

Building Transition State Models & Using ZPE

Essential Concepts

Nuclear coordinate (\mathbf{r}_i) – A vector (x_i, y_i, z_i) pointing to the location of atomic nucleus i in three-dimensional space. If the word “vector” bothers you, just think “three variables”.

Molecular geometry – Simultaneous locations of all nuclei (\mathbf{r}_i). For example, the geometry of a triatomic system is specified by assigning numerical values to three vectors: \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 .

Potential energy¹ – Total electronic energy, E_{tot} . This energy functions as a potential energy because its value is determined by the molecular geometry.

Potential energy surface (PES) – An imaginary graph showing how potential energy changes as a function of molecular geometry.

Gradient – A vector composed of the first derivatives of the PES, i.e., $(\partial E_{\text{tot}}/\partial \mathbf{r}_1, \partial E_{\text{tot}}/\partial \mathbf{r}_2, \dots, \partial E_{\text{tot}}/\partial \mathbf{r}_N)$. Note that $\partial E_{\text{tot}}/\partial \mathbf{r}_i$ is short-hand for a vector (three variables) defined by $(\partial E_{\text{tot}}/\partial x_i, \partial E_{\text{tot}}/\partial y_i, \partial E_{\text{tot}}/\partial z_i)$.

Stationary point – Any point on the PES where the gradient vector vanishes, i.e., where the gradient becomes the zero vector, $(0, 0, \dots, 0)$.

Curvature (second derivative) – $\partial^2 E_{\text{tot}}/\partial \mathbf{r}_i \partial \mathbf{r}_j$. Note that this symbol is short-hand for a collection of nine differentials: $\partial^2 E_{\text{tot}}/\partial x_i \partial x_j, \partial^2 E_{\text{tot}}/\partial x_i \partial y_j, \dots, \partial^2 E_{\text{tot}}/\partial z_i \partial z_j$.

Minimum-energy geometry – Any stationary point on the PES where the curvature is completely positive, i.e., where $\partial^2 E_{\text{tot}}/\partial \mathbf{r}_i \partial \mathbf{r}_j > 0$ for all i and j .

Reaction coordinate – The lowest potential energy path across the PES connecting reactants and products.

Transition state (\ddagger) – Any stationary point on the PES that is also a saddle point, that is, a point where one curvature is negative (the curvature with respect to the reaction coordinate), and all other curvatures are positive. Because the curvature is negative along the reaction coordinate, the transition state is the maximum energy geometry on this coordinate.

Normal coordinates (ξ_i) – Curvatures can be described (and used) more easily if we change the coordinate system. Specifically, it is beneficial to combine x_i, y_i , and so on, to make *normal coordinates*, ξ_i , that have the special property that $\partial^2 E_{\text{tot}}/\partial \xi_i \partial \xi_j = 0$ when $i \neq j$. The curvatures calculated using normal coordinates are “pure” in the sense that the PES curvature with respect to any normal coordinate is defined by a single number, $\partial^2 E_{\text{tot}}/\partial \xi_i^2$. You are probably familiar with the normal coordinates of the water molecule: symmetric stretch, asymmetric stretch, and bend. The reaction coordinate for any chemical reaction is also a normal coordinate.²

Force constant (\mathbf{k}) and vibration frequency (ν) – When vibrations are treated as harmonic oscillations, each vibration corresponds to a particular normal coordinate (the combined motion of the nuclei is called a *normal mode*). The force constant is

¹ This discussion assumes that the potential energy surface defines the transition state’s location but arguably it is the free energy that does this. However, aside from some textbook examples, I have yet to come across a real world case where this distinction is important.

² Normal coordinates change with geometry because the curvature of the PES changes. If we increase the OH distance for one bond in water, the normal coordinates will no longer be symmetric.

the curvature with respect to that normal coordinate, $k_i = \partial^2 E_{\text{tot}} / \partial \xi_i^2$, and the vibration frequency, ν_i , is proportional to the square root of the force constant, $(k_i)^{1/2}$. Since one, and only one, $k_i < 0$ at a transition state, we can say a transition state is a stationary point with exactly one negative force constant, or equivalently, exactly one imaginary frequency.

Equilibrium geometry calculation – A calculation that searches for a minimum-energy geometry. In fact, most computer programs (*Spartan* included) actually search for a stationary point. Therefore, for careful research, one must test the final geometry by calculating the vibration frequencies and verifying that all frequencies are positive.

Transition state geometry calculation – A calculation that searches for a saddle point geometry. Three factors make transition state searches much more difficult than equilibrium geometry searches: 1) search algorithms typically assume that the coordinate with the lowest (least positive or most negative) force constant is the reaction coordinate, 2) the force constants are only estimated so the search is not based on reliable information, 3) automated procedures for locating transition states are not as reliable or mathematically efficient³ as procedures for locating minimum-energy geometries. Not every saddle point is a transition state so the putative transition state model must be subjected to two additional tests. First, the vibration frequencies must be calculated and there must be exactly one imaginary frequency. Second, the vibration motion associated with this frequency must convert the transition state into the expected reactants and products, i.e., the normal coordinate must be the reaction coordinate.

Procedure for Building Transition States

1. **Build a trial geometry.** This is an art. If you are lucky, you might be able to find a suitable structure in *Spartan's* database. If you are unlucky, you will have to use trial-and-error. A standard procedure is to constrain distances and angles to plausible values, e.g., 2.1 Å for a partial CC single bond and 1.5 Å for a partial CH bond, and then calculate your model's **equilibrium geometry** subject to these **constraints**. If the resulting model looks reasonable, you can remove the constraints and proceed.
2. **Calculate the reaction coordinate.** Calculate the vibration frequencies for your model by calculating **energy** and checking the **compute: IR** box. After the calculation is finished, **display: spectra** and check the vibration frequency at the top of the list. The value does not need to be imaginary (this is just a trial structure), but the atom motions should look like the reaction coordinate.⁴
3. **Calculate the transition state geometry.** If the trial model is acceptable, calculate the **transition state geometry** and **compute: IR**. After the calculation is finished, **display: spectra**. There should be exactly one imaginary frequency. The motion associated with this frequency should look like the reaction coordinate.

³ Low efficiency is partly due to the nature of the PES itself. A PES normally tends to be "flatter" near a transition state than near an equilibrium geometry.

⁴ Atom motions may be hard to see. Add more **steps** to slow motion down and/or increase **amp** to make motions larger. Zooming the model to a larger size also helps.

Procedure for Calculating and Using ZPE

This procedure can be combined with step #3 of the previous one by checking the **print: thermodynamics** box and entering **FREQSCALE=0.90** in the **options** box before submitting the transition state geometry calculation.

If you have already performed the transition state and IR calculations, just open the **Setup: Calculations** window, make the additional entries that are needed, and submit the calculation. The results will be added to **display: output**.

ZPE, and all other thermodynamic quantities (temperature corrections, entropies, free energies) can be found in **display: output**, but an easier way to obtain these data is to **display: spreadsheet** and **add** a column for **E** and another for **ZPE**. Energy units can be set as desired at this point and it is most convenient to obtain both quantities in kcal/mol.

ZPE is a form of kinetic energy (vibrating nuclei at 0 K), so ZPE just gets added to E_{tot} to give the energy of the molecule at 0 K. Reaction barriers and energies are calculated as follows:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= (E_{\text{tot}} + \text{ZPE})_{\text{final}} - (E_{\text{tot}} + \text{ZPE})_{\text{initial}} \\ &= (E_{\text{tot},f} - E_{\text{tot},i}) + (\text{ZPE}_f - \text{ZPE}_i)\end{aligned}$$

The third equation may be less convenient to use, but it is interesting because it shows how you can determine how much of the energy change is due to a change in “potential” energy (E_{tot}) and how much is due to a change in ZPE.