Solvent Effects in MOLCAS

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1.- Effects of solvation on the potential energy surfaces

Solvatochromic effect: $\Delta E_{solvated} = \Delta E_{gas} + \Delta G^{*}_{excited} - \Delta G_{ground}$

2.- Reaction Field Methods: cavity + dielectric continuum

Spherical cavities: Kirkwood model
Adapted cavities: Polarized Continuum Model (PCM)

3.- More advanced models:

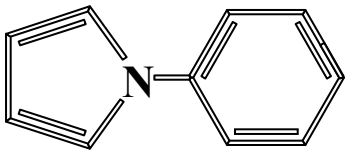
QM/MM, etc

Solvent Effects in Photophysics

Photoadiabatic reactions and the TICT phenomenon

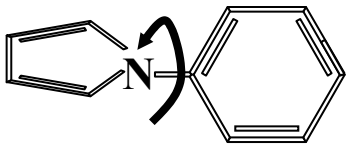
N-phenilpyrrole

~0º



S_1 LE (C_2)

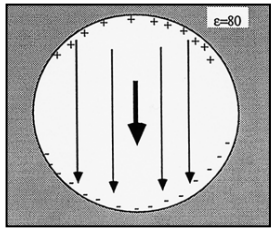
90º



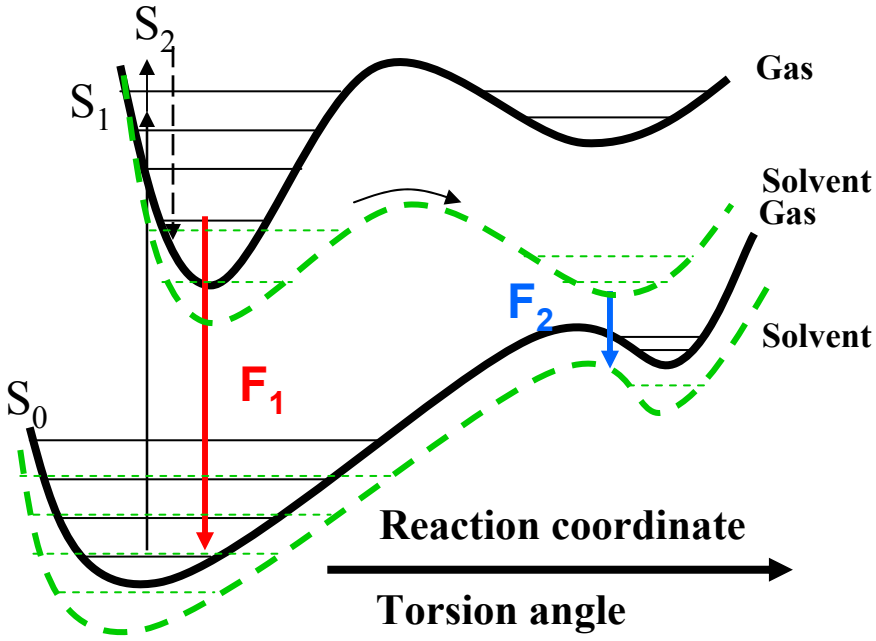
S_1 TICT (C_{2v})

TICT (Twisted Intramolecular Charge Transfer)

Gas phase	LE (C_2)	TICT (C_{2V})
Theo Dip (D)	-0.81	10.2
Max. Emi. (eV)	4.07	4.64
Exp (eV)	**4.08 (F_1)**	



Acetonitrile	LE (C_2)	TICT (C_{2V})
Theo Dip (D)	-1.14	13.4
Max. Emi.(eV)	4.07	3.72
Exp (eV)	**4.05 (F_1)**	**3.65 (F_2)**



CASSCF/CASPT2, B. Proppe *et al.*, *J. Phys. Chem. A.* 104, 1608 (2000)

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2.- Reaction Field Methods: cavity + dielectric continuum

Spherical cavities: Kirkwood model

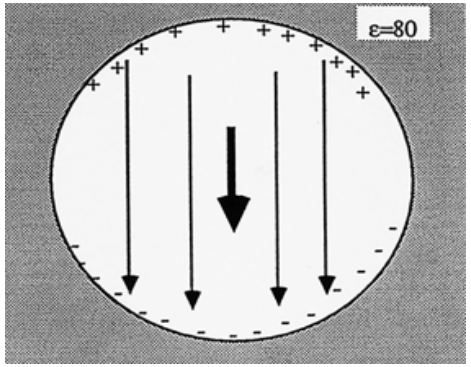
Adapted cavities: Polarized Continuum Model (PCM)

3.- Further models:

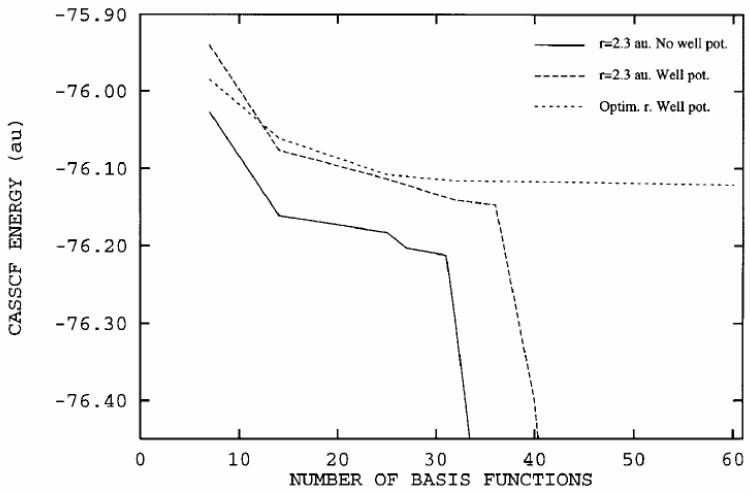
QM/MM, etc

Reaction Field Methods: cavity + dielectric continuum

Methods that surround the quantum problem with electric fields, charges, dipoles or polarizabilities. ***Implicit models: Reaction Field methods,PCM, etc***

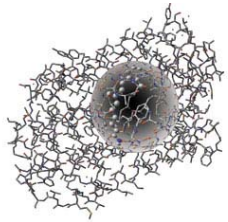


- The environment is simulated by a polarizable continuum out of the cavity
- The continuum can be a dielectric, distributed polarizabilities, etc.
- The molecule reacts to the surroundings and create a reaction field which mimics the solvent effect.



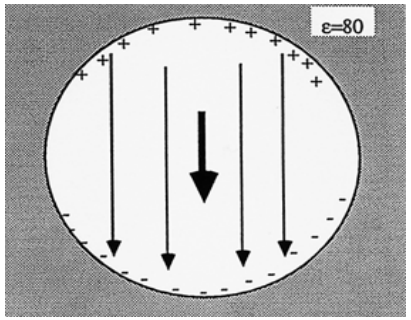
- Energetic collapse: if large basis are used the charge can be placed outside the cavity boundaries, and the energy may collapse
- In general the result depends on the cavity size and they are basically qualitative

- Improvements: supermolecule approach (explicit solvation shell)



Reaction Field Methods: cavity + dielectric continuum

Onsager-Kirkwood Model: $H = H_0 + H_{RF} + H_{WP}$



- Spherical cavity (r = a) sorrounded by a dielectric continuum

$$E = E^0 - \frac{1}{2}\sum_{l,m} M_l^m F_l^m, \qquad F_l^m = c_l M_l^m$$

$$c_l(\epsilon) = -\frac{l!(l+1)(\epsilon-1)}{(l+1)\epsilon + l}\frac{1}{a^{2l+1}}$$

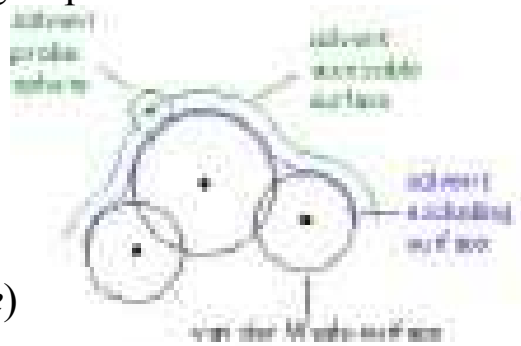
- Penalty gaussian functions (well potential) to avoid charge outside the cavity

$$E_{ex} = \iiint \rho(r,\theta,\phi) f(r)\, d\phi\, d\theta\, dr. \qquad f(r) = \sum_i \beta_i \exp\left(\alpha_i (r - R_i)^2\right)$$

Reaction Field Methods: cavity + dielectric continuum

Polarizable Continuum Model (PCM):

- Cavities as envelope of spheres centered on solute atoms or atomic groups
  - Pauling radii
  - UATM (united atom topological model) radii (default)
  - input sphere radii



- Solvation charges placed in the middle of small tiles (*tesserae*) drawn on the surface; the number of solvation charges can be gauged by changing the average area of tesserae (AAre in **SEWARD**).

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

$$E_{int}=\mathbf{V}^{\dagger}\mathbf{q}=\sum_{\mathbf{i}}^{\mathbf{N_{TS}}}\mathbf{V_i q_i} \qquad\qquad \mathcal{G}=E[\rho]+V_{NN}+\frac{1}{2}E_{int}$$

Solvent Effects for Excited States Nonequilibrium

Total reaction field of the ground state:

$$H_{\mathrm{RF,init}} = c_l(\epsilon_0) M^m_{l,\mathrm{init}}$$

Total reaction field of the excited state:

$$H_{\mathrm{RF}} = H_{\mathrm{RF,iner}} + H_{\mathrm{RF,op}}$$

$$E^{\mathrm{neq}}_{\mathrm{sol}} = \sum_{lm} F^m_{l,\mathrm{op,fin}} M^m_{l,\mathrm{fin}} + \sum_{lm} F^m_{l,\mathrm{iner,init}} [2M^m_{l,\mathrm{fin}} - M^m_{l,\mathrm{init}}]$$

- Inertial or low response: reaction field of the fixed nuclei after excitation or emission

  ↳ Obtained from the ground (initial) state reaction field (it does not change)

- Optical or fast response: reaction field of the changed electronic charge after excitation or emission

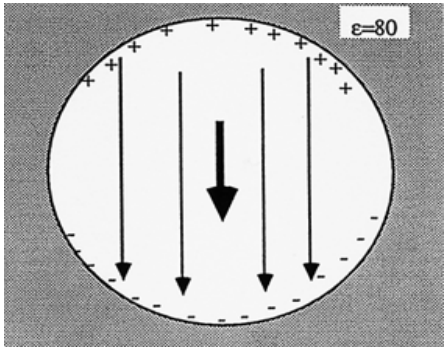
  ↳ Recomputed with the excited (final) state density using the optical dielectric ($\varepsilon = n^2$, n refraction index)

Reaction Field Methods: cavity + dielectric continuum

Onsager-Kirkwood Model in MOLCAS (ground states):

- SEWARD: definition of the cavity

```
&SEWARD  &END
...
RF-Input
Reaction  field
80  8.0  4
End  of  RF-Input
End  of  Input
```



- SEWARD: definition of the well potential

```
&SEWARD  &END
...
RF-Input
Reaction  field
80  8.0  4
End  of  RF-Input
Well  Int
4
1.0  5.0  12.0
1.0  3.5  13.0
1.0  2.0  15.0
1.0  1.4  17.0
End  of  Input
```

SCF

RASSCF

No input required. Reaction field computed self-consistently and stored in RUNFILE (RFRoot if SA-CASSCF)

CASPT2

RASSI

Other

RFPert keyword. Reaction field computed by SCF or RASSCF read from RUNFILE added perturbatively

Reaction Field Methods: cavity + dielectric continuum

PCM Model in MOLCAS (ground and excited states):

- SEWARD: definition of the cavity

```
&SEWARD  &END
...
RF-Input
PCM-model
Solvent
 Acetone
AAre
 0.2
End  of  RF-Input
End  of  Input
```

SCF, RASSCF → No input required. Reaction field computed self-consistently and stored in RUNFILE (RFRoot if SA-CASSCF)

CASPT2, RASSI, Other → RFPert keyword. Reaction field read from RUNFILE added perturbatively

- Excited (or final) states

slow part read from previous RUNFILE

RASSCF → Nonequilibrium keyword (RFRoot if SA-CASSCF)

CASPT2, RASSI, Other → RFPert keyword. Reaction field read from new RUNFILE added perturbatively

Reaction Field Methods: cavity + dielectric continuum

PCM Model in MOLCAS (ground and excited states):

SEWARD → RF-Input keyword

SCF

RASSCF → RFRoot if SA-CASSCF

cp $WorkDir/$Project.RUNFILE $TempDir/Initial_State.RUNFILE

CASPT2
RASSI
Other
→ RFPert keyword

Calculations of the initial state

ground state if absorption
excited state if emission

ln -fs $TempDir/Initial_State.RUNFILE RUNFILE

RASSCF → Nonequilibrium keyword
RFRoot if SA-CASSCF

CASPT2
RASSI
Other
→ RFPert keyword

Calculations of the final state

excited state if absorption
ground state if emission

Other methods to simulate the solvent

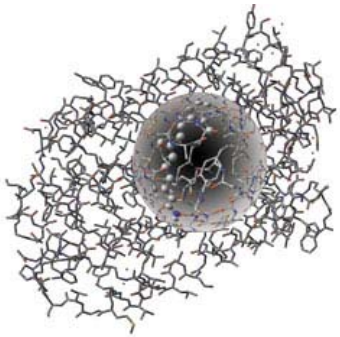
Methods that combine quantum and classical mechanics:

Explicit models: Quantum Mechanics / Molecular Mechanics (QM/MM)

$$H_{complete} = H_{QM} + H_{MM} + H_{QM/MM}$$

ONIOM **(in Gaussian):**
is divided in shells,
internal and more accurate QM,
and external charges or dielectric with MM

AM1/OPLS, QM/RISM, XSOL, etc..



The results will depend on the the accuracy of the force fields parametrized for MM, of the quality of the QM calculation, of the coupling of the shells, and of the design of the separation.

Molcas: new ESPF code: **QM + (Electrostatic potential, field, field deriv.)**

Coupled to Tinker or Amber

Methods that use exclusively quantum mechanics: (QM/MD) ***Car-Parrinello (1985)***

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