Computational Chemistry II 2022

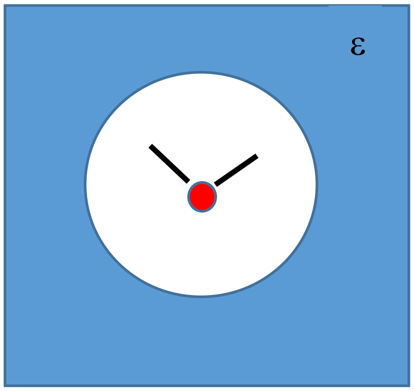
Text book Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

Chapter 7. Solvation(Cramer: chapter 11)

Not in the gas phase

So far all the calculation have been in gas phase, but chemistry is seldom done in gas. The most common environment is water or some other solvent. 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 its 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)

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

For dipole moment

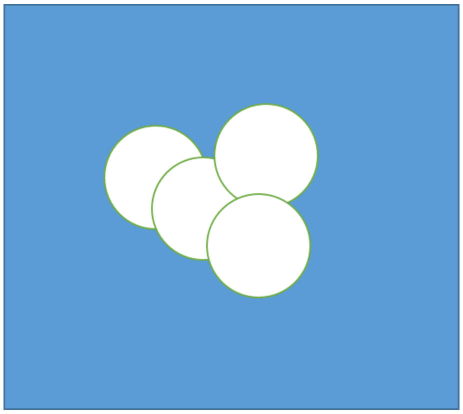
$$G = -\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\frac{\mu^2}{R^3}$$

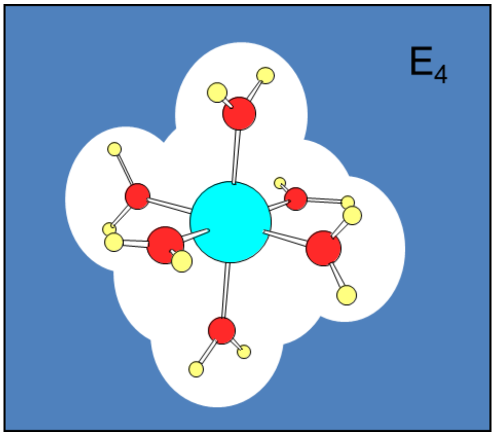
This looks simple but remember that the dipole moment will depend on the environment (polarization), so the solvent will increase the dipole moment. Luckily, the solvent model can be included easily to the HF/DFT equations. The Fock operator for the dipolar term is

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

Now the self-consistent iteration needs to include 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 can be built of several spheres each centered of a heavy atom (C,O,N etc.).





This 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 Poison or Poison-Bolzmann equation. The Poison eguation 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 does 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 inconsistency with 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.

These models has also additional parameters for hydrogen bonding, both the acceptor and donor H-bonds.

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 and later) 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

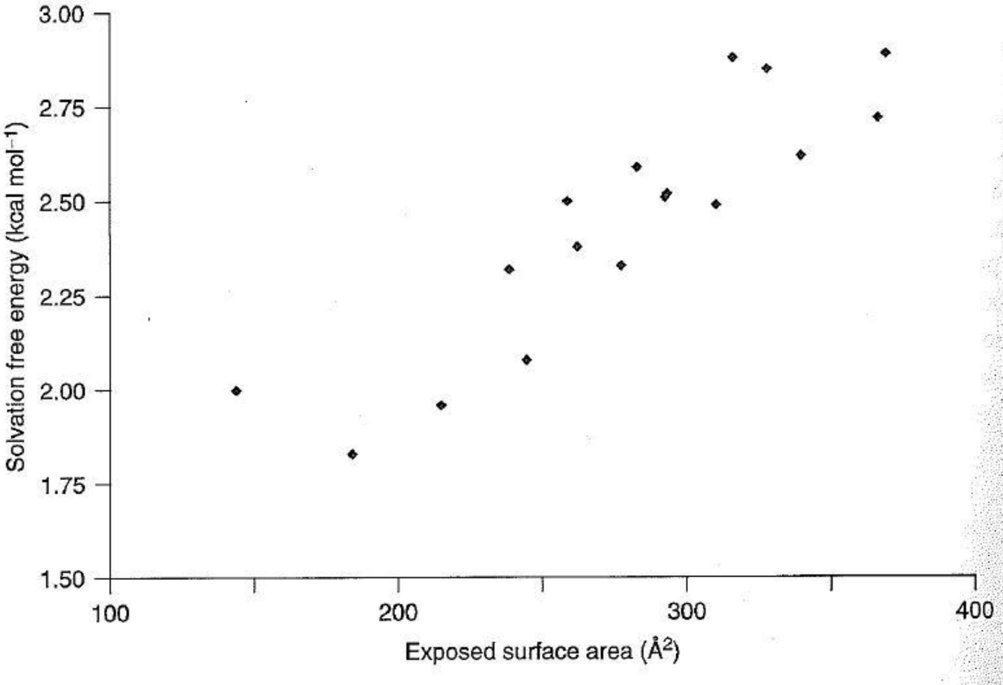


Figure 11.8 Approximately linear relationship between solvation free energy and solvent-accessible surface area for linear and branched alkanes. A best fit line passing through zero has a slope of 8.6 cal mol^{-1} Å^{-2}, which may be taken as the σ value for alkane surface area in Eq. (11.22) (Giesen,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

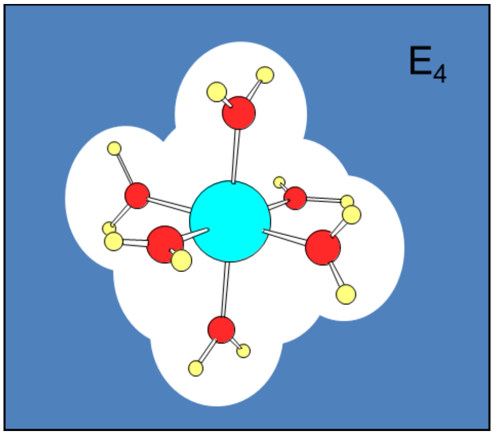
```
!CPCM(water)
%cpcm
     smd true            # turn on SMD
     solvent "water"   # specify the name of solvent from the list

end
```

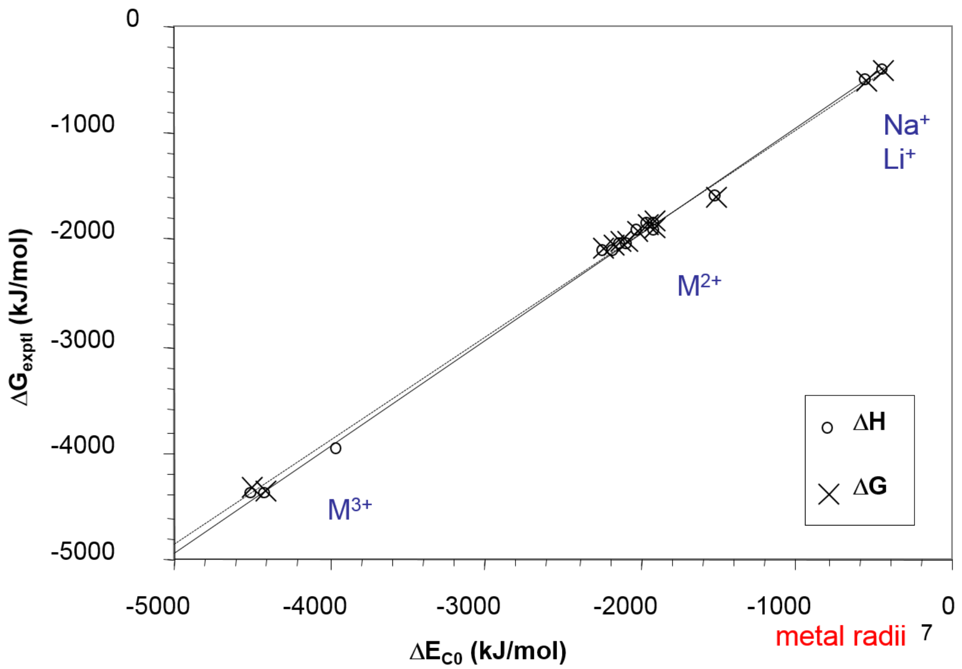
Explicit waters or solvent molecules

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.

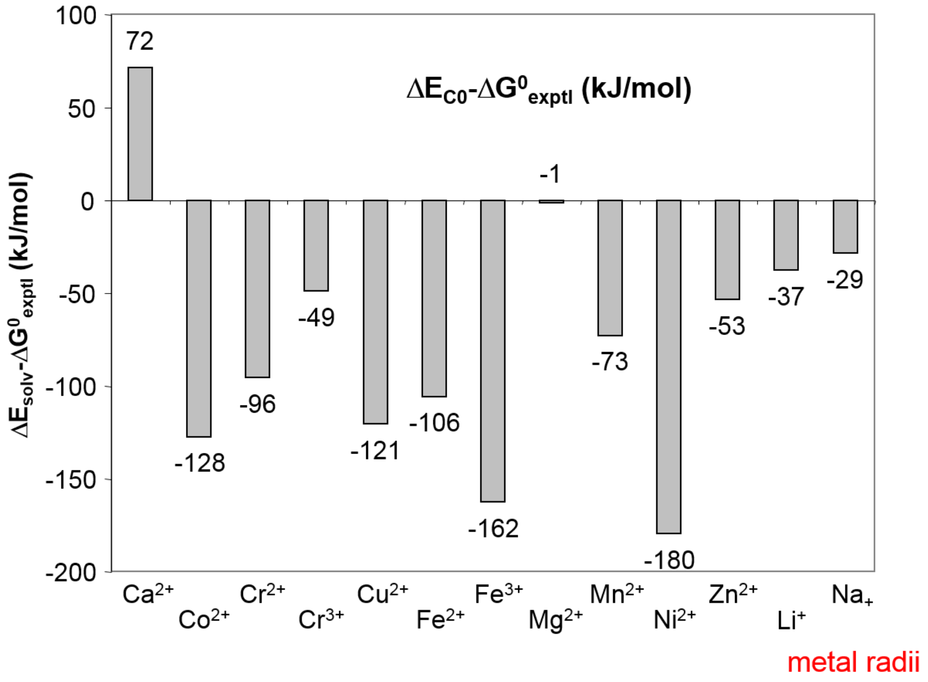
If one wants to study the solvation of an atom (a metal atom) it is much better to add the first solvation shell of water molecules to the system.



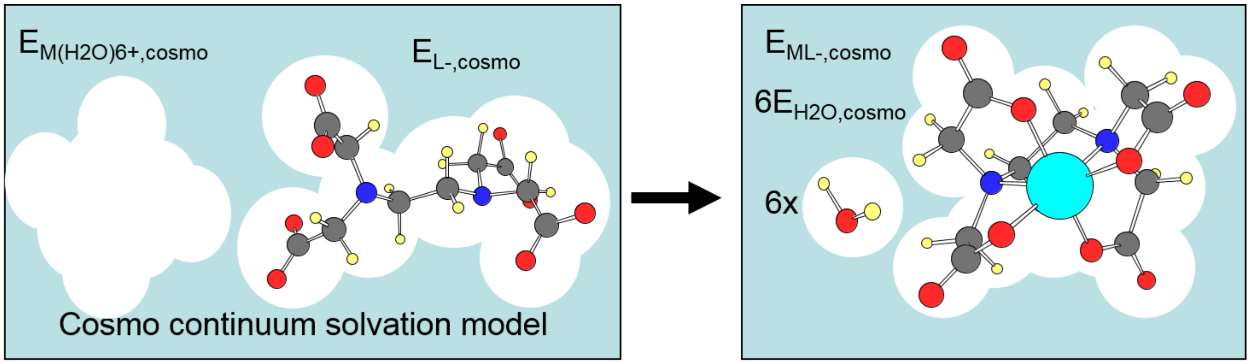
The metal solvation calculations will work quite well



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.

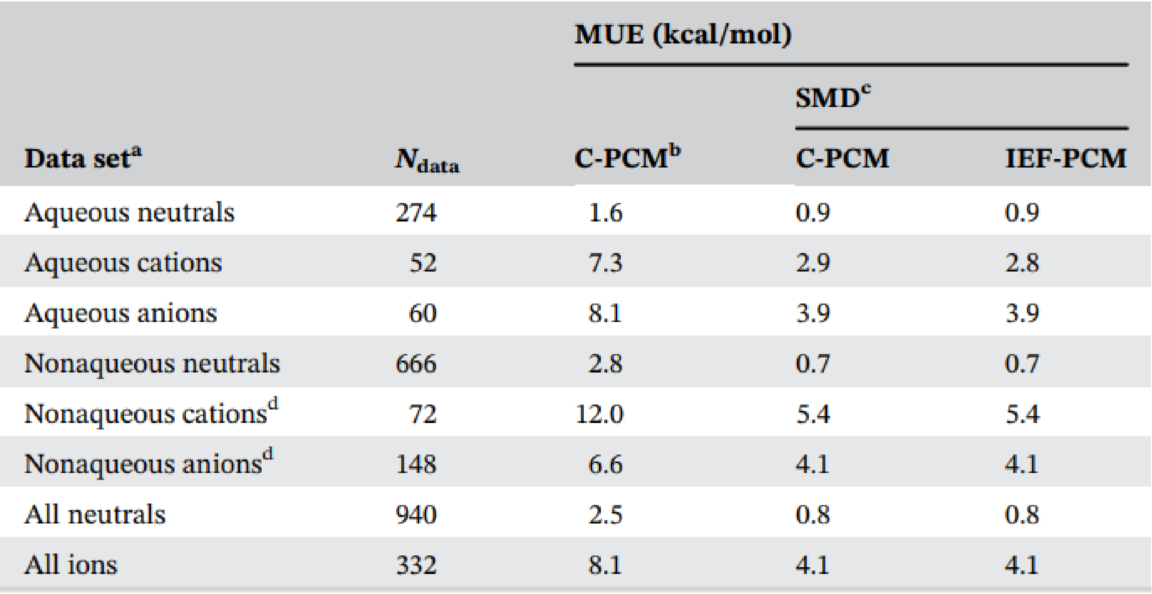


In general, if a 2- or 3- valent ion is under-coordinated the "free" sites should be covered with water molecules.

Accuracy

There is an excellent review of solvation models by J.M. Herbert, WIREs Comput. Mol. Sci. e1519 (2021). It have long discussion of different solvation models and it is more up-to-date than the Cramer's book.

Below is an accuracy test table. As one can see the SMD improves the results significantly.



Data set[a]	N_{data}	MUE (kcal/mol)		
			SMD[c]	
		C-PCM[b]	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

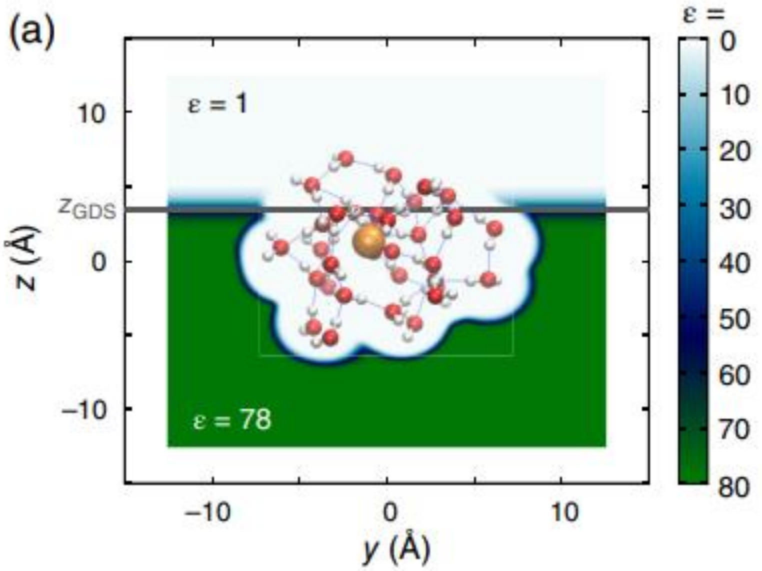
Mean unsigned errors (MUEs) versus experiment, for solvation energies ($\Delta_{solv}G\circ$) computed using various models. From J.M. Herbert, WIREs Comput. Mol. Sci. e1519 (2021), DOI: 10.1002/wcms.1519

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 modifications of solvent models to include the non-isotropic systems. There is some discussion on those in Cramer’s book 11.4.3. and in the Herbert’s review. The non-isotropic solvation models are very interesting when wet surfaces are studied.



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 ε(r), interpolating between εout = 1 above the Gibbs dividing surface (GDS) and εout = 78 below it, with εin = 1 inside of the solute cavity. The horizontal line indicates the position of the dividing surface, zGDS = 3:5Å. 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 so accurate with standard models. The next level models are often commercial but the Orca is an exception. The methods are rather black-box type so it is not easy to know what is really in them.

The CPCM+SMD is a strongly recommended method.