Theoretical models for the solvent effect

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8. Excited electronic states in solution

The dynamics of the solvent response
Absorption: the Franck-Condon approximation
Relaxations and Emissions
Excited states in solution: solvation dynamics

1. Excitation of solute electrons ($S_0 \rightarrow S_1$)

2. Polarization of solvent electrons (instantaneous)

3. Deformation of solvent intramolecular bonds (1st solvation shell, weak, units of fs)

4. Orientational ordering of solvent molecules: rotational and translational (10^{-1} to 10^2 ps)

5. Deformation of the bonds of the solute (supposed simultaneous with the previous process)

6. Relaxation of solute electrons ($S_1 \rightarrow S_0$)
Solvation dynamics: the continuum picture

Dielectric response of a polar solvent

Frequency dependent permittivity

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

\[ \varepsilon(\infty) \ll \varepsilon(0) \]

Partition of the solvent polarization into fast (electronic motions) and slow (molecular and nuclear motions) contributions

\[ \vec{P} = \vec{P}_{\text{fast}} + \vec{P}_{\text{slow}} \]

Electronic (deformation) polarization

Orientational polarization (only for polar solvents)
Electronic transition in a polar solvent

Nonequilibrium

Only the solvent electrons have readjusted: the solvent molecules are still frozen in the initial positions

Franck Condon (vertical) excited state

Solvent relaxation

GS (Equilibrium)

New equilibrium

Solvent molecules are now completely equilibrated with the excited state
The Franck Condon approximation: a nonequilibrium PCM

- Partition of the solvent charges into fast (electronic motions) and slow (molecular and nuclear motions) contributions
- Consideration of the different times involved: in a vertical electronic transition only the fast term will be in equilibrium with the final state

\[ q_{\text{r.fin}} = q_f(\rho_{\text{fin}}) + q_s(\rho_{\text{ini}}) \]
The nonequilibrium electrostatic problem

1. Equilibrium ground state:
   free energy $G^{GS}$ and slow charge $q_s(GS)$

2. Nonequilibrium excited state in the presence of the fixed slow charges:

   \[
   \begin{align*}
   -\Delta V &= 4\pi \rho^{exc} \\
   -\text{div}(\varepsilon_\infty \cdot \nabla V) &= 0 \\
   V_i - V_e &= 0 \\
   \left(\frac{\partial V}{\partial n}\right)_i - \varepsilon_\infty \left(\frac{\partial V}{\partial n}\right)_e &= 4\pi \sigma_s
   \end{align*}
   \]

   Fast charges
   \[
   q_f = -K(\varepsilon_\infty) \cdot (V^{exc} + V_s)
   \]

   Potential due to the solute in the excited state
   Potential due to the slow charges $q_s$

   Transition energy:
   $G^{exc} - G^{GS}$

   Two distinct calculations are required
Excitation energies: the QM description

Two classes of approaches to calculate excitation energies:

- **State Specific (SS):**
  - The energy of the excited state is explicitly calculated
    (CI, MCSCF, …)

- **Linear Response (LR):**
  - Excitation energies as poles of a linear response function of the molecule
    (CIS, TDDFT, …)
State specific versus Linear Response

In vacuo:
LR and SS give the same expressions for excitation energies

In solution (within continuum solvation models):
LR and SS give different expressions

• State Specific (SS):
The energy of the excited state is explicitly calculated
(CI, MCSCF, …)

• Linear Response (LR)
Excitation energies as poles of a linear response function of the molecule
(CIS, TDDFT, …)

Each excited state has its own solvent reaction field: for each state we need to do a separate calculation

We can solve simultaneously for all the excited states

Disadvantage: less accurate than SS
If the medium is too viscous to allow solvent molecules to reorganize, emission arises from a state close to the Franck–Condon state.

If the time required for the reorganization of solvent molecules around the solute is short with respect to the excited-state lifetime, fluorescence will be emitted from an excited molecule in equilibrium with its solvation shell.
The experimental evidence: Time dependent Stokes Shift

Time-resolved Stokes shift experiment: a short light pulse is used to electronically excite a probe solute.

Relaxation of the solvent is monitored measuring the time dependent frequency shift of the solute’s emission spectrum.

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

If the geometry of the solute does not significantly change in the excited state:

Time evolution of the variation of solvation free energy between ground and excited state from calculation.
The coupling of internal (geometry) and external (solvent) relaxation

Franck-Condon (vertical) excited state

Relaxed excited state

Flux of electronic charge in the excited state

Immediatly after the excitation, the solute geometry and the solvent orientational polarization are still those of the ground state (nonequilibrium)

An example: Para nitroaniline

Charge transfer
Larger dipole moment
Larger stabilization in a polar solvent

It is reasonable to assume that the geometrical relaxation of the solute in the excited state is accompanied by a complete relaxation of the solvent (full equilibrium)
9. Solute-solvent specific effects

Bulk versus specific interactions
The “supermolecule” approach
Short and long range effects
As first step, any theoretical model requires the definition of the interactions acting among particles.

**Isolated molecule**

electrons and nuclei to form the molecule

**Liquids**

molecules to form the solution

– Bulk polarization
– Site binding or specific solvation
– …
Bulk vs specific solvation

Bulk (averaged) effects

Local (specific) effects

Macro- and micro-solvation
To understand solvent effects at the molecular scale, some questions need to be addressed:

✓ How does solvation at the solute surface differ from that of bulk?
✓ Are there local rigid structures of solvent at the solute surface?
✓ What are the time scales for solvent dynamics at the solute surface?

No significant differences between surface and bulk: continuum models

Rigid and/or persistent solvent structures at the surface: ?
Solvent structures at the surface

Supermolecule = solute surrounded by some explicit solvent molecules
It properly accounts for short-range effects.

The different components of the new composite system can be described at the same level (QM) or using an hybrid approach: a better level for the solute and a more approximated level for the solvent molecules (semiempirical or MM)
How many explicit solvent molecules are needed?

From the chemical analysis of the system:

N-methyl acetamide in water: three possible H-bonds, two on the O(C) and one on the H(N).

From MD simulations:

O-Hw RDF: On average, two hydrogen atoms of two water molecules hydrate the carbonyl group by means of hydrogen bonding.

(N)H-OW: The integration number up to the first minimum gives 1 water molecule H-bonded to the H(N).
The Supermolecule

Which configuration?

◊ **From QM geometry optimizations**: the most stable configuration

  Proper description for strongly interacting solute-solvent systems giving rise to stable clusters.

  The structure of strong H-bonded solute-solvent can be properly described with QM geometry optimizations

◊ **From MD or MC simulations**: Better for weaker solute-solvent interactions described by a more dynamic situation.
Clusters from MD simulation: how to select them?

First we perform an analysis of the radial and spatial distribution functions so to obtain information on how solvent molecules pack in “shells” around some specific atoms in the solute

An example: N-methyl acetamide in acetone

Spatial Distribution Function for the carbonyl oxygen of NMA

An homogeneous sphere-like distribution of methyl groups is found around the NMA oxygen
Clusters from MD simulation: how to select them?

Then we select solute-solvent clusters on the basis of a cutoff distance \( (r_{\text{cut}}) \) for the O(C)-H(acetone) pairs: each cluster included all solvent molecules having the hydrogen atom closer than \( r_{\text{cut}} \) to the NMA oxygen.

The value used for \( r_{\text{cut}} \) has to be chosen so the represent the first solvation shell (here 5 Å).
Clusters from MD simulation: how to select them?

The problem of statistical representativity has to be solved:
we cannot represent a liquid with a single cluster, we need to introduce averages on many different clusters obtained with the same cutoff method.
Clusters from MD simulation

This approach is quite demanding from a computational point of view:

calculations of the property of interest have to be repeated for all the clusters so to obtained an averaged value

It has the great advantage to properly describe weak solute-solvent specific interactions which cannot be represented by a single configuration obtained from a QM geometry optimization
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 largely reduced, or an hybrid QM/MM has to be introduced

2. The problem of statistical representativity becomes very difficult: increasing the dimension of the cluster we need more and more clusters so to get a correct picture of the liquid
The Supermolecule

How can we include long-range effects?

- Adding an “external” continuum:
  the solvated supermolecule

The main 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.
Some conclusive remarks
Solvation is an intrinsically dynamic and long-range phenomenon: statistical treatments involving averaging and fluctuations from averages are important.

Which Theoretical Model?

Not a unique answer!

The choice has to be preceded by a combined analysis on:

(i) the chemical system,
(ii) the properties of interest,
(iii) the required accuracy,
(iv) the computational cost
Which Theoretical Model?

- Solvent Model
  - Discrete
  - Continuum
- Theoretical Method
  - Static
  - Dynamic
- Interaction Potentials
  - Empirical
  - Quantum mechanical
Which Theoretical Model?

Continuum models represent a very effective approach to study solvent effects on energies/properties and reactivity of solvated systems.

However, these continuum models must be:

1. general (not limited in the form of the cavity or in the description of the solute)
2. coupled to different QM methods (for ground and excited states), as well as to their extensions to derivative approaches (for geometry optimizations and response properties)
3. able to model specific aspects of solvation like local-field effects or nonequilibrium
4. extensible to treat non-standard solvents
Which Theoretical Model?

There can be cases/phenomena in which a continuum description is not sufficient

New strategies

- QM methods for small solute-solvent clusters (1-10 molecules)
- Mixed MD and QM methods for larger clusters

In both cases the addition of an external continuum gives a simple but effective way to introduce long-range effects
Other combinations and/or hybridization of different approaches as well as new and more powerful formulations of continuum models will surely appear in the next future.
**QM Continuum models and computational packages**

<table>
<thead>
<tr>
<th>Model Type/Extension</th>
<th>Software Packages</th>
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<tbody>
<tr>
<td>PCM (DPCM, CPCM, IEFPCM)</td>
<td>Gaussian (from g98)</td>
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<tr>
<td></td>
<td>GAMESS (DPCM, IEFPCM)</td>
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<tr>
<td></td>
<td>MOLCAS (CPCM only)</td>
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<td>COSMO (Klamt)</td>
<td>MOPAC</td>
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<td>TURBOMOL</td>
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<tr>
<td>Extension of Onsager (Mikkelsen)</td>
<td>Dalton</td>
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