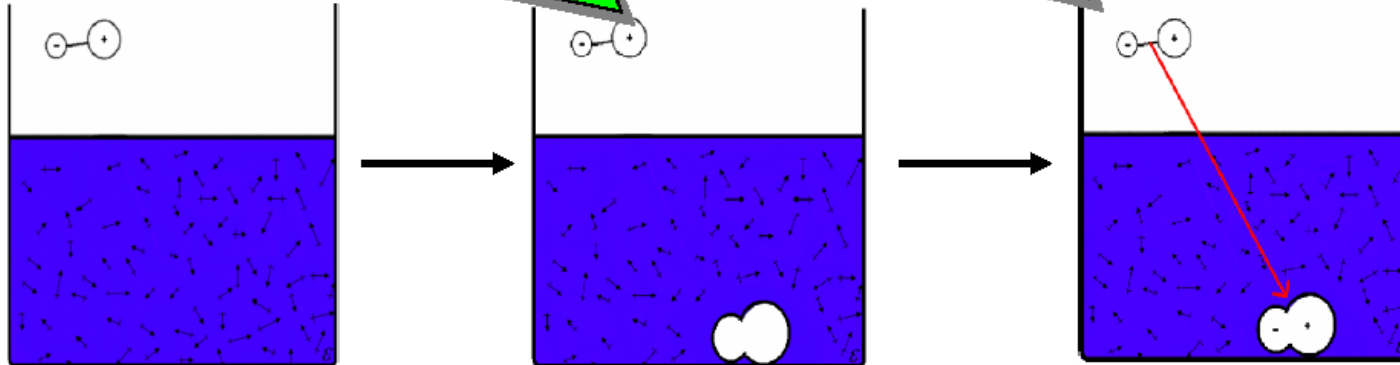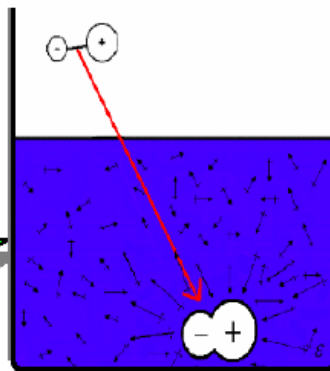# Solvation Models

What is solvation?

The process of moving a molecule from the gas phase to a condensed phase.

A solute shaped cavity of vacuum is introduced into the solvent.
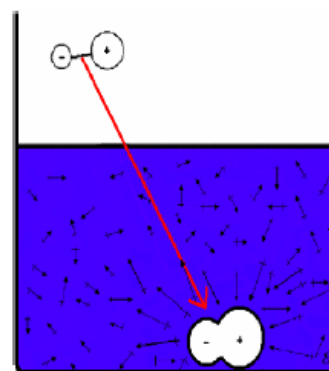
The solute charge density is placed in the solute cavity.

The solvent molecules reorient and polarize in response to the solute charge density

The solute polarizes in response to the solvent polarization

Solvent Effects

- Many reactions take place in solution

- Short-range effects
  - Typically concentrated in the first solvation sphere
  - Examples: H-bonds, preferential orientation near an ion

- Long-range effects
  - Polarization (charge screening)
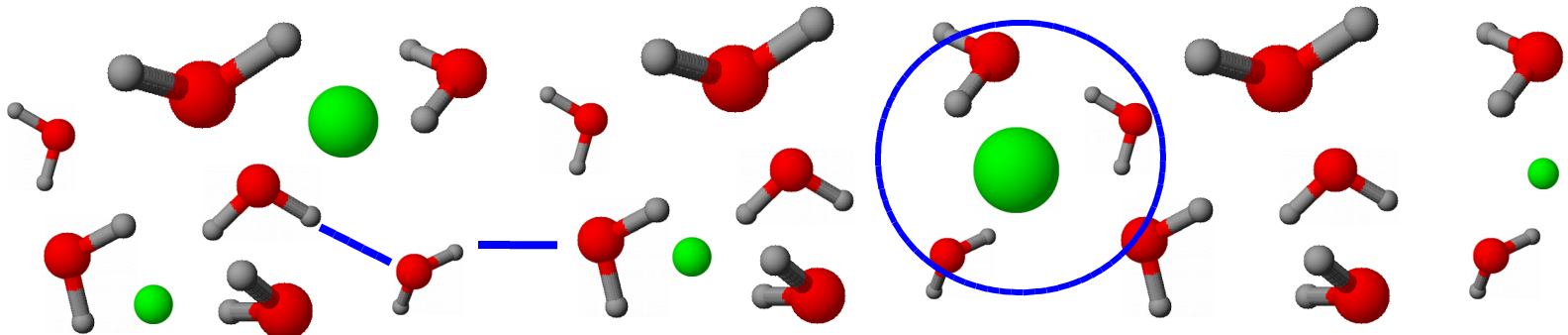
Solvation Methods in Molecular Simulations

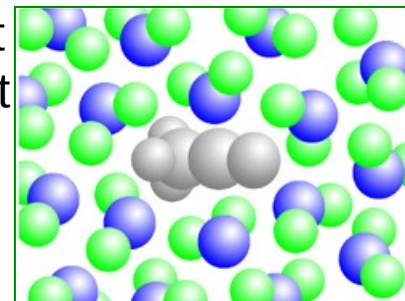• Explicit Solvent vs. Implicit Solvent

   Explicit: placing real molecules

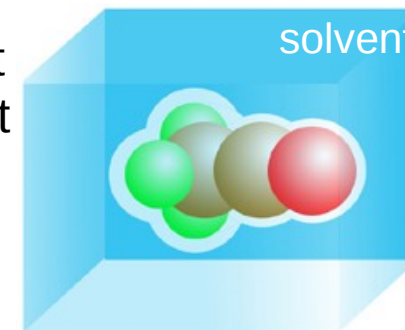   Implicit: treating the solvent as a continuous medium (Reaction Field

         Method)

Some are **hybrids** of the above two:
  – Treat first solvation sphere **explicitly** while treating
    surrounding solvent by a **continuum model**
  – These usually treat inner solvation shell quantum
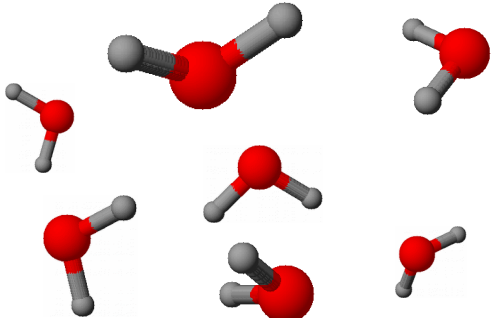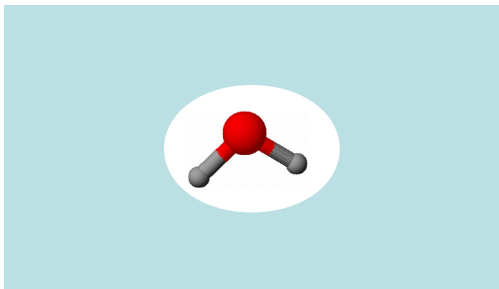   mechanically, outer solvation shell classically

explicit
solvent

implicit
solvent

solvent

Two Kinds of Solvation Models

Models	Explicit solvent models	Continuum solvation models
Features	All solvent molecules are explicitly represented.	Respresent solvent as a continuous medium.
Advantages	Detail information is provided. Generally more accurate.	Simple, inexpensive to calculate
Disadvantages	Expensive for computation	Ignore specific short-range effects. Less accurate.

Continuum (Reaction Field) Models

- Consider solvent as a uniform polarizable medium of fixed dielectric constant ε having a solute molecule **M** placed in a suitably shaped cavity.

- Solute induces polarization at the interface of cavity.

- This polarization acts back on the solute changing its wavefunction.

- Various solvation models use different schemes for evaluation of solvation effects.

- Problems arise when electrostatics do not dominate solvent-solute interactions

Models Differ in 5 Aspects

1. Size and shape of the solute cavity

2. Method of calculating the cavity creation and the dispersion contributions

3. How the charge distribution of solute **M** is represented

4. Whether the solute **M** is described classically or quantum mechanically
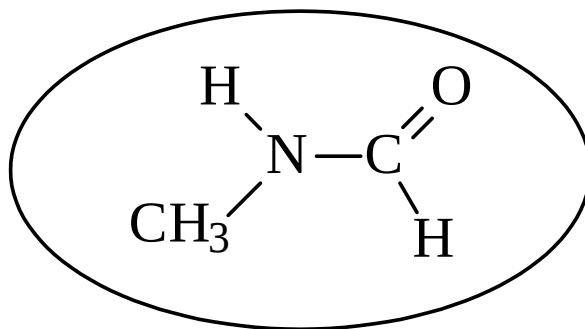
5. How the dielectric medium is described.

(these 5 aspects will be considered in turn on the following slides)
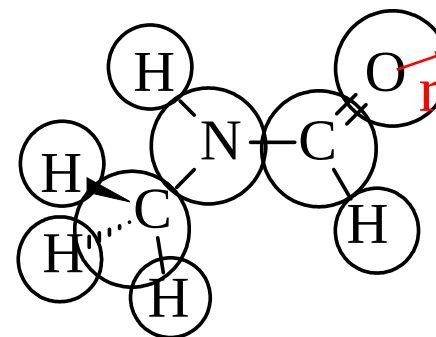
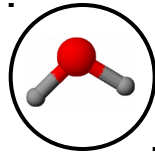# Solute Cavity Size and Shape

Spherical   Ellipsoidal   van de Waals
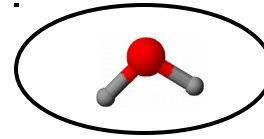(Born)   (Onsager)
(Kirkwood)
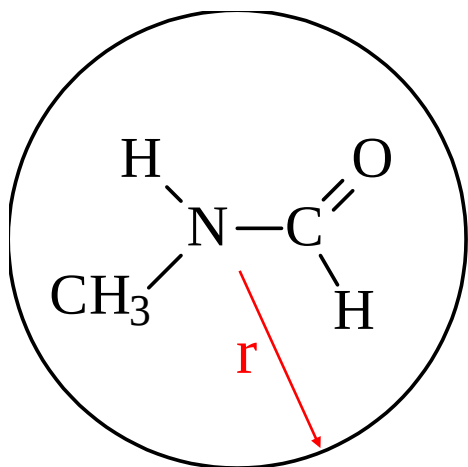
The Cavity

- Simple models

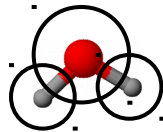Sphere
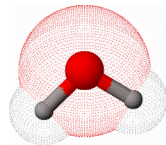
Ellipsoid
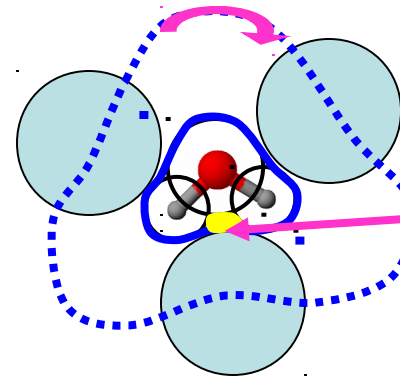
- Molecular shaped models

Van der Waals surface

Determined by QM wave function and/or electron density

Not accessible to solvent

Solvent accessible surface

Visualizing cavity

1. Geomview software (in the modules).

2. Works only with Gaussian 03

3. SCRF=(read) in the route section of the job

4."geomview" in the SCRF specification

5. Visualize the "tesserae.off" file

Tomasi Polarizable Continuum Model (PCM)

- Cavity based on union of spheres centered on each atom
  - ‣ Radius of sphere ~1.2 van der Waals radius

- Electrostatic interactions calculated numerically
  - ‣ Iterated

- Better approximations for cavity are the Connally surfaces

ϵ

Connally molecular
surface: crevices
smoothed out

$\in$

Connally solvent
accessible surface
(SAS): solvent
radius added
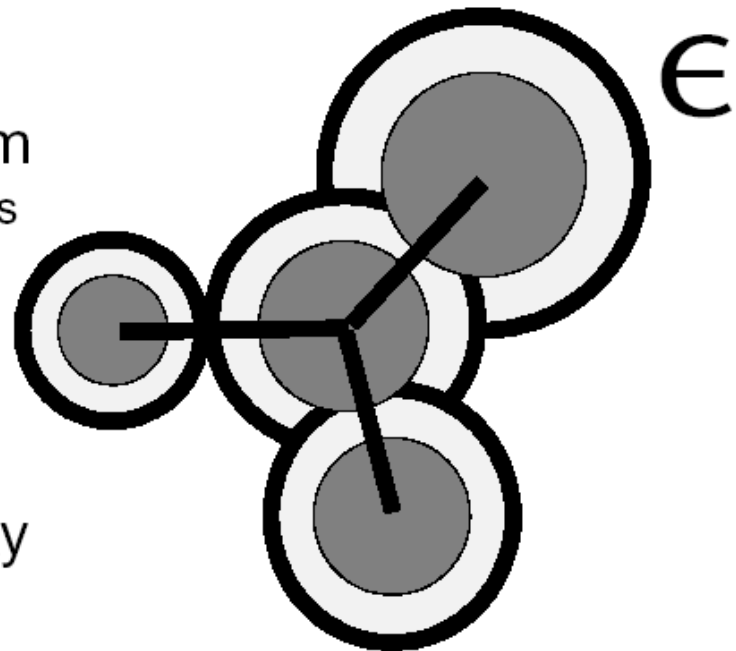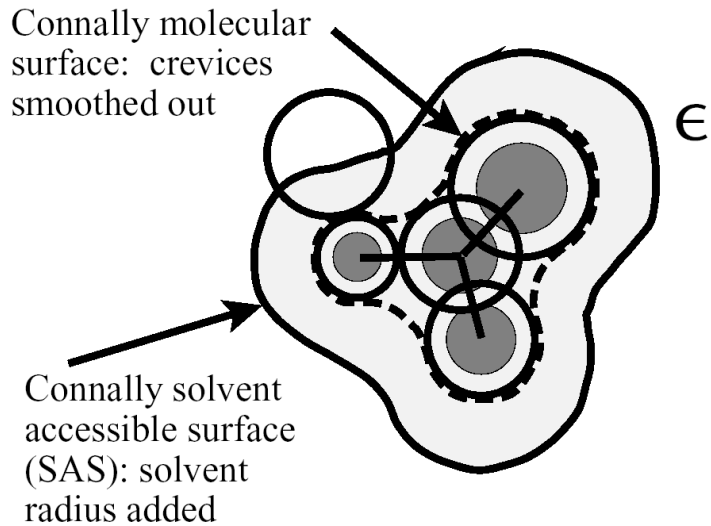
The walls of cavity determine the interaction interface (Solvent Excluded Surface, SES)

Size of the solvent molecule determines the Solvent Accessible Surface (SAS

Isodensity Polarized Continuum Model (IPCM)

- Cavity based on isosurface of electron density
  - ‣ SCF calculations on the cavity until converges
- Electrostatic interactions calculated numerically
- Self-Consistent Isodensity Polarized Continuum Model (SCI-PCM)
  - ‣ Cavity calculation embedded in SCF differently

Conductor like screening model

- Solute in virtual conductor environment
- Charge q on molecular surface is lower by a factor $f(\epsilon)$:

$$q = f(\epsilon)q^* \tag{1}$$

- where $f(\epsilon) = (\epsilon - 1)/(\epsilon + x)$; x being usually set to 0.5 or 0
- Implemented in Turbomole, ADF

Why Implicit Solvent?

| Method	Explicit Solvent (all-atom description)	Implicit Solvent (Continuum description)
Pros	• Full details on the molecular structures • Realistic physical picture of the system	• No explicit solvent atoms • Treatment of solute at highest level possible (QM)
Cons	• Many atoms--> expensive • Long runs required to equilibrate solvent to solute • Often solvent and solute are not polarizable. • Large fluctuations due to use of small system size	• Need to define an artificial boundary between the solute and solvent • No "good" model for treating short range effects (dispersion and cavity)

Explicit QM Water Models

- Sometimes as few as 3 explicit water molecules can be used to model a reaction adequately:
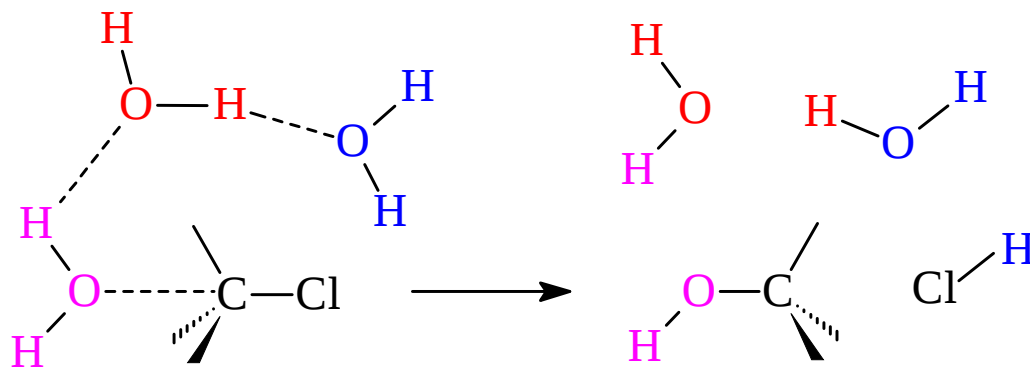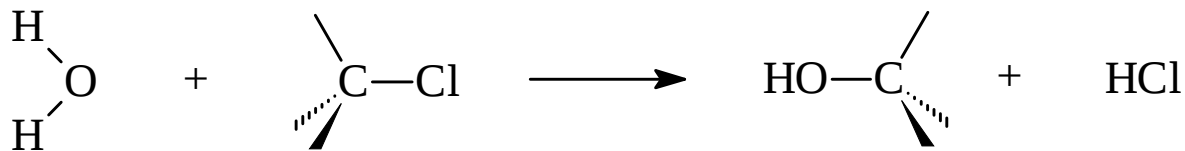
Could use HF, DFT, MP2, CISD(T) or other theory.

Explicit Hybrid Solvation Model
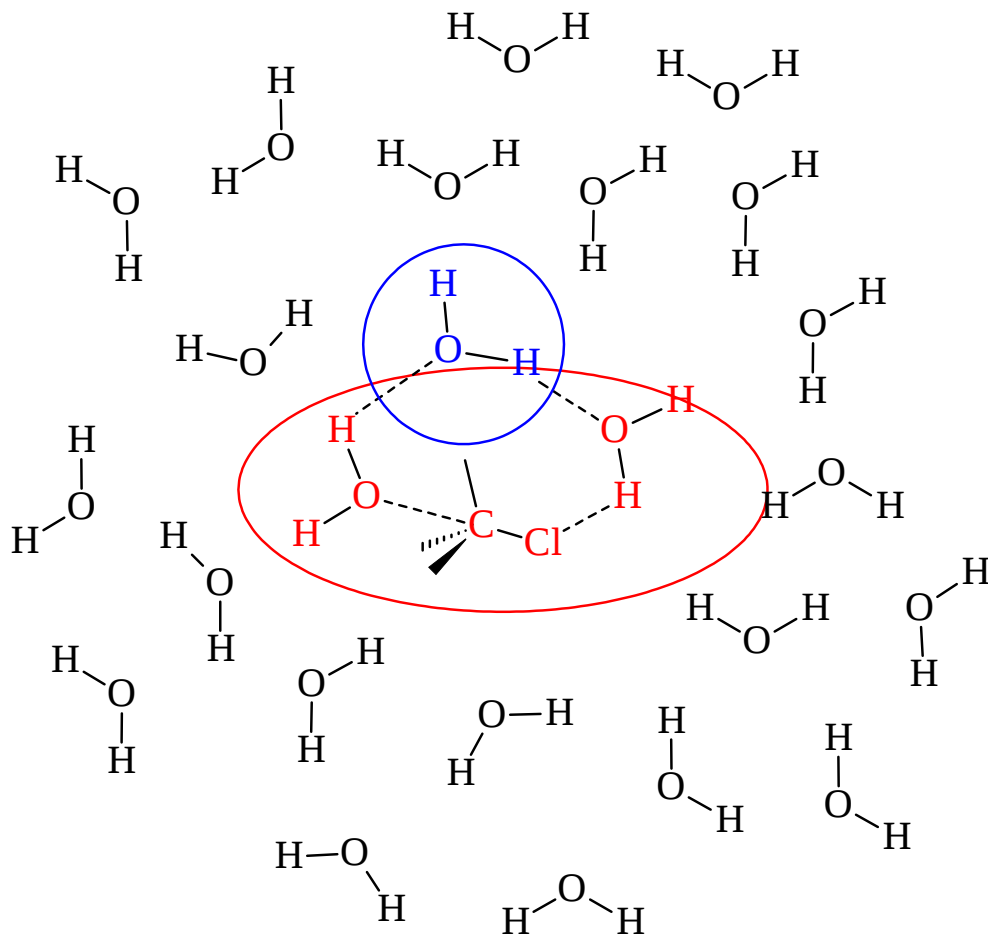
Red = highest level of theory (MP2, CISDT)

Blue = intermed. level of theory (HF, AM1, PM3)

Black = lowest level of theory (MM2, MMFF), or Continuum

Practical task

1. Model the Cl − + CH 3 Br → CH 3 Cl + Br −
2. Find the energy barrier for the reaction
3. Select any solvent from Gaussian library (be not concerned about solubility of species or chemical relevance)
4. Assume Sn1 and Sn2 reaction pathways
5. Use "SCRF=(solvent=XY)" in the route section of the calculation

Procedure

1. Use B3LYP 6-31+g(d,p) method
2. Usage of difuse functions when dealing with anions is crucial!
3. Use ultrafine integration grid
4. Use Frequency calculations to be sure where on PES you are
5. For the scan use the distance between C and Cl as RC
6. Negative value of step defines two atoms approaching

Turbomole

1. Prepare job using define module (see presentation 6 for help)

2. Setup COSMO using cosmoprep module

3. Set epsilon to 78.4 and rsolv to 1.93

4. Leave all other values at their default

5. Define radii of atoms using "r all o" for optimized values

6. Optimize all geometries