

Computational Chemistry II 2021

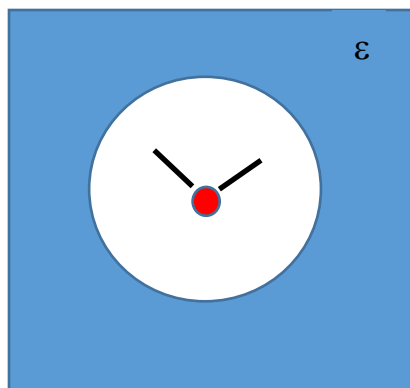
Text book Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

Chapter 7. Solvation(Cramer: chapter 11)

Not in the gas phase

So far all the calculation have been in gas phase, but the chemistry happen seldom done in gas. The most common environment is solution. So are most of the calculation we have done useless. No, since we can rather easily model the environment of the molecule. If the solvent has low dielectric constant and it's molecules do not form hydrogen bonds the situation is easy. The most important interaction between the molecule and solution is the **electrostatic interaction**. The average electrostatic interaction of a continuum can be described with the dielectric constant, ϵ , of the material.

The simplest solvation model is a (spherical) cavity of the continuum that have the dielectric constant of the solvent.



With this solvation model it is very easy to compute the interaction energy of the molecule and solvent.

For charged system it is (here the charge is q , the radius is R)

$$G = -\frac{1}{2}\left(1 - \frac{1}{\epsilon}\right)\frac{q^2}{R}$$

For dipole moment

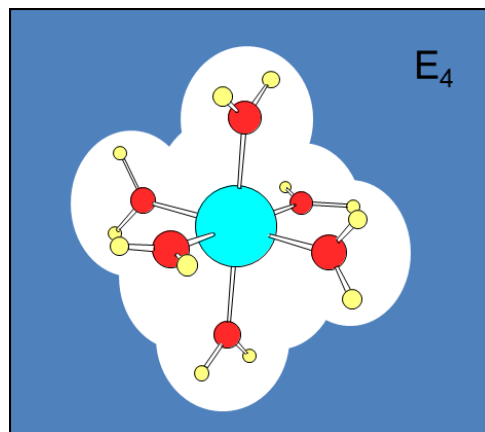
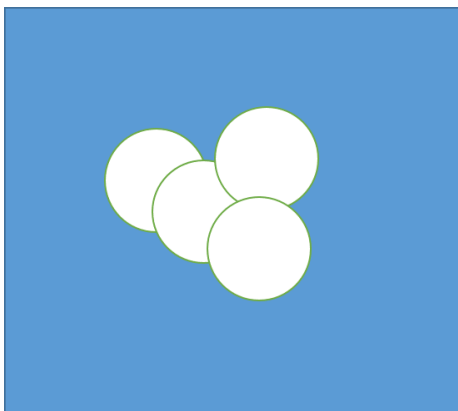
$$G = -\left(\frac{\epsilon - 1}{2\epsilon + 1}\right)\frac{\mu^2}{R^3}$$

This looks simple but remember that the dipole moment will depend on the environment (polarization), so the solvent will increase the dipole moment. Luckily, the solvent model can be included easily to the HF/DFT equations. The Fock operator for the dipolar term is

$$\left[F_i - \left(\frac{2(\epsilon - 1)}{2\epsilon + 1}\right) \frac{\langle \Psi | \mu | \Psi \rangle^2}{R^3} \right] \varphi_i = e \varphi_i$$

Now the self-consistent iteration need to include also the dipole moment. The approach is called self-consistent reaction field (SCRF). In addition, the higher multiple moments can be included.

Naturally, the single spherical cavity is not very realistic. A more realistic cavity fill be built of several spheres each centered of a heavy atom (C,O,N etc.).



The boundary problem cannot be solved analytically. A grid of the system is build and a dielectric constant is assign to each grid point. (Inside the cavity, the ϵ is usually 2-4 (not 1)). Next one need to evaluate the electric field in these grid

points using the Poisson or Poisson-Boltzmann equation. The Poisson equation is

$$\nabla\epsilon(r) \cdot \nabla\phi(r) = -4\pi\rho(r)$$

Where ϕ is the electric field. This electric field will affect to the electronic structure.

Orca is using the CPCM solvation model, which needs the dielectric constant, refractive index and appropriate radius of the atoms. Most of these has been automatized so one can do solvation calculation with command like: ! CPCM(water)

Usually one do not need to worry about the atomic radius, reasonable values for all elements is included to the CPCM package. Warning: In some models radius have been fitted only to water then there is small error in the other solvents.

In general, the simple solvation model will work well for low dielectric solvents that do not form hydrogen bonds. Unfortunately, water is not one of these.

The dielectric energy of CPCM is reported in the output.

Non-electrostatic interactions

The electrostatic part is the most important contribution but also the non-electrostatic interactions matters. Especially in the case of non-polar solvents. The non-electrostatic models are usually not included to standard solvation models. The models are mostly based on Solvent Accessible Surface Area (SASA).

$$G = \sum_i A_i \sigma_i$$

Where A_i is the SASA of a molecule or chemical group and σ_i is some surface tension. The σ_i 's are parameters of the model. In the figure below a solvation free energy with respect of the exposed surface are plotted for linear and branched alkenes. The data set is rather linear and the surface tension can be obtained from the slope.

There is a good discussion of this in the Cramer's book (Chapter 11.3.2). The COSMO-RS model will include also SASA type terms

but the model is commercial. Now Orca (4.0) is using the **Cramer's SMD model**. SMD is a universal solvation model, in the sense that it is applicable to any charged or uncharged solute in any solvent or liquid medium for which a few key descriptors are known. See chapter 9.27 in Orca manual.

See: <http://www.cosmologic.de/products.html>

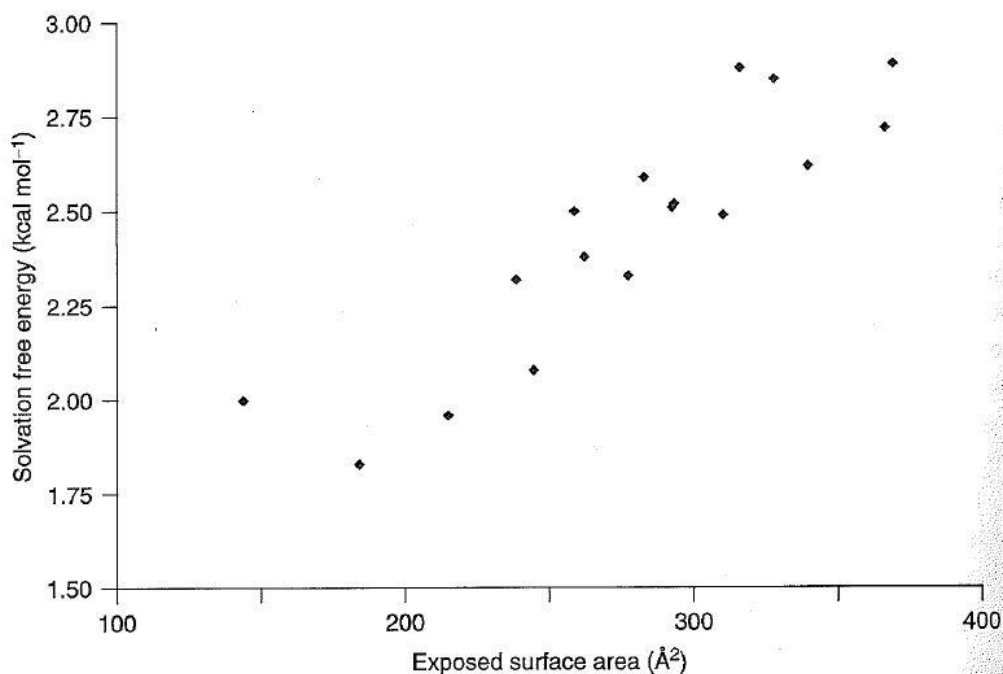


Figure 11.8 Approximately linear relationship between solvation free energy and solvent-accessible surface area for linear and branched alkanes. A best fit line passing through zero has a slope of $8.6 \text{ cal mol}^{-1} \text{ \AA}^{-2}$, which may be taken as the σ value for alkane surface area in Eq. (11.22) (Giesen, Cramer, and Truhlar 1994)

The Cramer's group SMx and COSMO-RS type model are often needed for realistic solvation energies. The model building requires a lot of effort and thus often these models are commercial. The latest version of Orca (v 4.0) have the (CPCM+)SMD model so it will also report the cavity and dispersion corrections. These have been reported as Free-energy (Cav+disp). The total solvation energy is the sum of the Dielectric energy and cavity correction.

The SMD model have very large library of solvents (totally 179) so you will very likely find your solvent of interest.

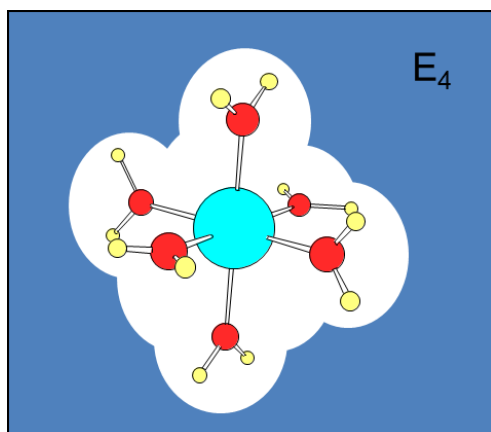
The usage of CPMD+SMD is easy:

```
!CPCM(water)
%cpcm
  smd true      # turn on SMD
  solvent "water" # specify the name of solvent from the list
end
```

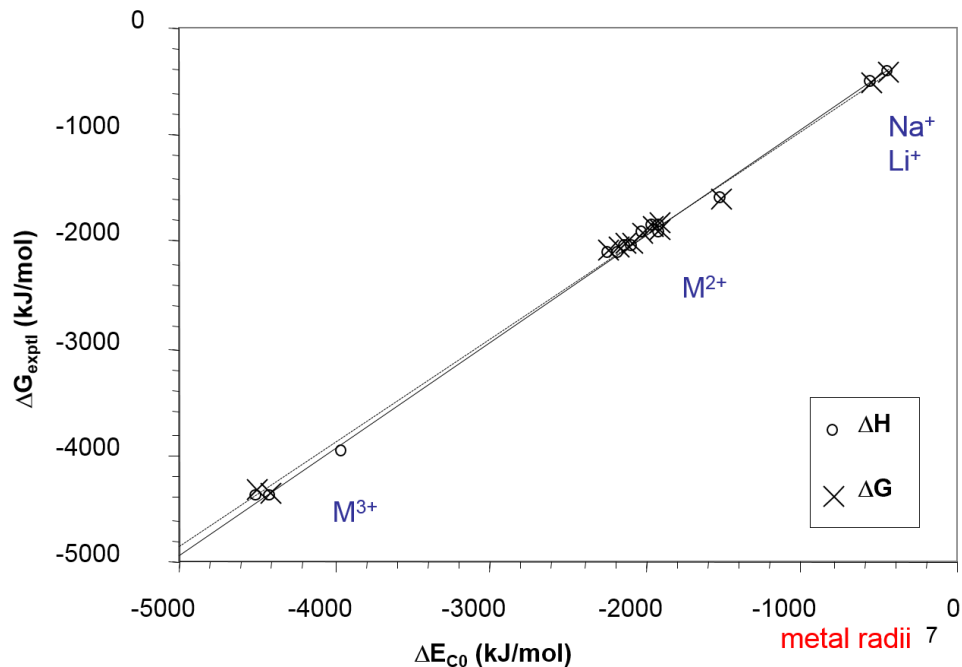
Explicit waters or solvent molecules

As said above water is a difficult case for solvation models. Luckily, one can improve the description by adding explicit water molecules to the system.

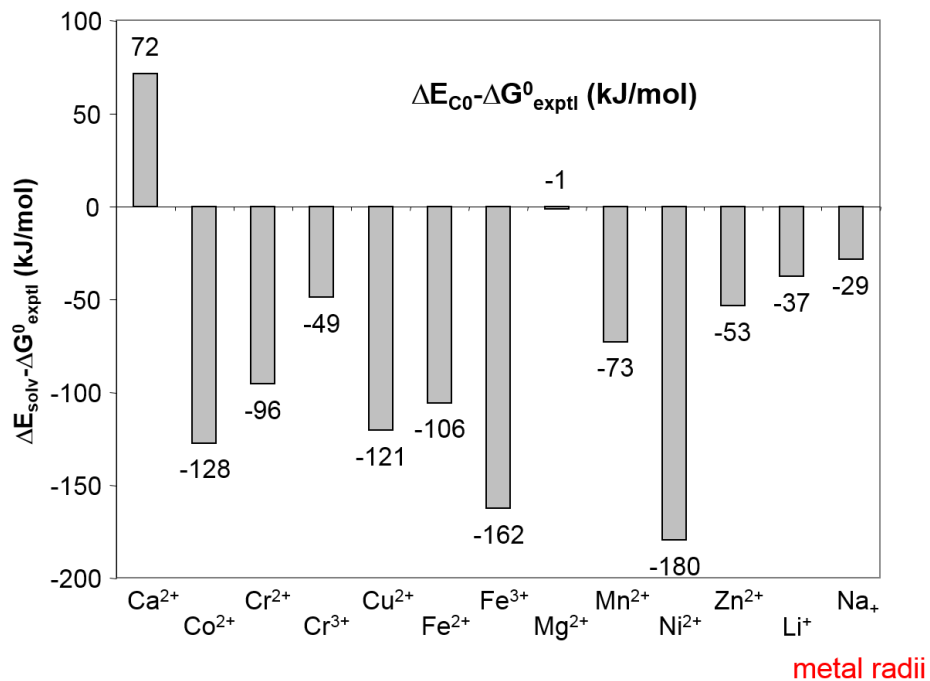
If one wants to study the solvation of an atom (a metal atom) it is much better to add the first solvation shell of water molecules to the system.



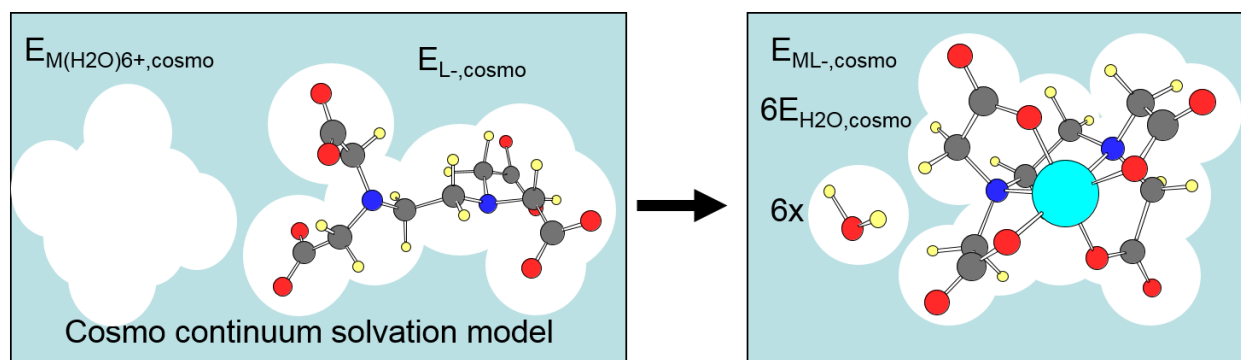
The metal solvation calculations will work quite well



The relative energies are very good but the absolute energies are not that great



The usage of added waters applies also to more complex systems.



In general, if a 2- or 3- valent ion is under-coordinated the “free” sites should be covered with water molecules.

Accuracy

| Data set ^a | N_{data} | MUE (kcal/mol) | | |
|---------------------------------|-------------------|--------------------|------------------|---------|
| | | C-PCM ^b | SMD ^c | |
| | | | C-PCM | IEF-PCM |
| Aqueous neutrals | 274 | 1.6 | 0.9 | 0.9 |
| Aqueous cations | 52 | 7.3 | 2.9 | 2.8 |
| Aqueous anions | 60 | 8.1 | 3.9 | 3.9 |
| Nonaqueous neutrals | 666 | 2.8 | 0.7 | 0.7 |
| Nonaqueous cations ^d | 72 | 12.0 | 5.4 | 5.4 |
| Nonaqueous anions ^d | 148 | 6.6 | 4.1 | 4.1 |
| All neutrals | 940 | 2.5 | 0.8 | 0.8 |
| All ions | 332 | 8.1 | 4.1 | 4.1 |

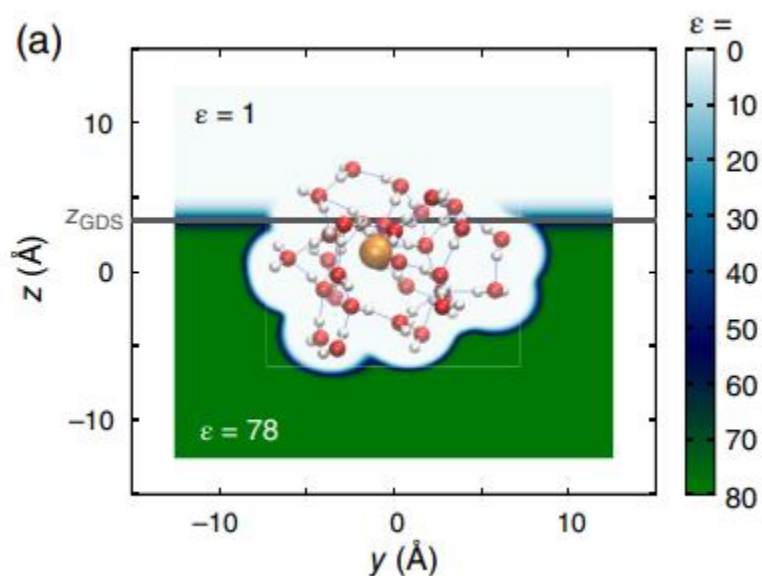
Mean unsigned errors (MUEs) versus experiment, for solvation energies ($\Delta_{\text{solv}}G^\circ$) computed using various models. From J.M. Herbert, WIREs Comput. Mol. Sci. e1519 (2021), DOI: 10.1002/wcms.1519

Vibrations and solvation

The vibration analysis can be done using the solvation models. The (some) vibrational frequencies will lower and the dipole moments will increase. Many features will be improved but for example the Thermochemistry is not correct, the frequent shifts are usually too small.

Non-isotropic media

The present standard solvation models do not handle non-isotropic systems. There are several modification of solvent models to include the non-isotropic systems. There is some discussion on those in Cramer's book 11.4.3.



A semicontinuum description of chlorate ion at the air water interface, in which the atomistic solute is ClO_3^- -(H_2O)₃₀. The background color shows the function $\epsilon(r)$, interpolating between $\epsilon_{\text{out}} = 1$ above the Gibbs dividing surface (GDS) and $\epsilon_{\text{out}} = 78$ below it, with $\epsilon_{\text{in}} = 1$ inside of the solute cavity. The horizontal line indicates the position of the dividing surface, $z_{\text{GDS}} = 3.5 \text{ \AA}$. From J.M. Herbert, WIREs Comput. Mol. Sci. e1519 (2021), DOI: 10.1002/wcms.1519

Summary: The solvation models are very fast way to include approximately the effect of the solvent to the quantum chemical models. The computations are very easy but not very accurate with standard models. The next level models are often commercial but the Orca is an exception. The CPCM+SMD in Orca is a strongly recommended method.