

The Potential Energy Surface

In this section we will explore the information that can be obtained by solving the Schrödinger equation for a molecule, or series of molecules. Of course, the accuracy of our solutions will be highly dependent on the exact basis set and method used.

The Basics

Let us start by looking at the energy E . When we solve the Schrödinger equation under the Born-Oppenheimer (BO) approximation we assume *the nuclei are fixed*, and we solve for the electrons, we obtain an energy E which is dependent on the frozen position of the nuclei. If I represent all the nuclear positions by a collective coordinate R , I get an *energy $E(R)$ dependent on the frozen nuclear positions*. All this means is, that if I move the nuclei slightly I will get a different energy $E(R')$ because the interactions inside of H will be slightly different. For example the electrostatic interaction between the nuclei will be different because the distance between them has changed. If I join these points up I have a function E dependent on the collective coordinates R called the potential energy curve or the *Potential Energy Surface (PES) $=E(R)$*

You are already familiar with this concept, the dissociation curve of a diatomic represents a potential energy curve $E(R)$, that is, E dependent on R , see **Figure 1**. In a diatomic there is only one "R" the distance between the two nuclei. As the nuclei get close together, they repel each other (two positive charges repel) and the energy goes up. As the nuclei become stretched and the electrons no longer form a bond, the electron-nuclear attraction decreases, the energy goes up and the molecule dissociates.

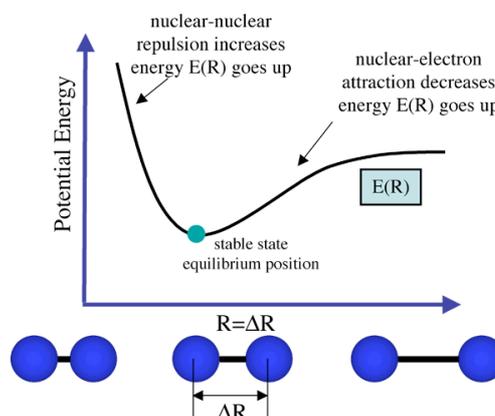


Figure 1 Potential energy surface

Somewhere in the middle the electrons and nuclei are able to arrange themselves so that they are stable, we say that the system is in *equilibrium*. When something is in equilibrium we say there are no net forces on the molecule (nothing pushing on them to make them want to move).

Once at the equilibrium geometry the molecule will not want to change, this is the stable state, and the structure that is computed or alternatively determined using X-ray crystallography. There will be slight differences between the computed gas-phase and X-ray solid state structure, because the X-ray structure will experience effects from surrounding molecules and co-crystallites, while the computed molecule will not. But how do we find the stable structure computationally? Normally we know roughly the structure of a molecule, but we don't know the exact stable state. If a crystal structure already exists we can use it as a starting point. If not, we make an informed guess and let the computer do all the hard work. Thus before we go any further we have to *optimise* the structure.

That is we solve the Schrödinger equation for the nuclear positions and electrons and find the energy $E(R)$. Then we move the atoms a little, solve the Schrödinger equation again obtaining a new energy $E(R')$ (I've represented the shifted collective coordinates by R'). Then we compare the energies and if the new energy is lower we "move" in that direction. Then we start our search again from this new nuclear configuration. In this way we gradually move toward the lowest energy structure. As the system moves there will be a sequence of different energies all dependent on the changing coordinates of the nuclei and electrons. The process of optimization is shown in **Figure 2**.

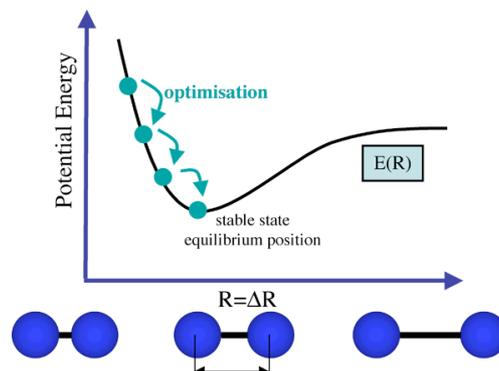


Figure 2 Optimisation along a potential energy surface

start: $H(R)\Psi(R) = E(R)\Psi(R)$
 step 1: $H(R')\Psi(R') = E(R')\Psi(R')$
 step 2: $H(R'')\Psi(R'') = E(R'')\Psi(R'')$
 and $E(R) > E(R') > E(R'')$ and so on.

When the nuclei and electrons are in equilibrium, they experience no forces trying to shift them one way or another. When the nuclei and electrons are not in equilibrium their mutual interactions, ie nuclear-nuclear repulsion, nuclear-electron attraction, electron-electron interactions, through the potential $V(r) = V_{ne} + V_{ee} + V_{nn}$ are not stable, these interactions cause forces to be exerted on the nuclei and electrons making them shift into better positions. It is clear that there is a relationship between these forces, $F(R)$, and the interactions inside of $V(R)$ which through solving the Schrödinger equation $H\Psi = [T_e + V(R)]\Psi = E(R)\Psi$ contribute to $E(R)$, the equation for this is given below,

$$F(R) = \frac{-\partial E(R)}{\partial R}$$

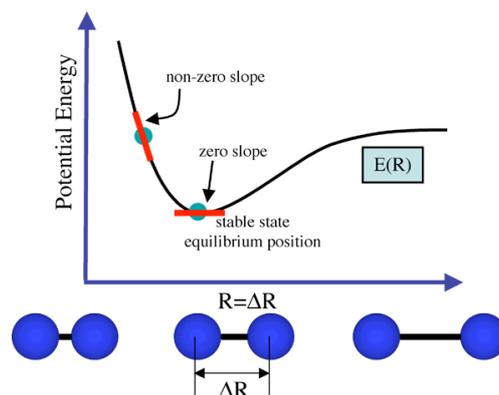


Figure 3 Potential energy surface

This just "says" that the molecule will experience forces $F(R)$ as long as a change in position (∂R) causes a change in energy, $\partial E(R)$. This equation is the first derivative, of the $E(R)$ function, and is the slope of the graph at any point. At equilibrium (when we have zero forces) the slope of the graph is zero, **Figure 3**. Thus we now have a criteria for searching for key structures of a molecule, the structure we want is the one at which the first derivative of the PES is zero.

However, I hope you remember from your pre-university days that while the first derivative of a function tells us the slope, it doesn't tell us if we are at a maximum or a minimum point! For example consider the case where there is a barrier to dissociation in our one dimensional example, **Figure 4**, both the maximum of the barrier (the transition state) and the minimum (the ground state) have a slope of zero.

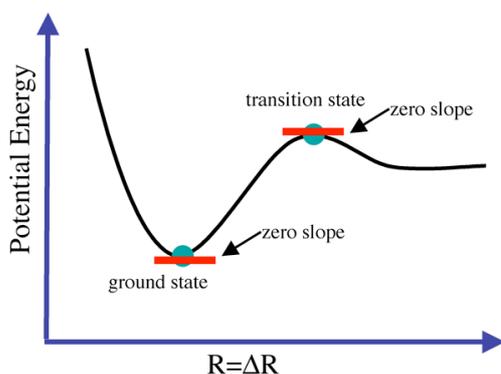


Figure 4 Ground state and transition state structures both have a zero slope (or zero first derivative of the PES)

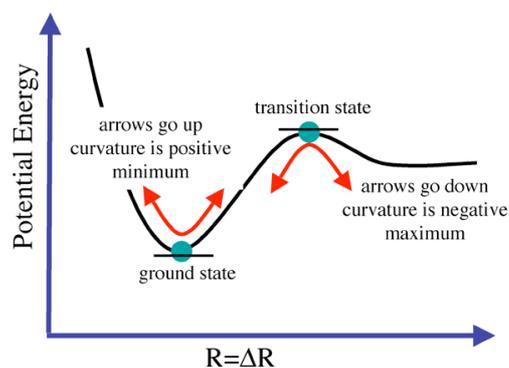


Figure 5 The second derivative gives the curvature of the surface and identifies maxima from minima

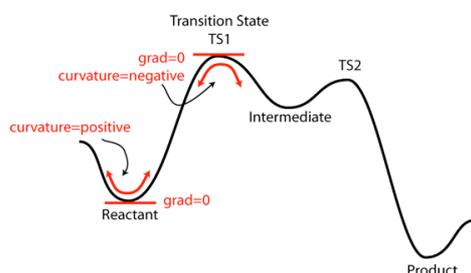


Figure 6 One dimensional reaction path

We will have to take the second derivative, if the second derivative is positive we have a minimum and if the second derivative is negative we have a maximum. The second derivative gives the *curvature* of the function, how this works is shown in **Figure 5**.

function $f(x)$

$$\text{first derivative } f'(x) = \frac{df(x)}{dx}$$

$$\text{second derivative } f''(x) = \frac{d^2 f(x)}{d^2 x}$$

if $f'(x) = 0$ then max or min

if $f''(x) \Rightarrow 0$ then max

if $f''(x) \Leftarrow 0$ then min

Now consider how this might look for a more general reaction mechanism, **Figure 6**. Those points on a potential energy surface where the first derivative is zero are called *critical points*, they are the points we think of as being important in a step wise mechanism.

The potential energy surfaces we have seen so far have been presented as one dimensional. This then maps out the energy versus a single coordinate, a bond stretch in the case of the diatomic dissociation curve. However the PES for a large molecule is significantly more complex, it is a function of energy vs *every* coordinate. What do I mean by every coordinate? Well, each atom has its position defined by its (x,y,z) coordinates, therefore for a single molecule there will be $3N$ coordinates (N =number of atoms). Normally we remove the center of mass motion leaving $3N-6$ independent coordinates (3 translational and 3 rotational coordinates are removed). So although we have drawn a diagram of energy vs one coordinate, the real potential energy surface is a function of $3N-6$ coordinates. (does this remind you of the $3N-6$ vibrations in a non-linear molecule!)

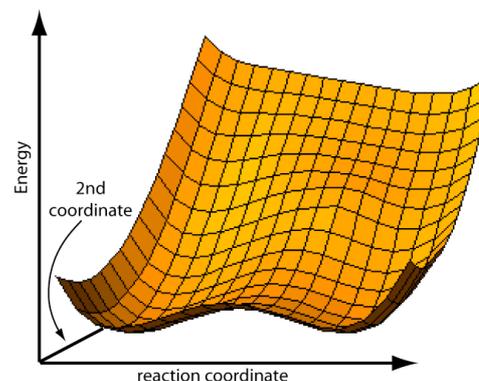


Figure 7 Two dimensional PES

Consider for example a small molecule, NH_3 , this will have $3 \times 4 - 6 = 6$ independent coordinates. How good are you at imagining 7 (6+energy) dimensional space? Because we cannot draw or describe these high dimensional spaces very well, we like to simplify things, we use symmetry where we can, and try to look at key coordinates, rather than the whole potential energy surface, hence the "reaction coordinate". Physically we can only draw in three dimensions, so we can only ever represent in a picture at most two of the $3N-6$ dimensions that contribute to the PES, **Figure 7**.

Thus for a reaction path the vertical axis is energy and the horizontal axis is a *general reaction coordinate*. These types of pictures are useful but should be taken with a grain of salt. It is seldom that a single atom – atom distance (bond break or formation) "drives" a chemical reaction, there will be other contributing bonds and angles, and the primary contributor to the reaction coordinate can change. These diagrams are "cartoons", vastly simplified pictures of a rather complex process!

Now that we have a multi-dimensional surface dependent on many coordinates, $E(R_1, R_2, R_3, \dots, R_N)$ how do we determine the stable geometries and transition states? Basically we still take first and second derivatives but now we do it for each coordinate, more on this next week. In reality potential energy surfaces are very complex creatures. While a particular diagram shows only a few intermediates and transition states, in reality the reaction could have many 10's of such structures. The "reaction mechanism" is really a path traversing a multidimensional landscape, a bit like a hiking track through the mountains. Finding the intermediates and transition states that we are interested in can be very difficult, and there is a great deal of on-going research into finding efficient ways of searching or mapping out potential energy surfaces.

Studying a Reaction Mechanism

Catalytic cycles are ideal cases for computational analysis. They are composed of elementary reaction sequences which can be studied in isolation. Catalysts are crucial because they open a lower activation energy pathways, but are problematic because we don't have a full understanding how this happens. Calculations are ideally suited to look at this kind of process, we can look for the low energy transition states, and then ask ourselves how to lower it further. This information can be fed back to experimental chemists who are trying to design complexes with enhanced catalytic ability. Alternatively we can look at destructive routes, isolating transition states for side reactions, and investigating ways of making them less stable.

Where do we start in studying a reaction mechanism? The reaction mechanism will generally have been predicted "on-paper", and our first step is to optimise all the relevant critical point structures along the reaction path. Often we have a good idea of the reactants and products because we will have the relevant crystal structures. In addition, because these are very stable species the optimiser will normally find them without difficulty. One problem that does occur is that the optimizer finds the nearest low energy structure, and this may not be the lowest energy structure! This is where the chemical knowledge of the user comes in. These first studies indicate the energy (or enthalpy) for the overall reaction (ie $E(\text{products}) - E(\text{reactants})$). If this is not negative, the reaction will not occur.

The optimised structures of the reactants and products are then modified to give us a starting "guess" for intermediates or transition states. We will tell the optimiser to

look for a minimum or transition state and let it run monitoring the calculation to ensure it is not doing something odd. Finding transition states and intermediates can be quite problematic. In addition, multiple isomers of a particular structure often exist, each one needs to be individually examined, and often energy differences will be small. This means the relative stability of structures can change depending on the local environment, the method used and the basis set. Optimised structures have to be confirmed by a second calculation the "frequency analysis" which gives us the second derivatives. We must also ensure that we are following the "right" reaction path, ie that the transition state we have found connects a particular reactant and product. This is achieved by carrying out an "Intrinsic Reaction Coordinate" or IRC analysis.

Geometry optimisation is expensive compared to just evaluating the energy. We have seen that each step in an optimisation requires an energy determination, moreover we also have to evaluate the gradient which is more expensive again. In practice we will first obtain a general understanding of the structures and mechanism using a lower level method and basis set, and then improve our computational description, refining our initial results. It is also important not to waste time and resources, thus we will need to determine the lowest computational level at which good quality result can be obtained. We normally do this for the reactants and products, testing methods and basis sets, and deciding on the best ones to use for the whole mechanism.

At this point it is good to re-iterate that there are essentially two optimisations occurring. The first optimises the electronic structure to obtain the wavefunction, this is the SCF cycle, or a single point (SP Gaussian keyword) calculation. The second steps through possible geometries to find the most stable nuclear structure, to obtain the geometry. This is the optimisation (OPT Gaussian keyword).

Extensive studies have shown, that the geometry converges quickly with respect to the basis set and method. This means that increasing the method or basis set does not significantly change the final geometry. In addition some of the higher level methods have not been implemented with an optimiser, or it carrying out a geometry optimisation would be prohibitive. Thus it is possible to evaluate the geometry at a lower level (say DFT) and then compute the energy (at this geometry) at a higher level (say CCSD(T)) to obtain more accurate energies and electron densities. This is also useful because in general, experimental results are bracketed by the lower level B3LYP and higher level CCSD results.

When this kind of process has been carried out it is indicated by a special notation, the level at which the energy (and wavefunction) has been calculated is given first, and separated from the level at which the geometry has been calculated by the symbol "//", for example:

- CCSD(T)/aug-cc-pVTZ//B3LYP/cc-pVDZ
a single point energy calculation at the CCSD(T)/aug-cc-pVTZ level
carried out on an optimised geometry at the B3LYP/cc-pVDZ level
- MP2/6-311+G(d,p)//HF/6-31G*
a single point energy calculation at the MP2/6-311+G(d,p) level
carried out on an optimised geometry at the HF/6-31G* level

There are other methods, that use a series of calculations at a lower level and attempt to extrapolate to produce a very accurate energy. Typically such methods aim for "chemical accuracy" which is defined at 1 kcal/mol = 1.184 kJ/mol. Two such methods are the Gaussian-n methods (for example G1 and G2) and the CBS

(Complete Basis Set) methods (for example CBSQB3). Such methods tend to start by computing a geometry and zero-point energy correction and then compute the energy with a very good basis set at a low level, and progress to computing the energy with a low level basis set at high level. Information is fed into an analytic expression to obtain the final extrapolated energy. I'm not going to discuss these any further, but you should be aware such methods exist.

The critical points are then joined up to produce an energy diagram, and to obtain an overall picture of the reaction. Frequently we have to re-evaluate our initial "on-paper" mechanism. Thus we can *propose* a mechanism using chemical intuition and experience, however we do not *know* that this is the path the reaction takes. We may have indirect experimental evidence. Computations provide a powerful tool, enabling us to *validate or refute* the proposed mechanism with a significant level of confidence. For example, large barriers mean that a reaction will not follow that particular route. The rate determining step is identified as the step having the highest barrier along the lowest energy reaction path.

Once a reaction path has been determined analysis of the mechanism can follow. We now have access to structural information, energies, and properties dependent on the electron density, such as population and MO analysis, we will be examining some of these later. Analysis of the structures and properties can lead to valuable insight, and to a fundamental understanding of the processes occurring. Insight can be obtained into complexes it is impossible to experimentally isolate.

So far we have focused on the potential energy surface, and characterising a reaction mechanism, however there are many other uses for calculations that basically evaluate an energy. I'm not going to go into much detail here, but you should be aware that being able to calculate energies gives us access to a substantial amount of information, for example:

- Atomisation energies
- Atomic energies
- Ionization energies
- Electron affinities
- Relative configurational stabilities
- Bond dissociation energies

Case 1: Hydroamination of Aminoalkynes

Organometallics 2006, 25, 5533–5539

Organolanthanide-Catalyzed Hydroamination/Cyclization Reactions of Aminoalkynes. Computational Investigation of Mechanism, Lanthanide Identity, and Substituent Effects for a Very Exothermic C–N Bond-Forming Process

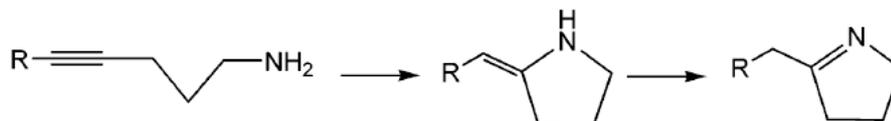
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Catalytic Cycles and Potential Energy Surfaces (Lanthanide Chemistry)

Hydroamination is N–H bond addition over an unsaturated C–C multiple bond, an alkyne in this case. The use of lanthanides as catalysts has recently seen significant advances. However, lanthanide catalytic mechanisms differ from their more conventional TM cousins which are dominated by oxidative addition and/or reductive elimination pathways. Lanthanides typically have a single primary oxidation state and interactions are dominated by electrostatic rather than covalent considerations.



Mechanism

- ◆ description of mechanism
- ◆ discussion of energy profile
- ◆ not discussing thermodynamical aspects now
- ◆ IRC means of confirming correct TS
- ◆ analysis of structures not isolateable experimentally
- ◆ changing metal or the R groups

Computational Details

- ◆ B3LYP is a DFT method (discussed more later), commonly used method
 - ECP of Stuttgart/Dresden used for Ln atom
 - Good quality ECP
 - Justification for including 4f electrons in PP
- ◆ All other atoms use all-electron 6-31G** basis
 - 6 GTOs for each core orbital
 - 4 GTOs split into pattern 3:1 requiring variation of 2 parameters for valence orbitals
 - included one set of polarisation functions on all atoms (including H)
- ◆ PES data
 - IRC not be discussed, method for confirming found correct TS
 - Frequency calculation (to confirm nature critical points)
- ◆ Codes and Machines
 - Specifies code used G98
 - Specified machines calculation run on IBM-SP and Origin 3000 systems