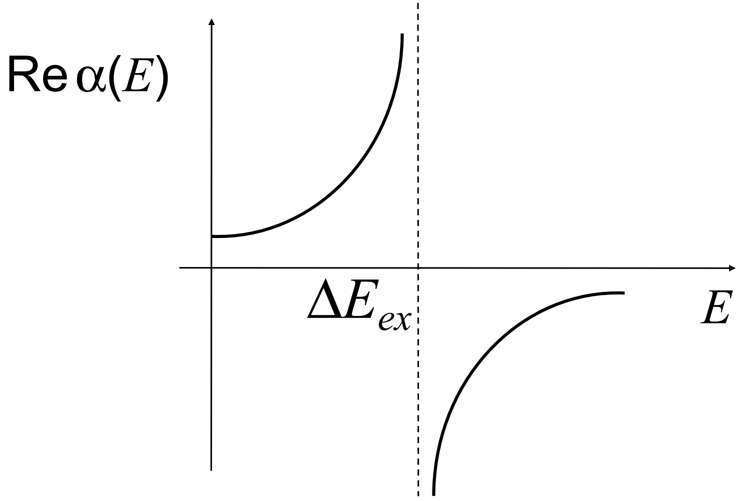
Inversion of the order in the electronic states ($L_a < L_b$) in water with equilibrium

# Electronic excitations: which QM approach?

- State Specific (SS):
  - The wavefunction of the excited state is explicitly calculated together with the energy
  - CASSCF, CI, ….



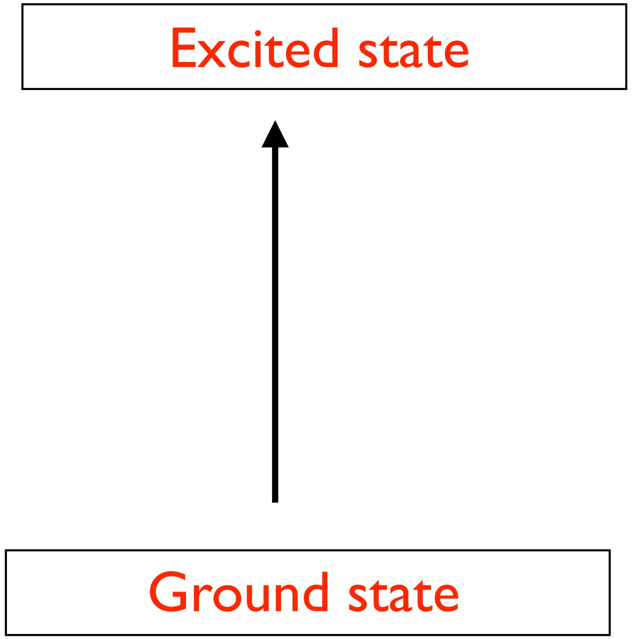
- Linear Response (LR)
  - Excitation energies as poles of a linear response function of the molecule, no need of the excited state wavefunction
  - TDDFT, EOM-CC , ...



For isolated systems the two approaches are "equivalent" (in the limit of exact states).

Is that still valid for solvated systems?

# The State-Specific (SS) formulation



Excited state

$$E_{exc};\mathbf{P}_{exc} \Leftrightarrow \mathbf{q}_{in}^{ASC}(\mathbf{P}_{GS})+\mathbf{q}_{dyn}^{ASC}(\varepsilon_{\infty};\mathbf{P}_{exc})$$

Energy & density are obtained self-consistently with the environment response for both ground & excited states

Ground state

$$E_{GS};\mathbf{P}_{\mathrm{GS}} \Leftrightarrow \mathbf{q}^{ASC}(\varepsilon;\mathbf{P}_{GS})$$

A nonequilibrium scheme is used

The inertial response remains frozen in the GS

The dynamic response relaxes in the EXC

# The linear response formulation

The TDDFT version

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) + (ia|f_{\mathrm{xc}}|jb)$$

$$B_{ia,jb} = (ia|bj) + (ia|f_{\mathrm{xc}}|bj)$$

$$\underset{K_{ia,jb}}{\boxed{(ia\,|\,jb) + \left(ia\middle|\, f_{xc} \,\middle|\, jb\right)}} = \int d\vec{r}\,' \int d\vec{r}\, \phi_i^*(\vec{r})\phi_a(\vec{r}) \left[ \frac{1}{\left|\vec{r} - \vec{r}\,'\right|} + \frac{\delta^2 E_{xc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')} \right] \phi_j^*(\vec{r}\,')\phi_b(\vec{r}\,')$$

# The solvated TDDFT

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Orbitals $\varphi_r$ and orbital energies $\varepsilon_r$ are obtained in the presence of the environment

$$\begin{cases} A_{ia,jb} = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + K_{ia,jb} + C^{Env}_{ai,jb} \\ B_{ia,bj} = K_{ia,bj} + C^{Env}_{ai,bj} \end{cases}$$

Additional term induced by the environment response

$$C^{env}_{ai,jb} = \int d\vec{r}\,\phi_i^*(\vec{r})\phi_a(\vec{r}) \sum_l q_l^{ASC}\left[\phi_j^*\phi_b\right] \frac{1}{\left|\vec{r} - \vec{s}_l\right|}$$

The response of the solvent to the excitation is obtained using a “transition density”

The LR approach is not equivalent to SS (when the embedding is polarizable)

# Can we recover a state-specific response within a TDDFT scheme?

## TDDFT densities

Transition density matrix

$$T^{TDDFT}_{\mu\nu} = \sum_{ia} \left( X_{ia} + Y_{ia} \right) c_{\mu i} c_{\nu a}$$

Transition properties

From Ground State density matrix …

$$\mathbf{P}_{GS}$$

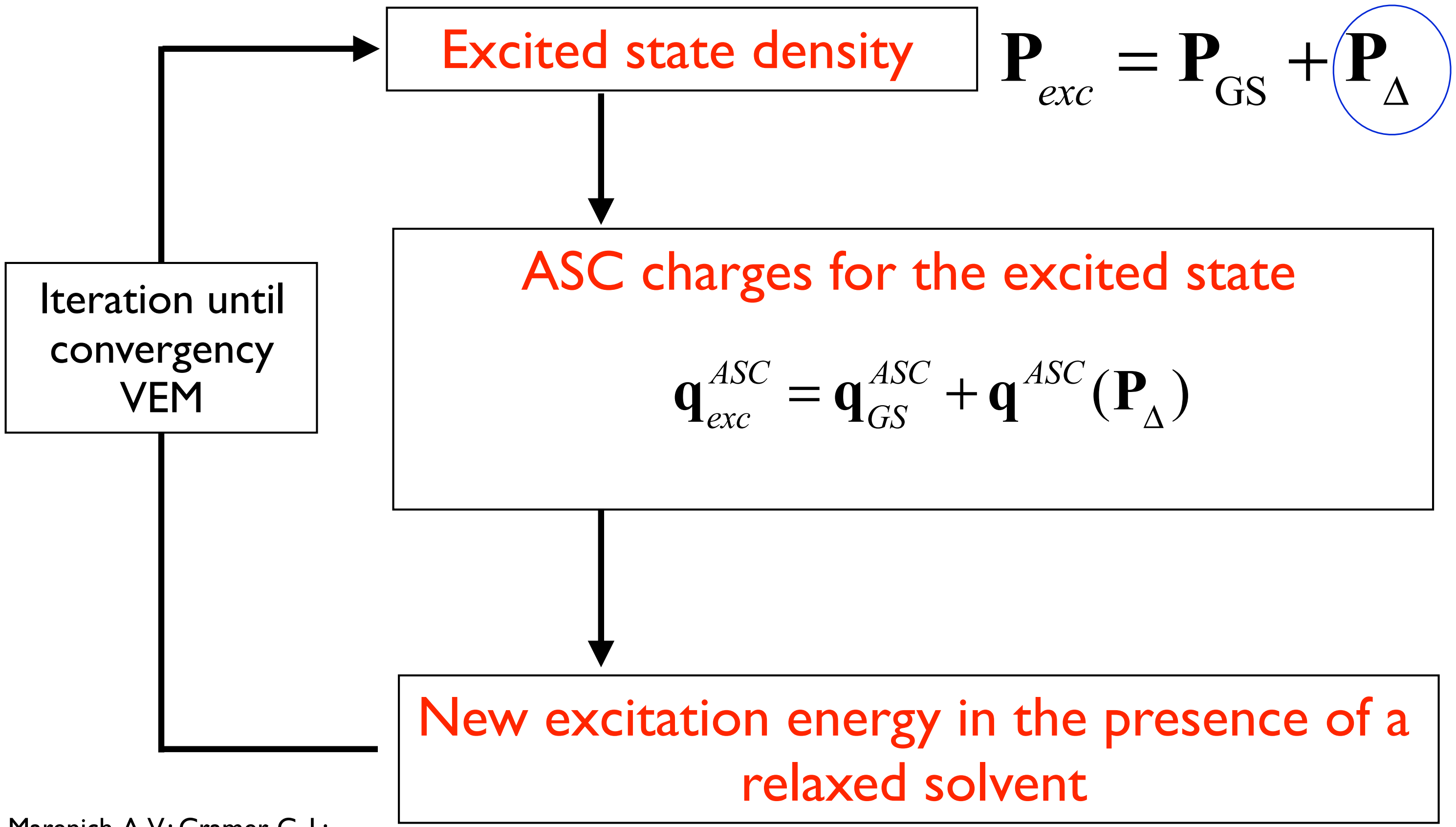
… to Excited State density matrix

$$\mathbf{P}_{EX} = \mathbf{P}_{GS} + \mathbf{P}^{\Delta}$$

$$P^{\Delta}_{\mu\nu} = \sum_{pq} P^{\Delta}_{pq} c_{\mu p} c_{\nu q} \quad \left\{ \begin{array}{ll} P^{\Delta}_{ij} = -\frac{1}{2} \sum_{a} \left( Y_{ai} Y_{aj} + X_{ia} X_{ja} \right) & \text{occ-occ} \\ P^{\Delta}_{ab} = \frac{1}{2} \sum_{i} \left( Y_{ai} Y_{bi} + X_{ia} X_{ib} \right) & \text{virt-virt} \\ P^{\Delta}_{ia} = -Z_{ia} & \text{occ-virt: Zeta-Vector contribution} \end{array} \right.$$

# Can we recover a state-specific response within a TDDFT scheme?

We start from an "unrelaxed" excitation energy obtained with the solvent polarization frozen in the ground state



Excited state density

$$\mathbf{P}_{exc} = \mathbf{P}_{GS} + \boxed{\mathbf{P}_{\Delta}}$$

ASC charges for the excited state

$$\mathbf{q}_{exc}^{ASC} = \mathbf{q}_{GS}^{ASC} + \mathbf{q}^{ASC}(\mathbf{P}_{\Delta})$$

New excitation energy in the presence of a relaxed solvent

Iteration until convergency VEM

Marenich, A.V.; Cramer, C. J.; Truhlar, D. G.; Guido, C. A.; Mennucci, B.; Scalmani, G.; Frisch, M. J. Chem. Sci. 2011, 2 , 2143

First-order correction: cLR

Caricato, M.; Mennucci, B.; Tomasi, J.; Ingrosso, F.; Cammi, R.; Corni, S.; Scalmani, G. J. Chem. Phys. 2006, 124, 124520

# Linear Response vs. State-Specific solvation

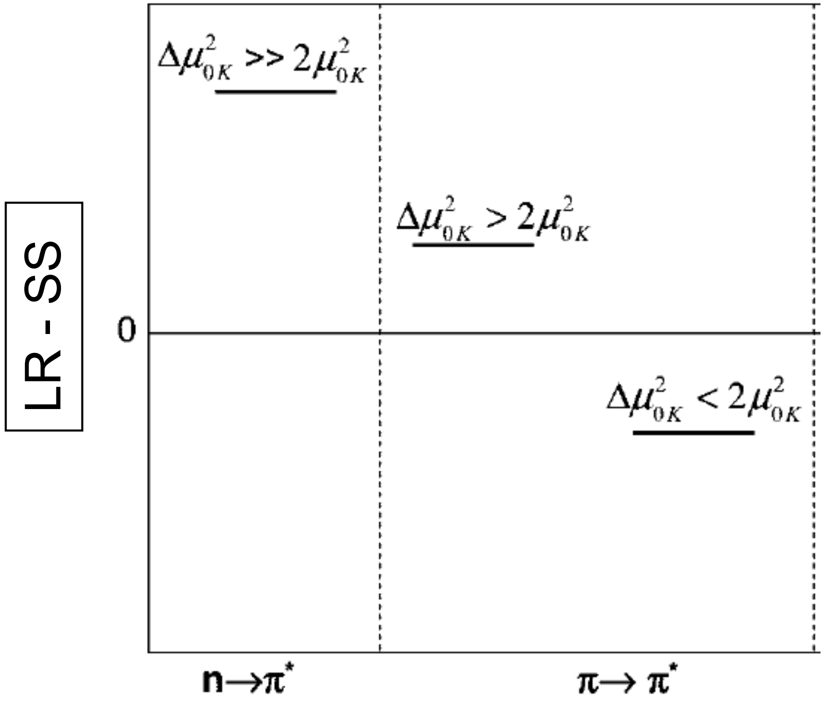
Cammi, R.; Corni, S.; Mennucci, B.; Tomasi, J. J. Chem. Phys. 2005, 122, 104513

Corni, S.; Cammi, R.; Mennucci, B.; Tomasi, J. J. Chem. Phys. 2005, 123, 134512

Lunkenheimer, B.; Köhn, A. J. Chem. Theory Comput. 2013, 9, 977

Schwabe, T. J. Chem. Phys. 2016, 145, 154105

An analysis based on the difference between the variation of the dipole from GS to Exc and the corresponding transition dipole



SS effects are dominant for excitations involving an important charge redistribution

LR effects are dominant for very bright excitations (without important charge redistributions)

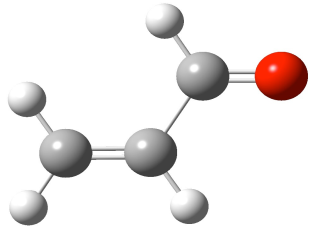
# Linear Response vs. State-Specific solvation

Frozen Solvent

LR/SS response

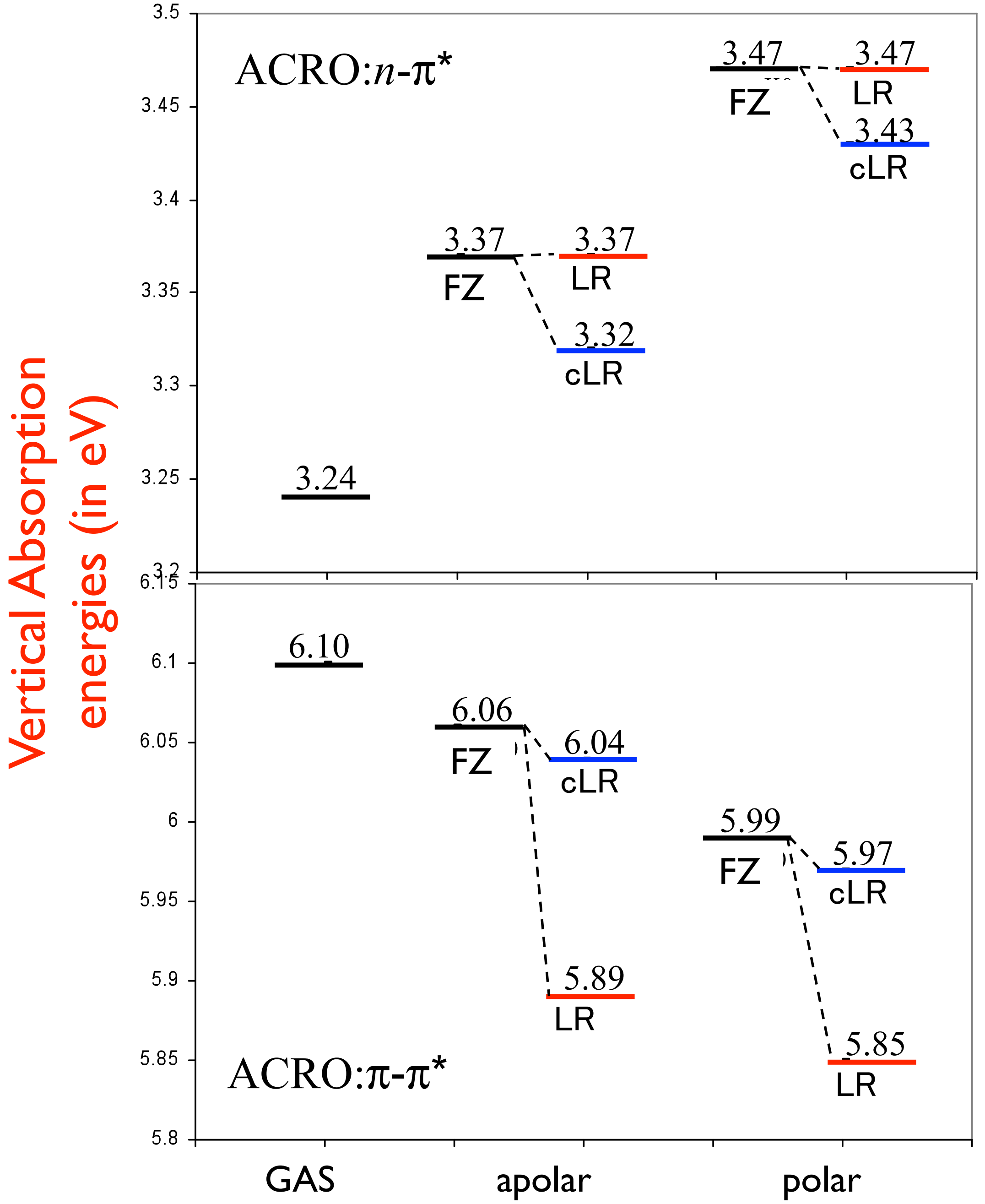
$$\omega_{0i}^{\mathrm{LR}} = \omega_{0i}^{(0)} + R^{\mathrm{LR}}(X_{0i}),$$

$$\omega_{0i}^{\mathrm{SS}} = \omega_{0i}^{(0)} + R^{\mathrm{SS}}(P_{0i}^{\Delta}),$$

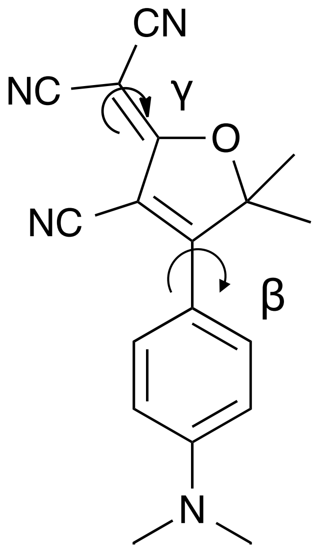


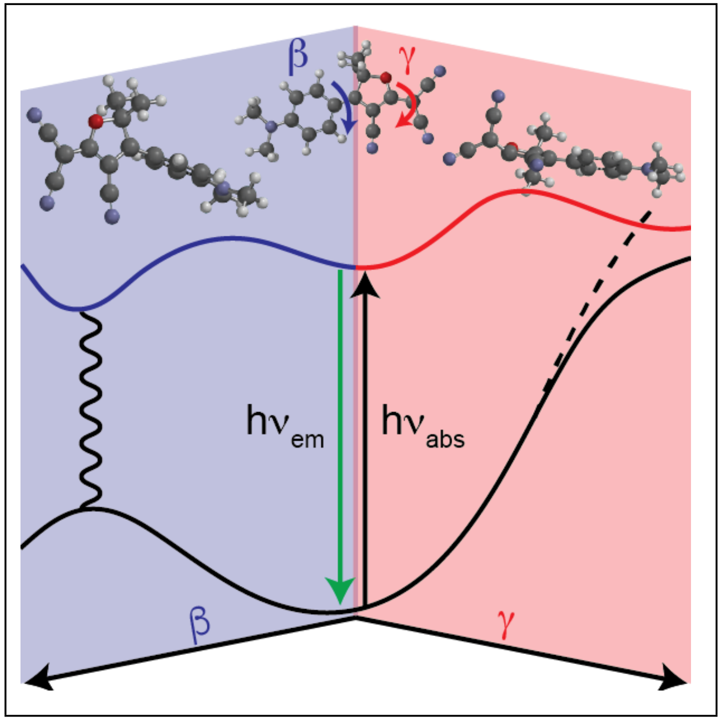
ACRO (CIS/PCM)

| | $n \rightarrow \pi^*$ | $\pi \rightarrow \pi^*$ |
|---|---|---|
| $\Delta\mu_{0i}$ | 4.169 | 2.296 |
| $\mu_{0i}$ | 0.000 | 5.412 |



# Excited-State Decay Pathways of Molecular Rotors





Polar solvent

Apolar solvent

EXPERIMENTALLY:

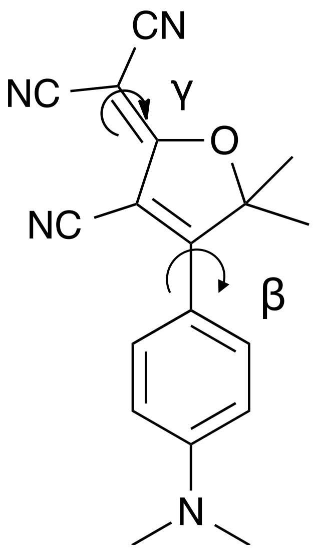
In **nonpolar solvents** relaxation occurs by twisting about C=C (γ) bond.

**Polar solvents** hinder this twist but allow a new deactivation pathway that leads to a dark intermediate β twisted ICT state from which the nonradiative relaxation occurs.

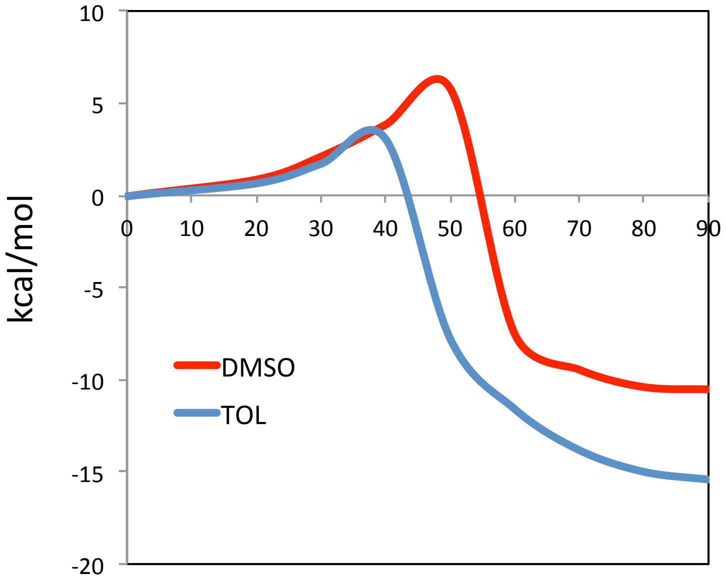
Suhina, T.; Amirjalayer, S.; Mennucci, B.; Woutersen, S.; Hilbers, M.; Bonn, D.; Brouwer, A. M. J. Phys. Chem. Lett. 2016, 7, 4285

# Excited-State Decay Pathways of Molecular Rotors

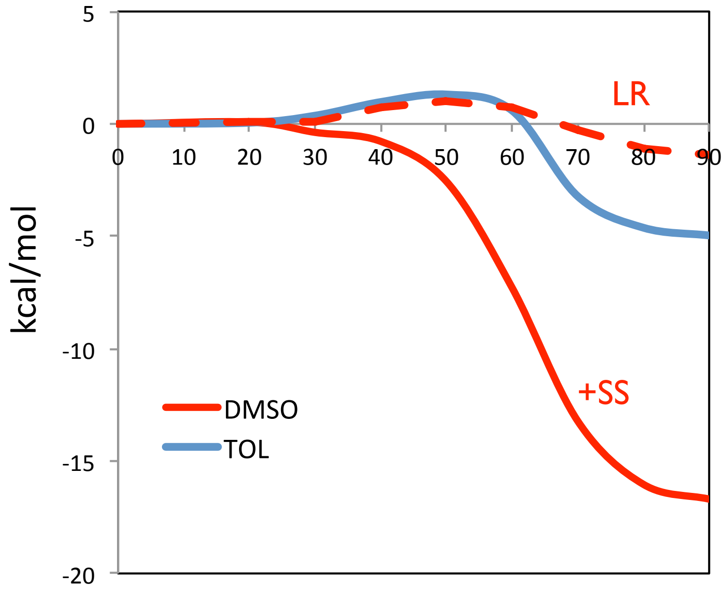
## The PCM results



Relaxed SCAN of $S_1$ along γ



Relaxed SCAN of $S_1$ along β



TDCAM-B3LYP/6-31+G(d)

**The polar DMSO** hinders the γ twist in favor of the deactivation pathway through the β twisting

BUT

only allowing the excited state polarization to relax (+SS)
we can get the right picture