

Lab 8

Solvation and Relativistic Effects

8.1 Overview

In this lab we will consider two separate topics.

The first topic that we will consider this lab is the influence of special relativity on chemical properties. The Schrödinger equation is not relativistic. It turns out that this leads to significant errors in some calculations. We will look at an approximate way to include relativity in our calculations. Further, we will consider when relativity is important and when it is not.

In the second topic we will study how to include the influence of a solvent in our calculations. We will describe the solvent first by discrete molecules and then later through a continuum model. The advantages and disadvantages of the two methods will be compared. A combination of discrete molecules and a continuum model is possible.

8.2 Relativistic Effects

Along with quantum mechanics, Einstein's theories of relativity form the basis for much of the new physics developed in the 20th century. Relativity comes in two flavours, general and special. General relativity usually applies to large masses and the theory of gravity. Gravity is so unimportant to the properties of molecules that we almost always neglect it and the influence of general relativity in computational chemistry calculations. Special relativity on the other hand can be very important.

Special relativity has two basic postulates: that the speed of light is constant in any given reference frame and that the laws of physics are invariant to choice of reference frame. The Schrödinger equation does not follow these postulates and as such is a nonrelativistic equation. An equation equivalent to the Schrödinger equation but also following the postulates of relativity was derived not long after the Schrödinger equation. This second equation is called the Dirac equation.

What happens if we describe a molecule with the Dirac equation rather than the Schrödinger equation? If we consider a very simple system, a nucleus with one electron we find that the energy of that electron that we get with the Dirac equation is lower than what we get with the Schrödinger equation. Furthermore, the difference the relativistic and nonrelativistic energies becomes bigger as the charge on the nucleus becomes bigger.

$$\left(\sum_i \left(c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 + \sum_N \frac{Z_N}{r_{iN}} \right) + \sum_{ij} \left(\frac{1}{r_{ij}} - \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{2r_{ij}} - \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2r_{ij}^3} \right) \right) \Psi = E\Psi \quad (8.1)$$

Figure 8.1: The Dirac equation of a molecule with the electron-electron interaction of Breit.

If we go to many-electron atoms things are a bit more complicated. The lowest energy electrons (the $1s$ electrons) are stabilized by relativity. However, now we also have the electrons interacting with each other. If an electron is stabilized its orbital is smaller and it shields the nucleus better. This means that other electrons feel the nucleus' charge less and they are destabilized. So, some electrons are stabilized and some are destabilized. Which electrons do what? It turns out that all s electrons are stabilized because their orbitals have some amplitude very near the nucleus and so they feel the nuclear charge at its strongest. p orbitals are not stabilized or destabilized much and d and f orbitals are destabilized. Thus, in comparison to a nonrelativistic calculation s orbitals are stabilized and contracted (smaller), p orbitals are not changed so much and d and f orbitals are destabilized and expanded. Once we go to molecules things become even more complicated but they can often be understood in terms of what happens to the atomic orbitals.

Relativity also has a second influence beyond stabilizing electrons. This second influence is spin-orbit coupling which does not exist in nonrelativistic descriptions of the world. As we will see in the next lab, spin-orbit coupling has an influence in NMR and EPR. Spin-orbit coupling appears in a lot of places because it breaks symmetry. Some forbidden electronic transitions become allowed once spin-orbit coupling is included.

These contractions and decontractions, stabilizations and destabilizations and spin-orbit splittings are called relativistic effects. Relativistic effects in chemistry are the term given to anything that arises because of special relativity. Relativity is always present in reality but we can calculate relativistic effects by simply calculating the same thing twice, once with a nonrelativistic approach and once with a relativistic approach.

Just like the one-electron atoms, the relativistic effects on the properties of a molecule become larger as the atoms in that molecule become heavier. It turns out that the errors created by neglecting relativity become unacceptably large once one of the atoms in a molecule is a $4d$ transition metal or heavier. Whether an error is unacceptably large or not will depend on the required accuracy but the cutoff described above should work in most cases where chemical phenomena are considered. If the phenomena of interest is caused by the presence of spin-orbit coupling (for example, g -factors) then of course spin-orbit coupling must be considered somehow.

8.2.1 Relativity and ADF

It turns out that the Dirac equation is pretty horrible to solve so we want to approximate it somehow. There are many ways to approximate the Dirac equation. Two are implemented in ADF. The first is called the zero-order regularized approximation or ZORA for short. The other, somewhat older, method makes use of the Pauli Hamiltonian.

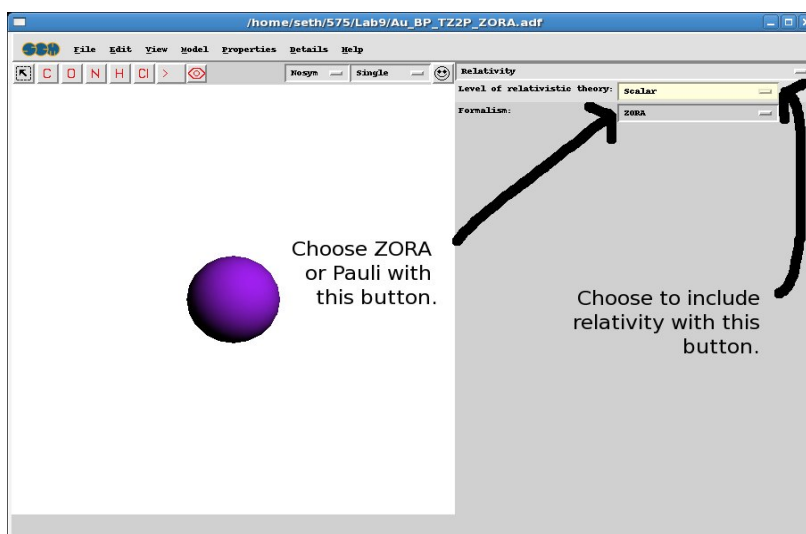


Figure 8.2: Choose to run a relativistic calculation.

To choose to perform a relativistic calculation, use the *Model: Relativity* menu option. This will produce just two buttons (figure 8.2). The first chooses what kind of relativity to include: None (the default) Scalar only or Scalar and spin-orbit coupling. The second button chooses the method of including relativity, ZORA or Pauli.

In general, we would recommend using the ZORA form, especially when very heavy elements ($5d$ transition metals and heavier) are involved but there are occasions when the Pauli method is appropriate.

Exercise 8.1 Calculate the energy of the Au atom with and without scalar relativistic corrections. The valence configuration of gold is $5d^{10}6s^1$ so don't forget to choose an unrestricted calculation and the correct spin polarization. Use a QZ3P basis set and the BP functional. Compare the energies of the $5d$ and $6s$ electrons and the $6p$ virtual orbital of Au in the two calculations. Which are stabilized, which are destabilized by relativity and how much? Gold is gold coloured (metallic yellow) because it absorbs violet light. The transition responsible for the colour of gold is $5d \rightarrow 6s$. If we make the rough approximation that the energy of this transition is equal to the difference in the eigenvalues of the $6s$ and $5d$ orbitals, what colour is nonrelativistic gold?

8.3 Solvation

In all of the calculations that we have done up to this point the molecules and atoms were isolated. We were studying molecules placed in a vacuum. This approach is a good approximation to a molecule in the gas phase. It is sometimes a good approximation to a solvated molecule. Often it is not. The solvent may play an important role in structure, reaction energies and many other issues of chemical importance. The question is, how to include the influence of the solvent? Including millions of solvent molecules in a calculation is not an

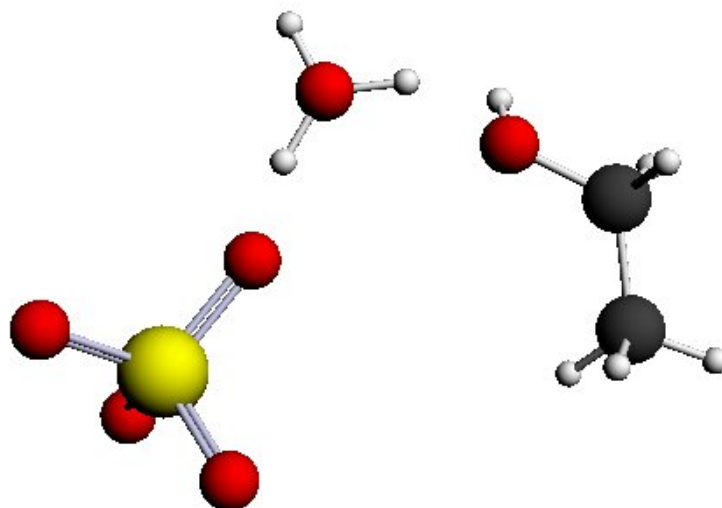


Figure 8.3: A molecule of H_2O shuttling a proton. The solvent molecule must be included in any calculation of this reaction.

option. The wide range of ways that have been tried to approximately include the influence of solvation in molecular calculations usually fall into one of two main classes: explicit solvent molecules and continuum models.

8.4 Explicit Solvation

While it is not possible to include a million molecules in a calculation, a few can be included. “A few” could mean 1 or 2 or 100 or 200 depending on how big the solvent molecules are and how big your computer is. Sometimes a small number of molecules is a suitable replacement for the bulk solvent. Sometimes a solvent molecule is of crucial importance to the property of interest. It may act as a ligand in a complex or actually take part in the reaction under investigation. Sometimes what the solvent molecules are doing is the topic that you are interested in. In these cases, solvent molecules must be included in a calculation.

Aside: These days, it is actually possible to include a million solvent molecules in your calculation if you describe those molecules in a very simple, non-quantum mechanical way. We will not consider this option here and will limit ourselves to describing explicit molecules quantum mechanically.

Exercise 8.2 Optimize the geometry of the ScCl_3 molecule. Repeat the calculation but this

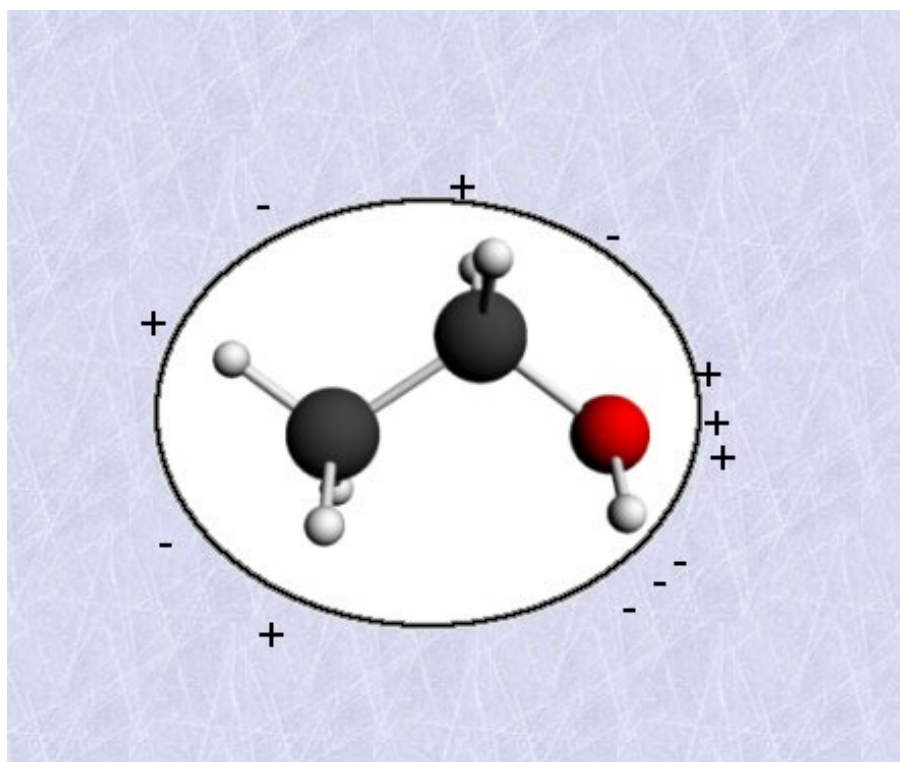


Figure 8.4: A molecule solvated by a continuum model of the solvent.

time add a molecule of H_2O . Repeat both of these calculations but with CH_4 in place of ScCl_3 . Compare the geometry of ScCl_4 and CH_4 in the gas phase with that of the same molecules “solvated” by a single H_2O molecule. Use the LDA functional and a DZP basis set. These calculations may require a fairly large number of geometry optimization steps. Change the default maximum value from 30 to a larger number of your choice in the *Details: Task: GeometryOptimization* option. It’s not obvious ahead of time exactly where the H_2O molecule should go. Make a good guess. The calculations including a solvent molecule might take a while (10-30 minutes on one processor) so it is recommended that they be run on 2 processors.

8.5 Continuum Models

Often a solvent molecule will not bond directly to the molecule of interest or participate in a reaction that is under investigation. The solvent can still be influential however by stabilizing a product, reactant or transition state. Solvent molecules will have a dipole moment or at least be polarizable. These dipolar or polarizable species will interact with charge build up in a molecule and stabilize it. A solvent may then affect the structure and properties of a molecule through this interaction especially if the solvent and/or molecule are especially polar. How a solvent will influence the progress of a reaction is difficult to predict ahead of

time because the solvent will interact differently with the reactants, products, intermediates and transition states of that reaction.

Including this “dipole/polarizable medium” interaction in a calculation through the addition of discrete solvent molecule is difficult because in order to do a reasonable job a very large number of solvent molecules must be included.

An alternative approach is to use a “continuum model” of the solvent. What is meant by “continuum model” is that we describe the solvent as a single continuous blob with appropriate electrostatic properties rather than as isolated molecules. The solvation is achieved by digging an appropriately sized hole out of the blob, putting the molecule into the hole and allowing the electrons and nuclei of the molecule to interact with the blob (figure 8.4).

Numerous different continuum models exist. The differences between each of these models will depend on the technical details of the calculation. A few choices can be made about how the blob will behave. For example, it can be treated as a dielectric or a conductor. Also, a number of choices about how to define the hole in the blob can be made. Several other choices can be made.

Each continuum model contains some parameters. It could be many or few. These parameters must come from somewhere. Often they fitted to experimental data. An experimental parameter that describes the dipole moment and polarizability of a solvent is the dielectric constant (see http://en.wikipedia.org/wiki/Dielectric_constant for more information on dielectric constants). This parameter is often used in a continuum model. Other parameters that can be applied include the size of the solvent and solute and the surface tension of the solvent.

Continuum solvation models are still an area of active research. See http://www.cosmologic.de/data/DOK_HTML/node219.html, <http://www.cup.uni-muenchen.de/oc/zipse/compchem/solv/pcm.html>, http://en.wikibooks.org/wiki/Computational_chemistry/Continuum_solvation_models and http://www.cfs.dl.ac.uk/docs/gamess_manual/chap8/node11.html for more details on four different approaches. The first of these approaches, the COSMO method, is the one implemented in ADF.

8.5.1 COSMO Calculations and ADF

In order to include a continuum solvent into a calculation using the COSMO method, first open the solvation option through the *Model: Solvation* menu option (figure 8.5). The window to the right will display some of the parameters and options of a COSMO calculation. Entries include the *solvent epsilon* (dielectric constant) *solvent radius*, solute atom radii and *solvent*. The *solvent* option gives a list of possible solvents to choose from. The default option is of course *None*. By choosing a predefined solvent a set of default parameters will be chosen. Sometimes the desired solvent is not listed. Further, parameterization of continuum models is an arcane subject and it may be that you have your own set of parameters that you believe to be better. The *UserDefined* option from the *solvent* list can be chosen and your new/alternative parameters entered.

Many other options and parameters of a continuum model can be selected and/or modified through the *Details: Solvation Details* menu option (figure 8.6).

In this lab course we not deal with all these parameters and will only make use of the list of solvents from the *Model: Solvation* menu option. If you would like to understand some

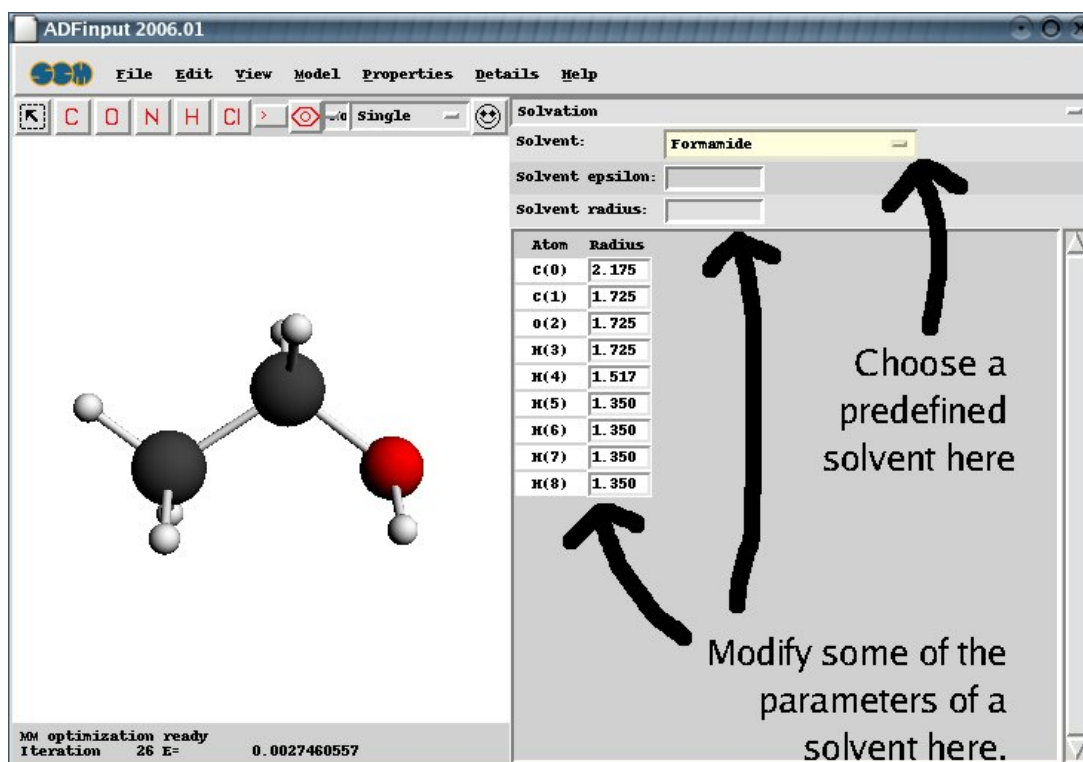


Figure 8.5: The basic solvation menu options.

of the parameters and options of COSMO in ADF consult the paper by Pye and Ziegler that describes how COSMO is implemented in the ADF program (C. C. Pye and T. Ziegler, *Theor. Chem. Acc.* **101**, 396 (1999))

Exercise 8.3 Optimize the geometry of ScCl_3 and CH_4 in water using a continuum model to describe the solvent. Compare the resulting geometry with those obtained for a molecule in a vacuum and in the presence of a single water molecule. Also compare the length of time each calculation took. Use the same basis set and functional as was used in the previous exercise.

8.6 Combination Calculations

A continuum model can include the influence of the many solvent molecules that surround a solute in a calculation but it cannot include the influence of a solvent molecule participating directly in a reaction or bonding directly to a solute molecule. On the other hand, including solvation effects through explicit solvent molecules will be able to reproduce the direct influence of a solvent molecule but will generally not be able to simulate the effect of the many surrounding solvent molecules.

The two differing approaches to solvation clearly each have their own advantages and disadvantages. There is nothing to say that both can't be used at the same time however.

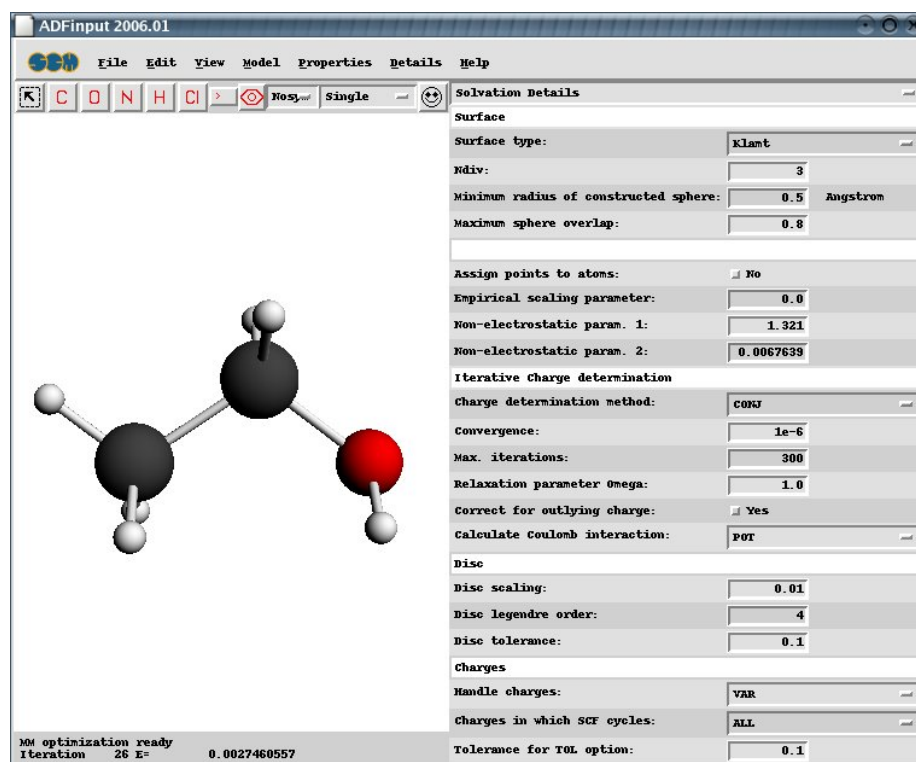


Figure 8.6: A couple of other options of the continuum model that you might like to play with.

In this way, we can take advantage of the good points of both methods while reducing the influence of their less attractive aspects.

In order to use both methods at the same time we would first build the molecule we are interested in, add in the explicit solvent molecules that are required and then surround the whole set of molecules by our continuum model for the solvent (figure 8.7).

Exercise 8.4 Optimize the geometry of ScCl_3 and CH_4 in the presence of a single molecule of H_2O and surrounded by a continuum model of H_2O . Use the same basis set and functional as you have applied to the previous exercises in this lab. Compare the geometries and calculation times obtained in the combination calculation with the previous results.

8.7 Projects

8.7.1 *The Influence of Scalar Relativistic Corrections on the Bond Lengths of Diatomic Molecules*

Calculate the bond lengths of the following group 1 diatomics with and without the inclusion of scalar relativistic corrections: K_2 , Rb_2 and Cs_2 . Perform the same calculations but this

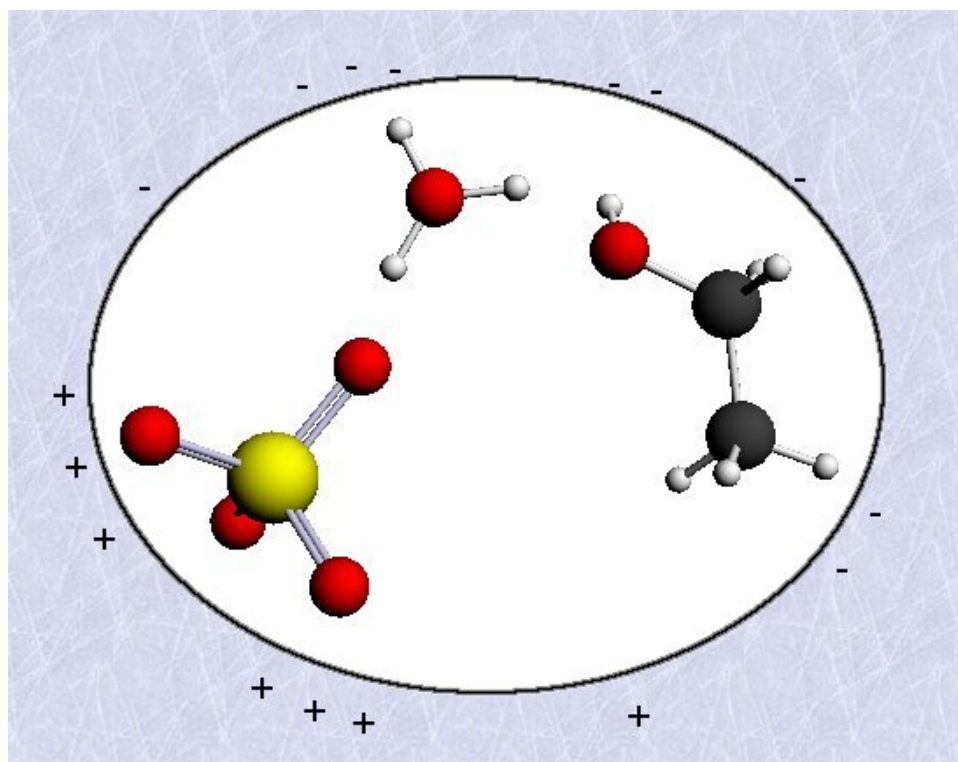


Figure 8.7: A system including a solvent molecule along with a continuum solvent model.

time consider three group 11 diatomics Cu_2 , Ag_2 and Au_2 . Perform the same calculations but this time consider three group 17 diatomics, Br_2 , I_2 and At_2 . Make a table of your results and include in your table the difference between the relativistic and nonrelativistic results. How do the relativistic effects change going down the periodic table? How do they change going across the periodic table?

Use a TZ2P basis set and the BP functional. The ZORA option is the best choice for relativistic contributions here.