THE CONCEPT OF THE POTENTIAL ENERGY SURFACE

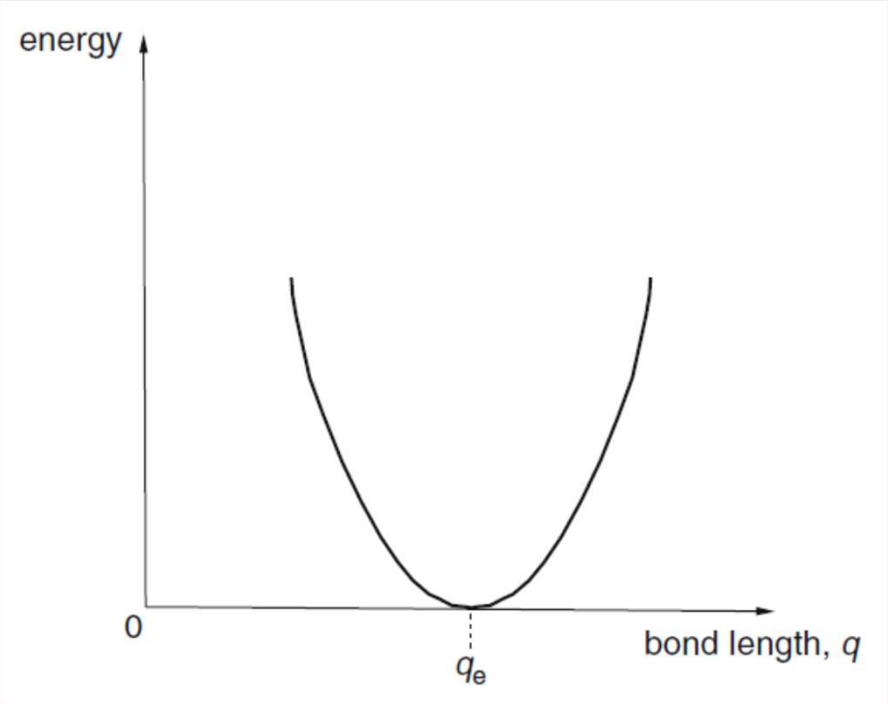
Chapetr 2

Everything should be made as simple as possible, but not simpler.
Albert Einstein

Abstract

- The potential energy surface (PES) is a central concept in comp. chem.
- A PES is the relationship – mathematical or graphical – between the energy of a molecule (or a collection of molecules) and its geometry.
- The Born–Oppenheimer approximation says that in a molecule the nuclei are essentially stationary compared to the electrons. This is one of the cornerstones of comp. chem. because it makes the concept of molecular shape (geometry) meaningful, makes possible the concept of a PES, and simplifies the application of the Schrodinger equation to molecules by allowing us to focus on the electronic energy and add in the nuclear repulsion energy later;

- We begin a more detailed look at comp. chem. with the PES because this is central to the subject.
- Consider a diatomic molecule AB. In some ways a molecule behaves like balls (atoms) held together by springs (chemical bonds);
- The stretched or compressed spring possesses energy,

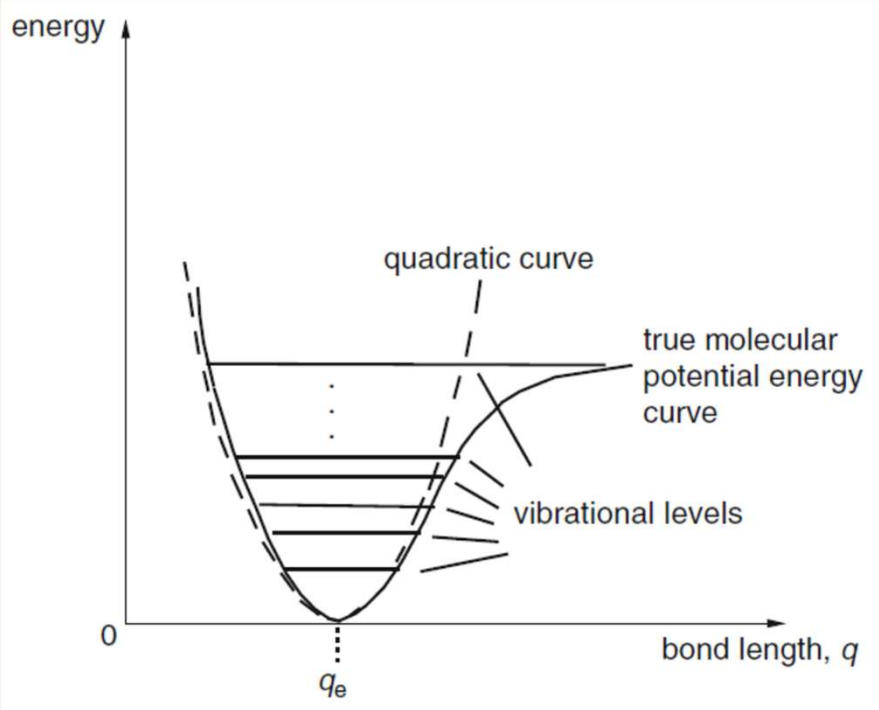


The potential energy surface for a diatomic molecule. The potential energy increases if the bond length q is stretched or compressed away from its equilibrium value q_e. The potential energy at q_e (zero distortion of the bond length) has been chosen here as the zero of energy

- Real molecules behave similarly to, but differ from our macroscopic model in two relevant ways:

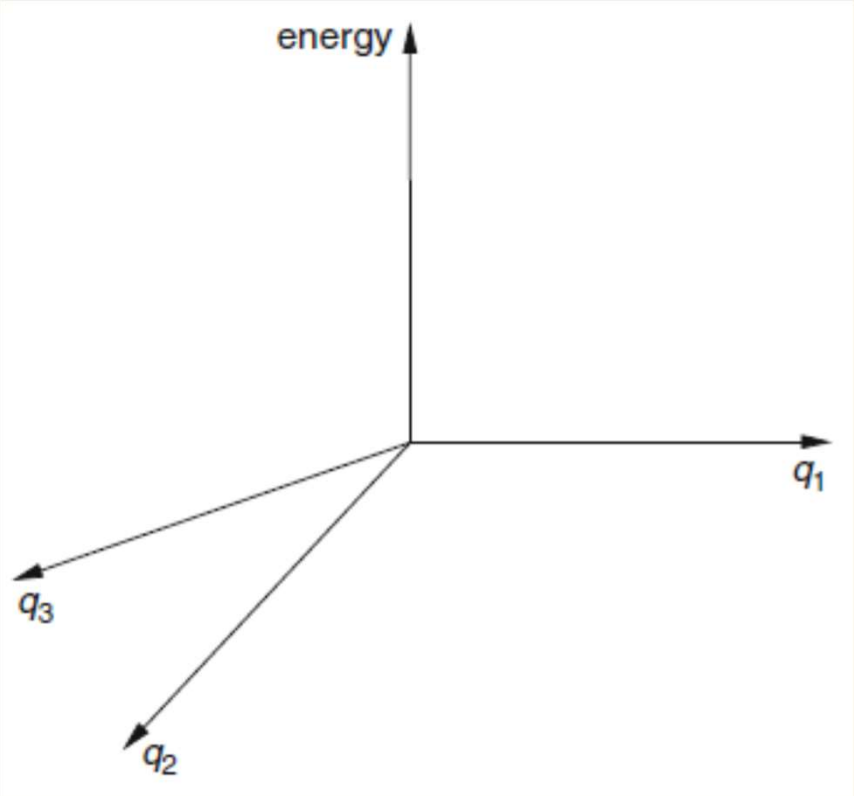
  (1) zero point energy

  (2) anharmonicity

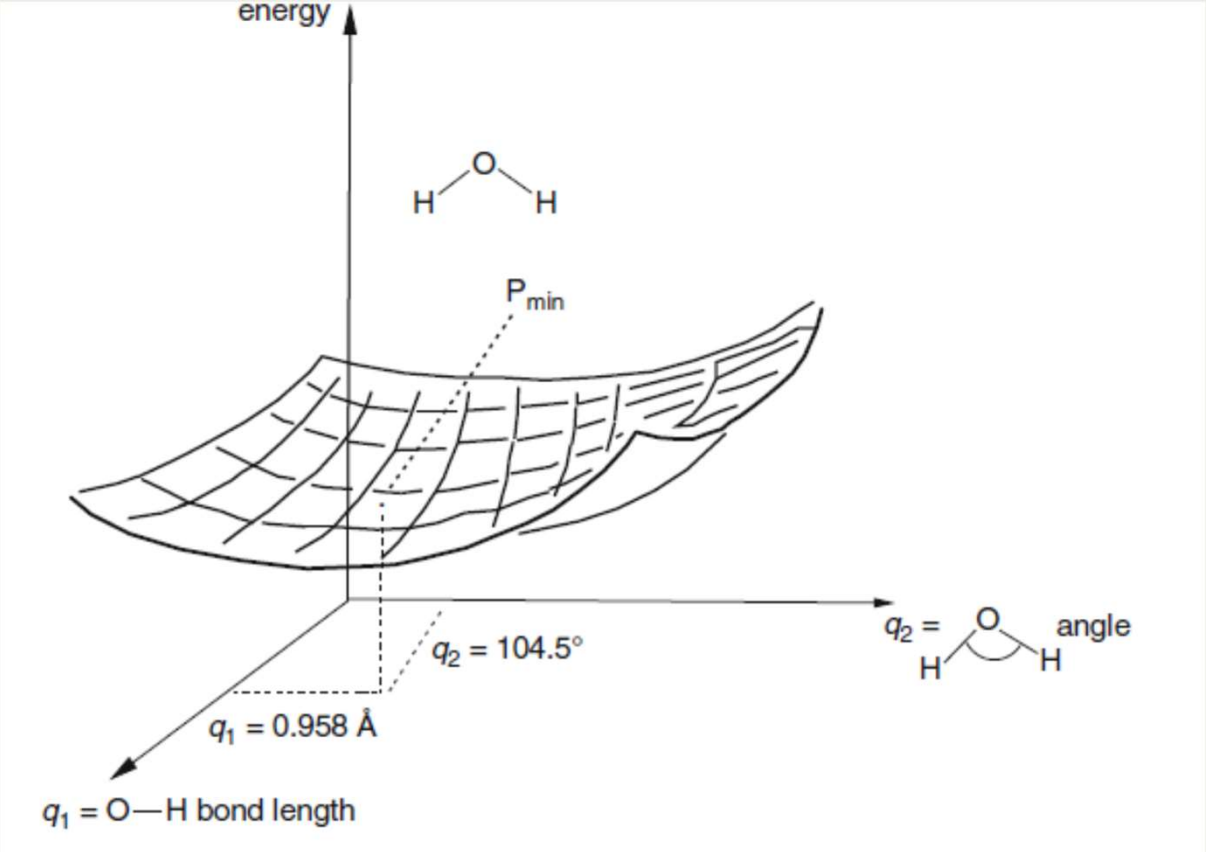


Actual molecules do not sit still at the bottom of the potential energy curve, but instead occupy vibrational levels. Also, only near q_e, the equilibrium bond length, does the quadratic curve approximate the true potential energy curve

- Figure (1) represents a one-dimensional PES in the two-dimensional graph of E vs. q. (one geometric parameter)
- water: the geometry is defined by two bond lengths and a bond angle. if we limit ourselves to C_{2V} symmetry (allowing the two bond lengths to be the same) then the PES for this triatomic molecule is a graph of E versus two geometric parameters, q_1= O–H bond length, and q_2 = H–O–H bond angle. a 2-D PES in the three-dimensional graph;
- a triatomic molecule of lower symmetry, HOF.
- three geometric parameters: the H–O and O–F lengths and the H–O–F angle.
- To construct a Cartesian PES graph for HOF: We would need four mutually perpendicular axes → a 4-D graph cannot be constructed in our 3-D space. we cannot draw it.
- The HOF PES: a 3-D “surface” in 4-D space (a hypersurface, or a potential energy hypersurfaces.
- Despite the problem of drawing a hypersurface, we can define the equation E=f (q_1, q_2, q_3) as the potential energy surface for HOF, (treat the hypersurface mathematically).
- on the AB diatomic molecule PES: the minimum PE geometry is the point at which dE/dq = 0.
- On the H_2O PES: the minimum PE geometry is defined by the point P_m, where $dE/dq_1 = dE/dq_2 = 0$.

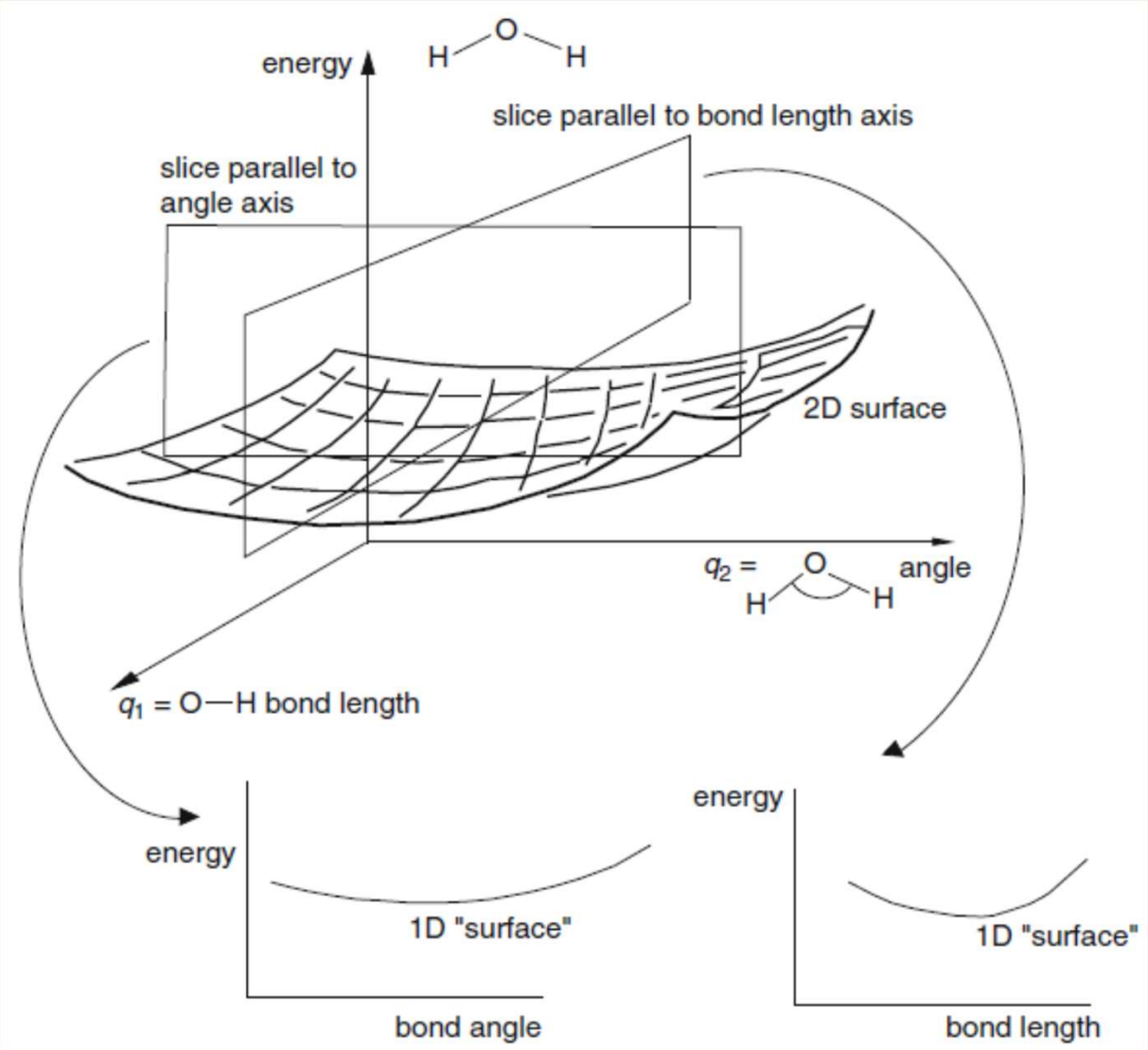


To plot energy against three geometric parameters in a Cartesian coordinate system we would need four mutually perpendicular axes. Such a coordinate system cannot be actually constructed in our three-dimensional space. However, we can work with such coordinate systems, and the potential energy surfaces in them, mathematically

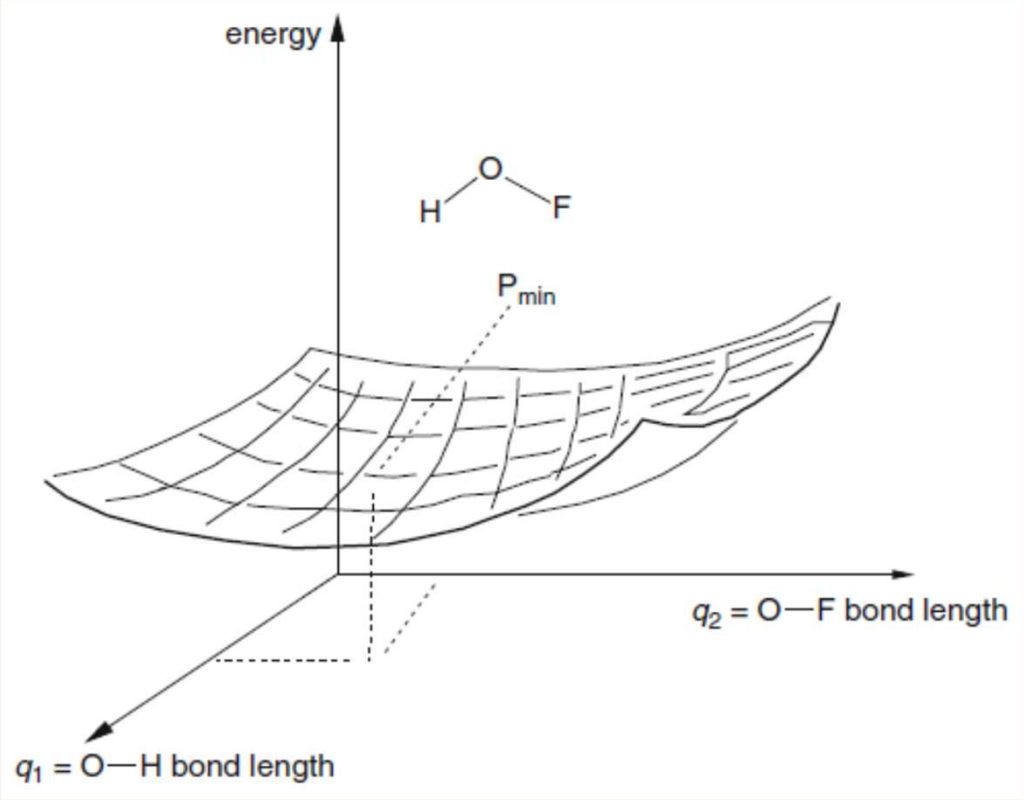


The H_2O potential energy surface. The point P_{min} corresponds to the minimum-energy geometry for the three atoms, i.e. to the equilibrium geometry of the water molecule

- for hypersurfaces we content ourselves with a line or a two-dimensional surface, in effect using a slice of a multidimensional diagram.
- For H_2O: The slice could be made holding one or the other of the two geometric parameters constant, or it could involve both of them, giving a diagram in which the geometry axis is a composite of more than one geometric parameter.
- We can take a 3-D slice of the hypersurface for HOF or even a more complex molecule and use an E versus q_1, q_2 diagram to represent the PES; we could even use a simple 2D diagram, with q representing one, two or all of the geometric parameters.
- these 2D and particularly 3D graphs preserve qualitative and even quantitative features of the mathematically rigorous but unvisualizable E = f(q1, q2, . . . qn) n-dimensional hypersurface.



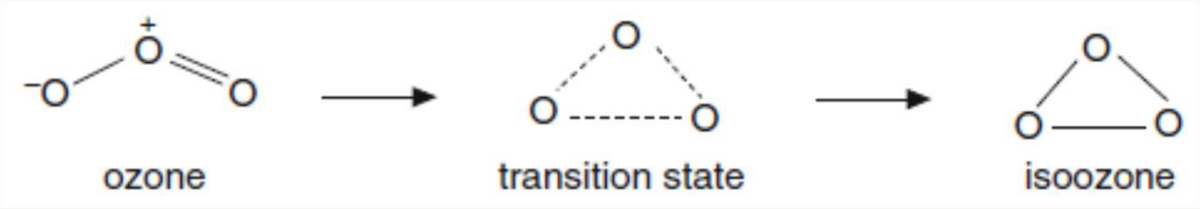
Slices through a 2D potential energy surface give 1D surfaces. A slice that is parallel to neither axis would give a plot of geometry versus a composite of bond angle and bond length, a kind of average geometry



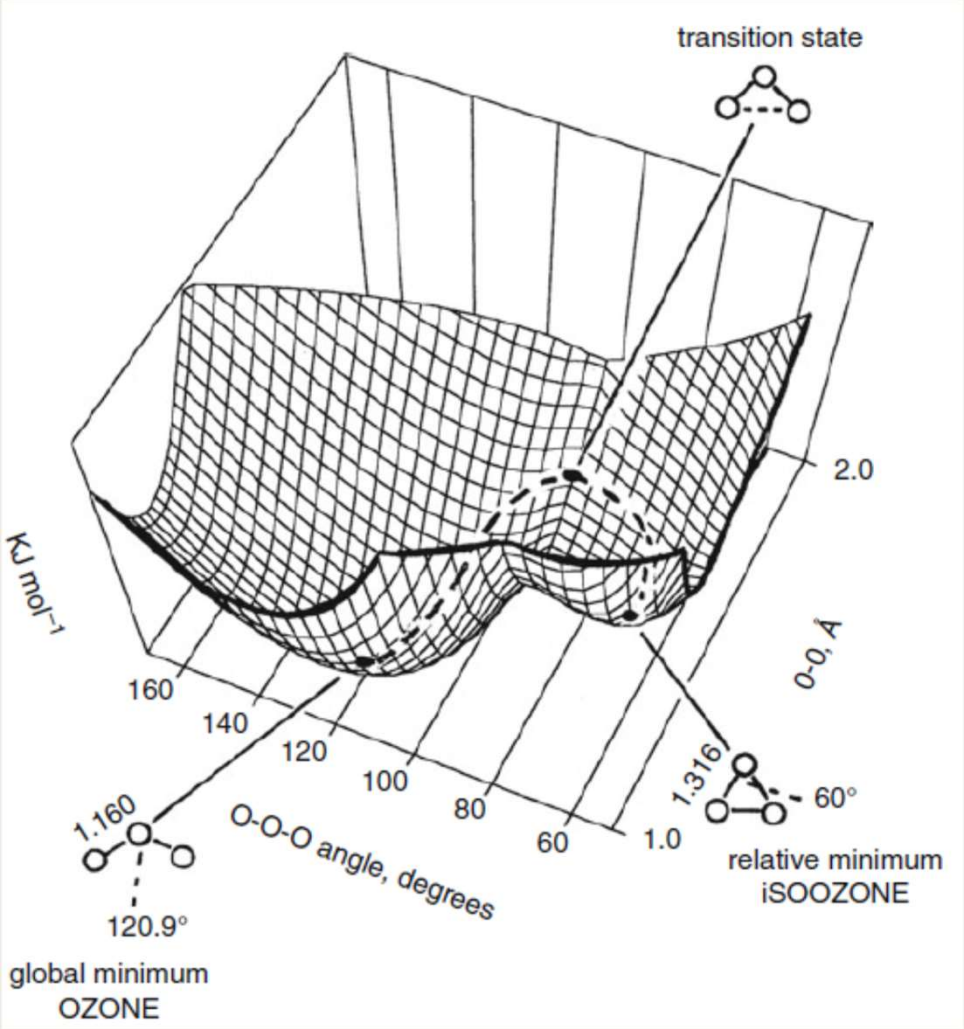
A PES for HOF. Here the HOF angle is not shown. This picture could represent one of two possibilities: (1) the angle might be the same (some constant, reasonable value) for every calculated point on the surface; this would be an unrelaxed or rigid PES. Alternatively, for each calculated point the geometry might be that for the best angle corresponding to the other two parameters, i.e. the geometry for each calculated point might be fully optimized; this would be a relaxed PES

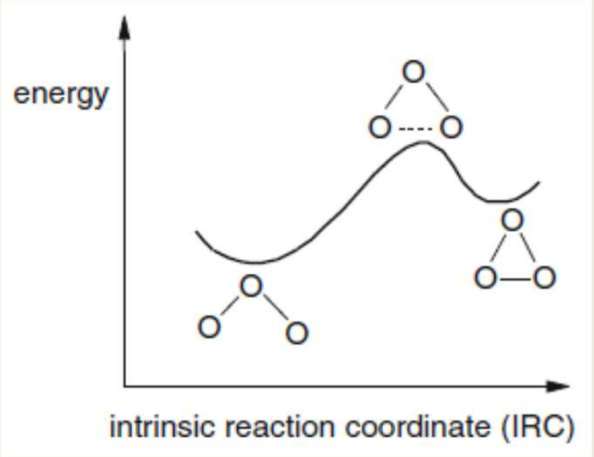
Stationary Points

- Among the main tasks of computational chemistry are to determine the structure and energy of molecules and of the transition states involved in chemical reactions:



- it seems reasonable that ozone might have an isomer (call it isoozone) and that the two could interconvert by a transition state as shown in the reaction.
- We can depict this process on a PES. PE must be plotted against only two geometric parameters, the bond length (we may reasonably assume that the two O–O bonds of ozone are equivalent, and that these bond lengths remain equal throughout the reaction) and the O–O–O bond angle.
- a 2D slice from this 3D diagram gives the energy/reaction coordinate type of diagram commonly used by chemists.
- The slice goes along the lowest-energy path connecting ozone, isoozone and TS. horizontal axis (the reaction coordinate) of the 2D diagram is a composite of Bo and An. In most discussions this horizontal axis is left quantitatively undefined; qualitatively, the reaction coordinate represents the progress of the reaction.





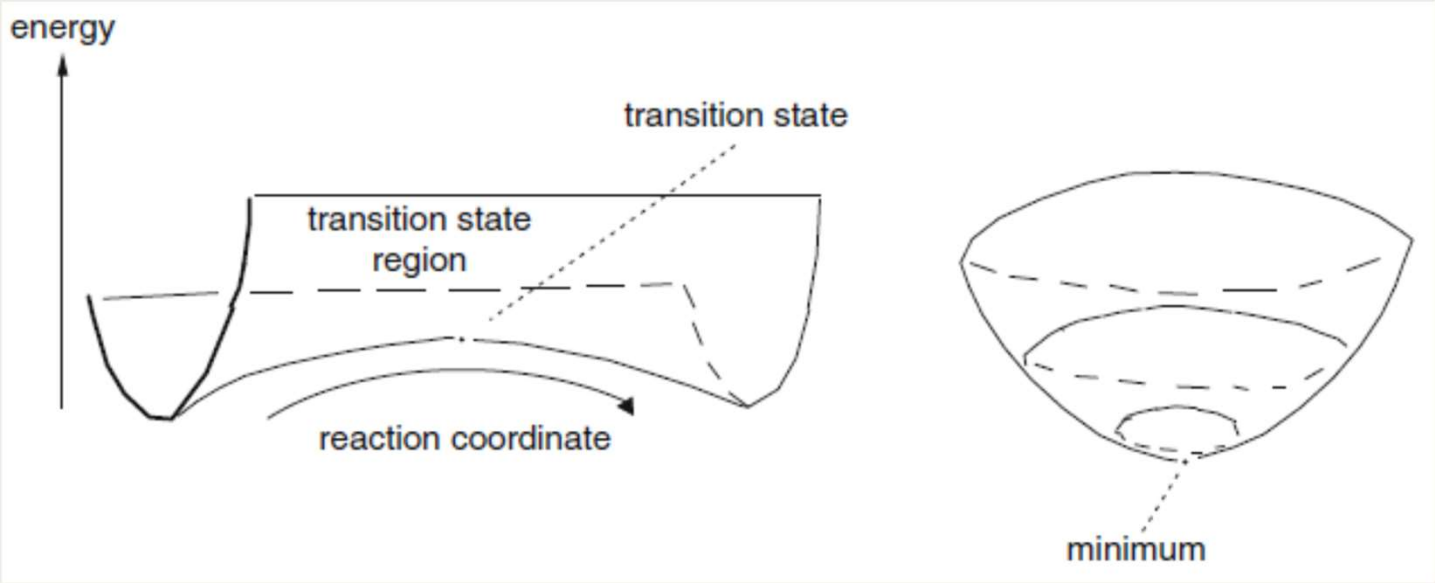
The ozone/isoozone potential energy surface (calculated by the AM1 method; a 2D surface in a 3D diagram. The dashed line on the surface is the reaction coordinate (intrinsic reaction coordinate, IRC). A slice through the reaction coordinate gives a 1D “surface” in a 2D diagram. The diagram is not meant to be quantitatively accurate

- The points on the PES corresponding to ozone, isoozone, and TS are called stationary points (SP).
- A SP on a PES is a point at which the surface is flat, i.e. parallel to the horizontal line corresponding to the one geometric parameter (or to the plane corresponding to two geometric parameters, or to the hyperplane corresponding to more than two geometric parameters). A marble placed …
- Mathematically, a stationary point is one at which the first derivative of the potential energy with respect to each geometric parameter is zero1:

$$\frac{\partial E}{\partial q_1} = \frac{\partial E}{\partial q_2} = \cdots = 0$$

- Minima or energy minima : stationary points that correspond to actual molecules with a finite lifetime, like ozone or isoozone.
- Maxima or energy maxima: stationary points that correspond to TSs, which exist only for an instant.
- Minima occupies the lowest-energy point in its region of the PES, and any small change in the geometry increases the energy.
- Ozone is a global minimum, since it is the lowest-energy minimum on the whole PES.
- Isoozone is a relative minimum, a minimum compared only to nearby points on the surface.
- The lowest-energy pathway linking the two minima,
- the reaction coordinate or intrinsic reaction coordinate (IRC; dashed line in Fig.) is the path that would be followed by a molecule in going from one minimum to another should it acquire just enough energy to overcome the activation barrier, pass through the transition state, and reach the other minimum.
- Not all reacting molecules follow the IRC exactly: a molecule with sufficient energy can stray outside the IRC to some extent.

- the transition state linking the two minima represents a maximum along the direction of the IRC, but along all other directions it is a minimum. This is a characteristic of a saddle-shaped surface, and the transition state is called a saddle point
- The saddle point lies at the “center” of the saddle-shaped region and is, like a minimum, a stationary point,
- since the PES at that point is parallel to the plane defined by the geometry parameter axes: we can see that a marble placed (precisely) there will balance.
- Mathematically, minima and saddle points differ in that although both are stationary points (they have zero first derivatives), a minimum is a minimum in all directions, but a saddle point is a maximum along the reaction coordinate and a minimum in all other directions.
- Recalling that minima and maxima can be distinguished by their second derivatives,



A transition state or saddle point and a minimum.

- For a minimum

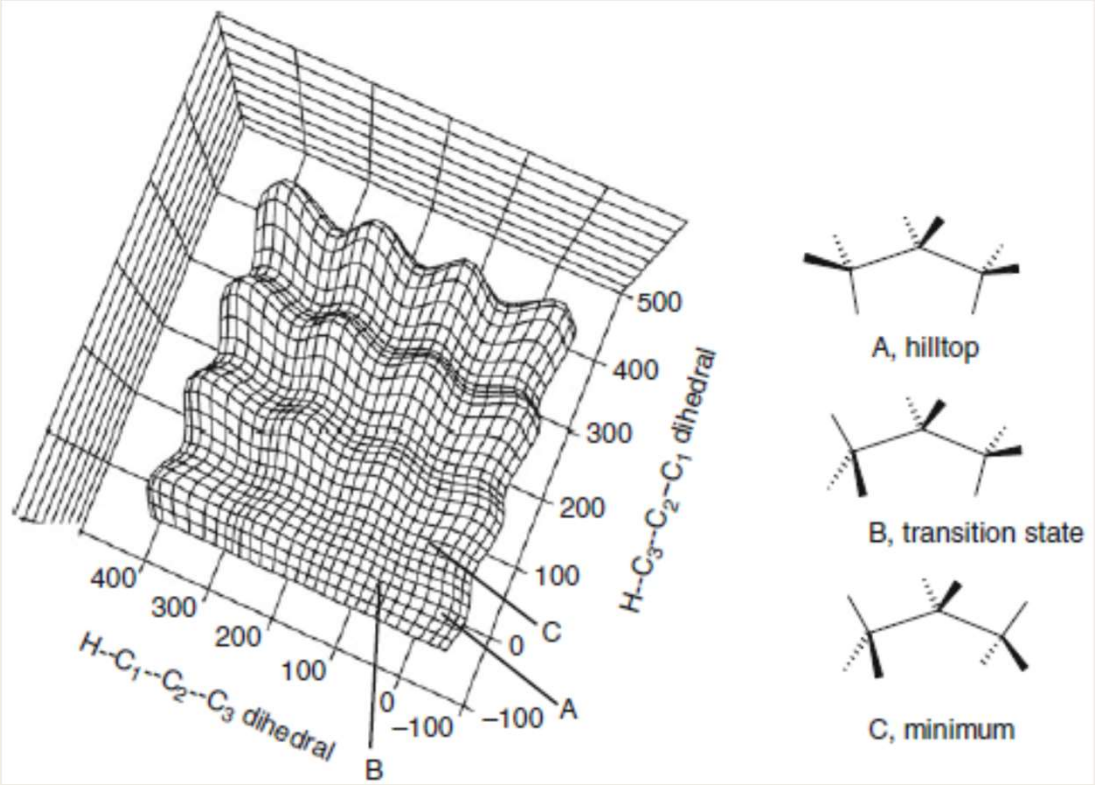
$$\frac{\partial^2 E}{\partial q^2} > 0$$ for all q

- For a transition state

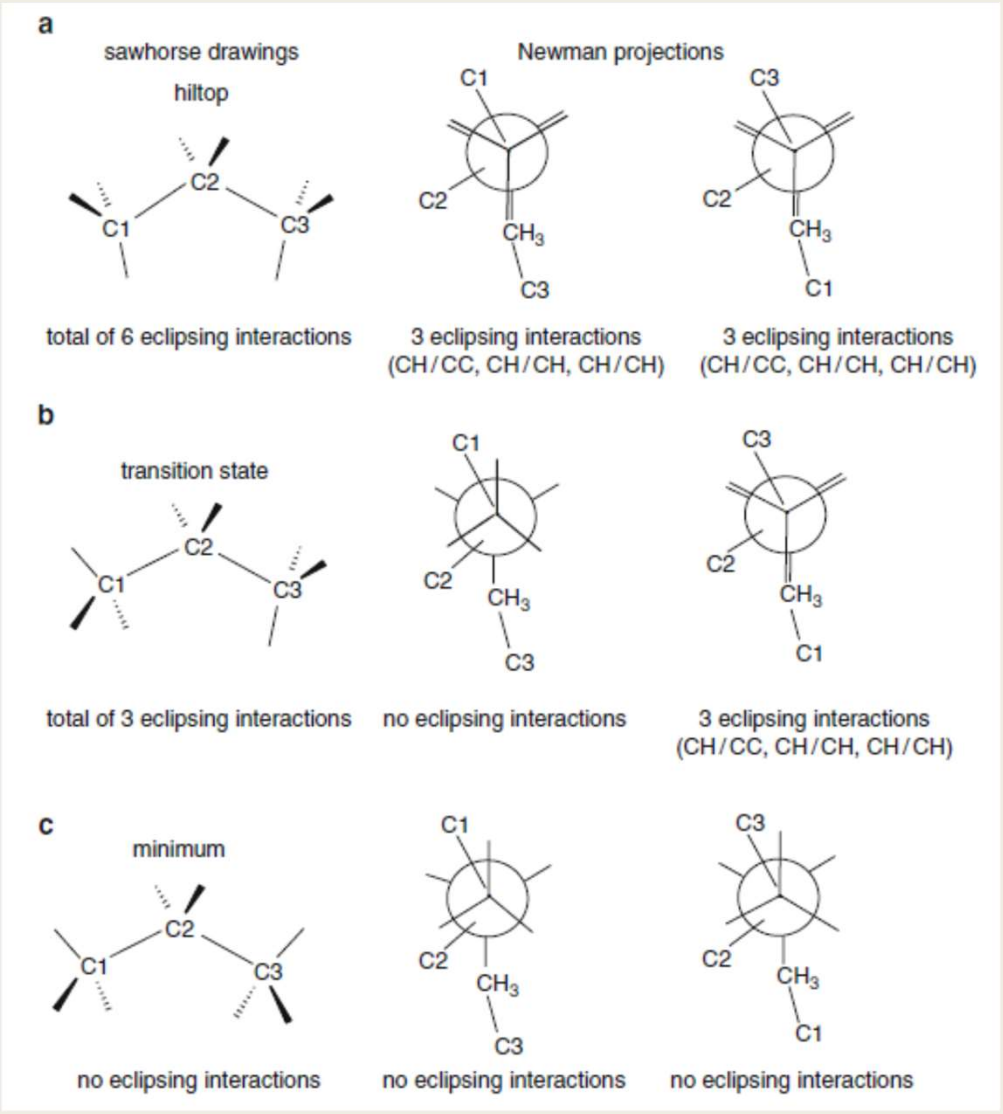
$$\frac{\partial^2 E}{\partial q^2} > 0$$ for all q, except along the reaction coordinate, and

$$\frac{\partial^2 E}{\partial q^2} < 0$$ along the reaction coordinate.

- A saddle point: the point on a PES where the second derivative of energy with respect to one and only geometric coordinate (possibly a composite coordinate) is negative,
- higher-order saddle points or hilltops: the points (for some PESs) where the second derivative of energy with respect to more than one coordinate is negative
- The propane PES:
- a second-order saddle point (A): The “doubly-eclipsed” conformation (is eclipsing as viewed along the C1–C2 and the C3–C2 bonds)
- a first-order saddle point (B): a “singly-eclipsed” conformation.
- Minimum (C): has no eclipsing interactions (There are no lower-energy structures on the C3H8 PES and so C is the global minimum).
- The potential energy surface for a chemical reaction has just been presented as a saddle-shaped region holding a transition state which connects wells containing reactant(s) and products(s) (reactants).



The propane potential energy surface as the two HCCC dihedrals are varied (calculated by the AM1 method). this is not a relaxed PES; however, changes in bond lengths and angles from one propane conformation to another are small, and the relaxed PES should be very similar to this one

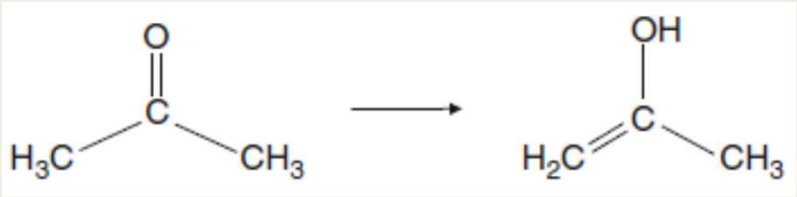


The stationary points on the propane potential energy surface. Hydrogens at the end of CH bonds are omitted for clarity

Geometry Optimization

- The characterization of a stationary point on a PES, that is, calculating its geometry (and energy), is a geometry optimization.
- The stationary point of interest might be a minimum, a transition state, or a higher-order saddle point.
- Locating a minimum is often called an energy minimization or simply a minimization
- locating a transition state is often referred to specifically as a transition state optimization.
- Geometry optimizations are done by starting with an input structure that is believed to resemble (the closer the better) the desired stationary point and submitting this plausible structure to a computer algorithm that systematically changes the geometry until it has found a stationary point.
- The curvature of the PES at the stationary point, i.e. the second derivatives of energy with respect to the geometric parameters may then be determined to characterize the structure as a minimum or as some kind of saddle point.

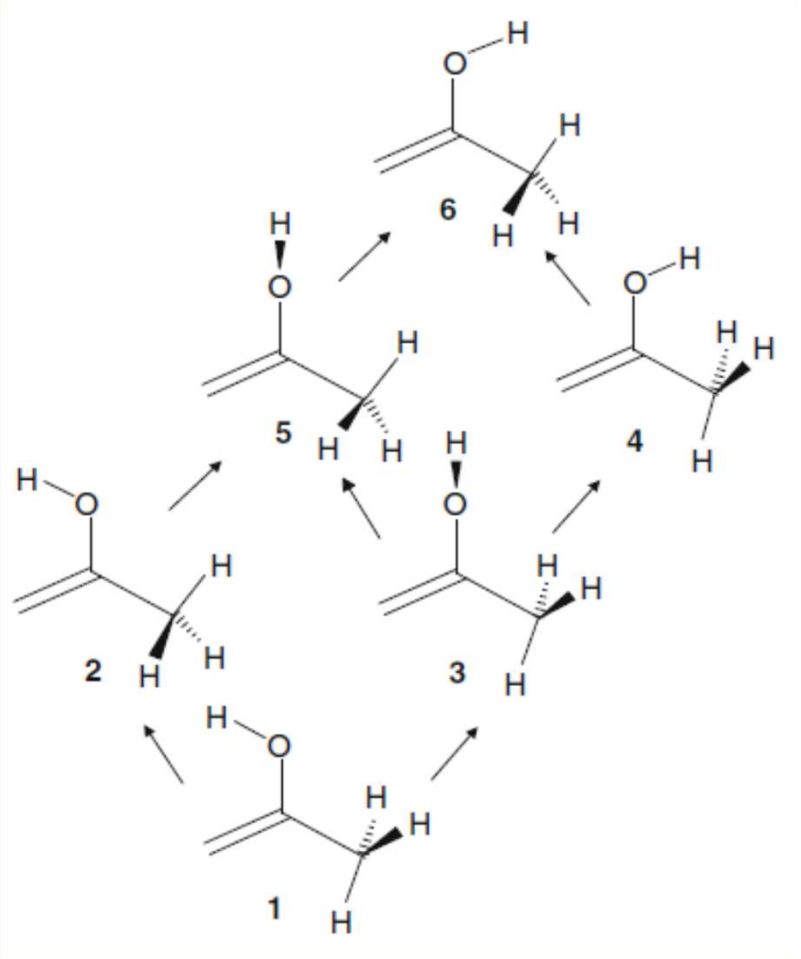
- Experimentally: ionization → neutralization of the radical cation → frozen the product in an inert matrix → IR spectroscopy



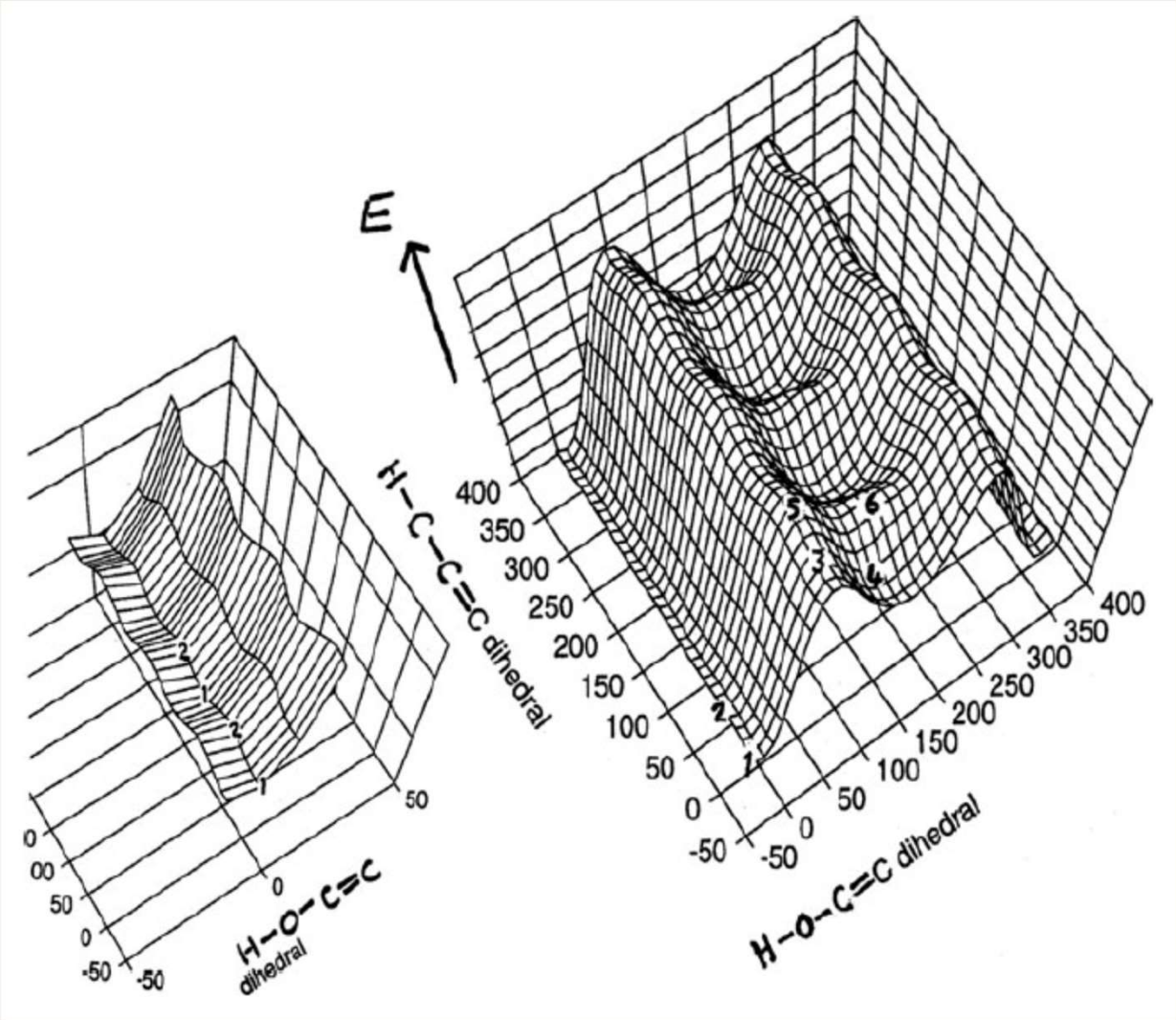
Propanone (acetone)

the enol isomer of propanone, 1-propen-2-ol

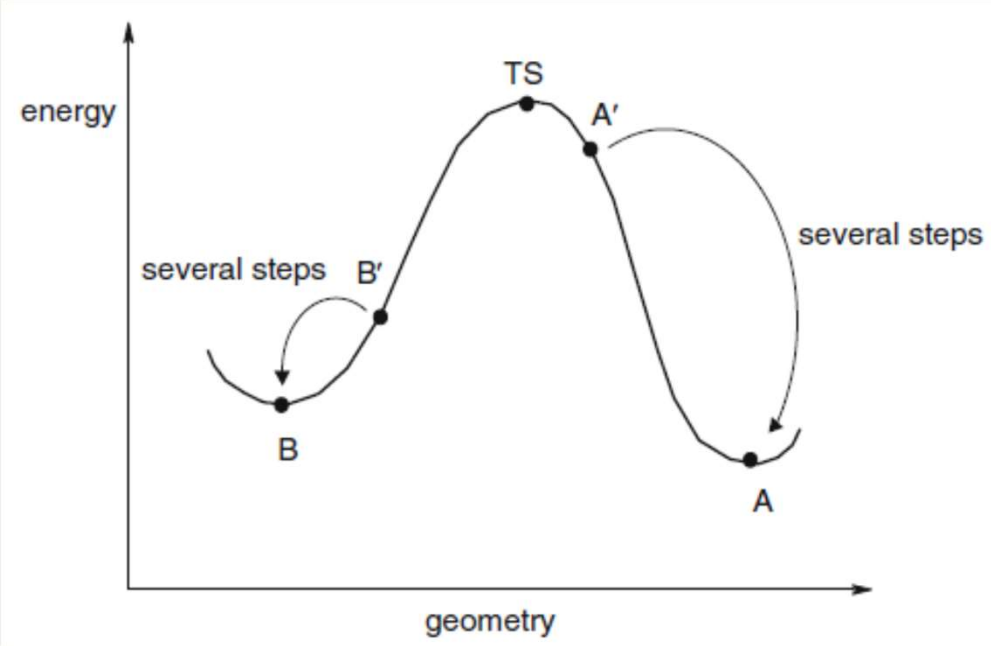
- which conformer should one choose for the calculation? Rotation about the C–O and C–C bonds creates six plausible stationary points



The plausible stationary points on the propenol potential energy surface. A PES scan indicated that 1 is the global minimum and 4 is a relative minimum, while 2 and 3 are transition states and 5 and 6 are hilltops. AM1 calculations gave relative energies for 1, 2, 3 and 4 of 0, 0.6, 14 and 6.5 kJ mol^{-1}, respectively (5 and 6 were not optimized). The arrows represent one-step (rotation about one bond) conversion of one species into another

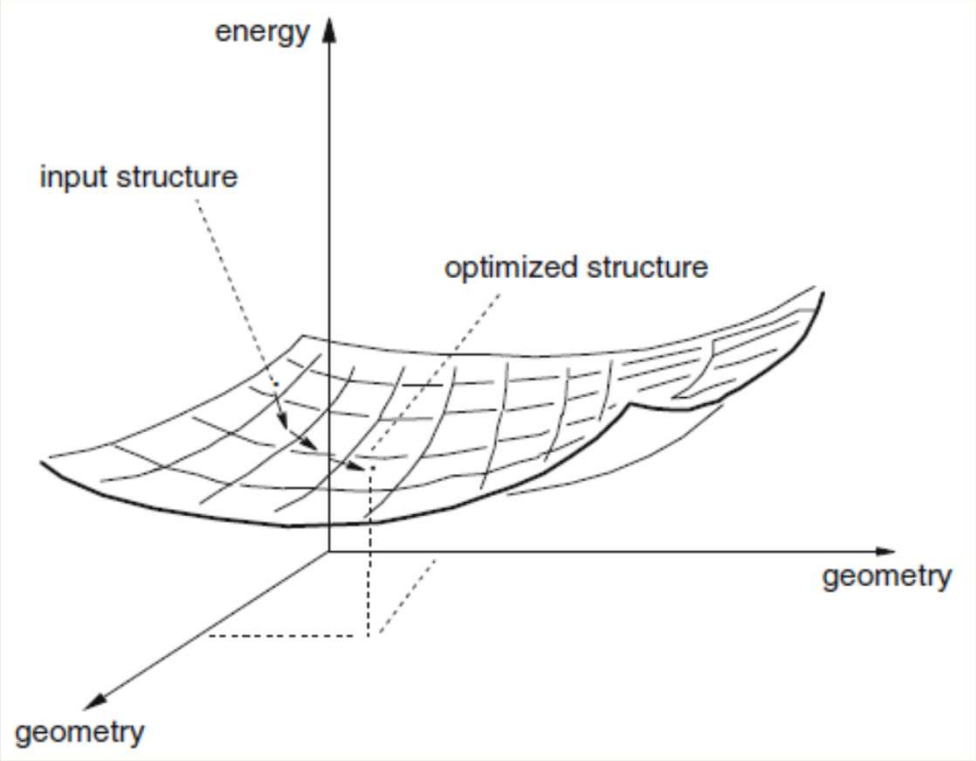


The 1-propen-2-ol potential energy surface (calculated by the AM1 method)

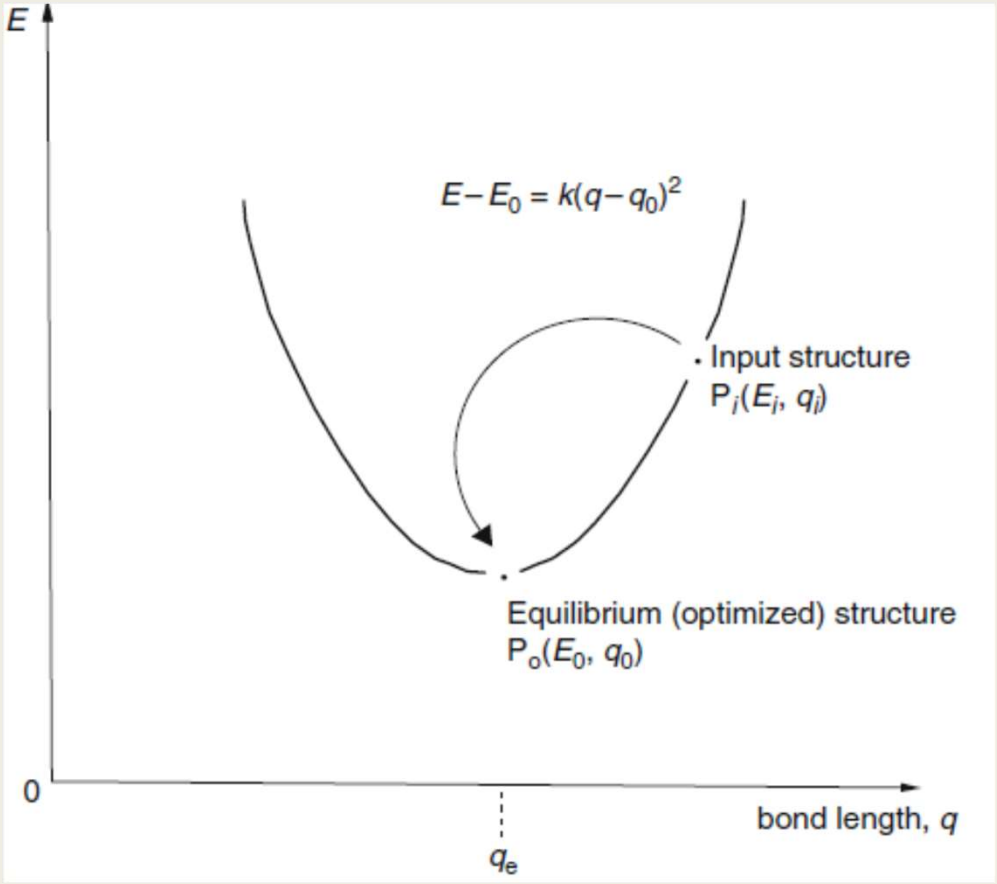


Geometry optimization to a minimum gives the minimum closest to the input structure. The input structure A’ is moved toward the minimum A, and B’ toward B. To locate a transition state a special algorithm is usually used: this moves the initial structure A’ toward the transition state TS. Optimization to each of the stationary points would probably actually require several steps.

- To be sure we have found a global minimum we must (except for very simple or very rigid molecules) search a potential energy surface (there are algorithms that will do this and locate the various minima).
- input structures: is usually done nowadays with an interactive mouse-driven program. An older alternative is to specify the geometry by defining the various bond lengths, angles and dihedrals, i.e. by using a so-called Z-matrix (internal oordinates).
- To move along the PES from the input structure to the nearest minimum:
  - 1D PES of a diatomic molecule: one simply changes the bond length → the lowest energy is found.
  - On any other surface, efficient geometry optimization requires a sophisticated algorithm.
  - One would like to know: in which direction to move, and how far in that direction
- It is not possible, to go from the input structure to the proximate minimum in just one step, but modern geometry optimization algorithms commonly reach the minimum within about ten steps, e
- The most widely-used algorithms for geometry optimization the first and second derivatives of the energy with respect to the geometric parameters.



An efficient optimization algorithm knows approximately in which direction to move and how far to step, in an attempt to reach the optimized structure in relatively few (commonly about five to ten) steps



The PE of a diatomic molecule near the equilibrium geometry is approximately quadratic function of the bond length. Given an input structure (i.e. given the bond length q_i), a simple algorithm would enable the bond length of the optimized structure to be found in one step, if the function were strictly quadratic

Assume (fairly good approximation) that near a minimum the PE is a quadratic function of q,

$$E - E_o = k\,(q - q_o)^2$$

At the input point $(dE/dq)_i = 2k(q_i - q_o)$

At all points $d^2E/dq^2 = 2k\ (= \text{force constant})$

$$(dE/dq)_i = (d^2E/dq^2)\,(q_i - q_o)$$

$$q_o = q_i - (dE/dq)_i/(d^2E/dq^2)$$

- For multidimensional PESs: far more sophisticated algorithms are used, and several steps are needed since the curvature is not exactly quadratic.
- Since the PES is not strictly quadratic, the second derivatives vary from point to point and are updated as the optimization proceeds.

- Optimizations are actually commonly done using Cartesian coordinates x, y, z.
- Consider HOF: there are nine geometric parameters, q1, q2, . . . , q9.
- the PES would be a nine-dimensional hypersurface on a 10D graph.
- The first and second derivatives of E with respect to q's are manipulated as matrices.

$$\mathbf{g}_i = \begin{pmatrix} (\partial E/\partial q_1)_i \\ (\partial E/\partial q_2)_i \\ \vdots \\ (\partial E/\partial q_9)_i \end{pmatrix} \quad \mathbf{H} = \begin{pmatrix} \partial^2 E/\partial q_1 q_1 & \partial^2 E/\partial q_1 q_1 \cdots & \partial^2 E/\partial q_1 q_9 \\ \partial^2 E/\partial q_2 q_1 & \partial^2 E/\partial q_2 q_2 \cdots & \partial^2 E/\partial q_2 q_9 \\ \vdots & \vdots \quad \cdots & \vdots \\ \partial^2 E/\partial q_9 q_1 & \partial^2 E/\partial q_9 q_2 \cdots & \partial^2 E/\partial q_9 q_9 \end{pmatrix} \quad \mathbf{q}_i = \begin{pmatrix} q_{i1} \\ q_{i2} \\ \vdots \\ q_{i9} \end{pmatrix} \quad \mathbf{q}_o = \begin{pmatrix} q_{o1} \\ q_{o2} \\ \vdots \\ q_{o9} \end{pmatrix}$$

force constant matrix (Hessian)
is important for: geometry optimization, characterization of stationary points and the calculation of IR spectra

$$\mathbf{q}_o = \mathbf{q}_i - \mathbf{H}^{-1}\,\mathbf{g}_i$$

- For n atoms: 3n Cartesians, 3n × 1 column matrices and H is a 3n × 3n square matrix (matrix division is not defined).
- An approximate initial Hessian is often calculated from molecular mechanics
- Since the PES is not really exactly quadratic, the first step does not take us all the way to the optimized geometry (matrix q_0). Rather, we arrive at q_1, the first calculated geometry
- the gradients are calculated analytically and the second derivatives are updated using the changes in the gradients – as

$$\frac{\partial^2 E}{\partial q_i \partial q_j} \approx \frac{\Delta(\partial E/\partial q_j)}{\Delta q_i}$$

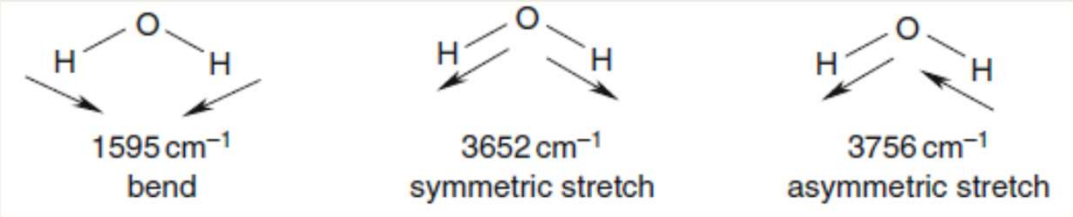
- Using q_1 and the new **g** and **H** matrices → geometry matrix q_2 is calculated.
- The process is continued until the geometry and/or the gradients (or with some programs possibly the energy) have ceased to change appreciably.

- Analytic calculation of second derivatives is relatively time-consuming and is not routinely done for each point along the optimization sequence, in contrast to analytic calculation of gradients.
- A fast lower-level optimization, usually provides a good Hessian and geometry for input to a higher-level optimization.
- Finding a transition state is a more challenging computational problem than finding a minimum. at the transition state the surface is a maximum in one direction and a minimum in all others, rather than simply a minimum in all directions.

Stationary Points and Normal-Mode Vibrations – Zero Point Energy

- Once a stationary point has been found by geometry optimization, check whether it is a minimum, a transition state, or a hilltop (by calculating the vibrational frequencies via finding the normal-mode frequencies)
- normal-mode frequencies are the simplest vibrations of the molecule, which, in combination, can be considered to result in the actual, complex vibrations that a real molecule undergoes.
- Essentially, a normal-modes calculation is a calculation of the infrared spectrum, although the experimental spectrum is likely to contain extra bands resulting from interactions among normal-mode vibrations.

- A nonlinear molecule with n atoms has 3n - 6 normal modes: three vectors describing the translational motion of the molecule as a whole (the translation of its center of mass) and the three vectors describing the rotation of the molecule (around the three principal axes needed to describe rotation for a three-dimensional object of general geometry)
- A linear molecule has 3n - 5 normal modes: three translational and two rotational vectors, as rotation about the molecular axis does not produce a recognizable change in the nuclear array.
- So water has 3n - 6 = 3(3) - 6 = 3 normal modes,
- HCN has 3n - 5 = 3(3) - 5 = 4 normal modes.
- At any moment an actual molecule of water will be undergoing a complicated stretching/bending motion, but this motion can be considered to be a combination of the three simple normal-mode motions.



- Consider a diatomic molecule A–B;

$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

- the frequency of a vibrational mode is related to the force constant
- So it is possible to calculate the normal-mode frequencies of a molecule, that is, the directions and frequencies of the atomic motions, from its force constant matrix (its Hessian).
- matrix diagonalization of the Hessian gives the directional characteristics (which way the atoms are moving), and the force constants themselves, for the vibrations.
- Matrix diagonalization: a process in which a square matrix A is decomposed into three square matrices (P, D, and P^{-1} in: $A=PDP^{-1}$)
- D is a diagonal matrix (all its off-diagonal elements are zero), P is a premultiplying matrix and P^{-1} is the inverse of P.

$$\mathbf{H} = \begin{pmatrix} \partial^2 E/\partial q_1 q_1 & \partial^2 E/\partial q_1 q_2 & \cdots & \partial^2 E/\partial q_1 q_9 \\ \partial^2 E/\partial q_2 q_1 & \partial^2 E/\partial q_2 q_2 & \cdots & \partial^2 E/\partial q_2 q_9 \\ \vdots & \vdots & \cdots & \vdots \\ \partial^2 E/\partial q_9 q_1 & \partial^2 E/\partial q_9 q_2 & \cdots & \partial^2 E/\partial q_9 q_9 \end{pmatrix}$$

$$= \underbrace{\begin{pmatrix} q_{11} & q_{12} & \cdots & q_{19} \\ q_{21} & q_{22} & \cdots & q_{29} \\ \vdots & & & \\ q_{91} & q_{92} & \cdots & q_{99} \end{pmatrix}}_{\mathbf{P}} \underbrace{\begin{pmatrix} k_1 & 0 & \cdots & 0 \\ 0 & k_2 & \cdots & 0 \\ \vdots & & & \\ 0 & 0 & \cdots & k_9 \end{pmatrix}}_{\mathbf{k}} \mathbf{P}^{-1}$$

- The 9×9 Hessian for a triatomic molecule (three Cartesian coordinates for each atom)
- **P** : whose columns are “direction vectors”
- **k** : give force constants
- columns 1, 2 and 3 of **P** and the corresponding k_1, k_2 and k_3 of **k** refer to translational motion of the molecule; these three “force constants” are nearly zero.
- Columns 4, 5 and 6 of **P** and the corresponding k_4, k_5 and k_6 of **k** refer to rotational motion about the three principal axes of rotation, and are also nearly zero.

- Columns 7, 8 and 9 of **P** and the corresponding k_7, k_8 and k_9 of **k** are the direction vectors and force constants, respectively, for the normal-mode vibrations:
- Three last columns of **P** are composed of the x, y and z components of vectors for motion of the three atoms in three vibrational modes
- Mass-weighting" the force constants, i.e. taking into account the effect of the masses of the atoms, gives the vibrational frequencies.
- the directions of the normal-mode frequencies are the eigenvectors, and their magnitudes are the massweighted eigenvalues, of the Hessian.

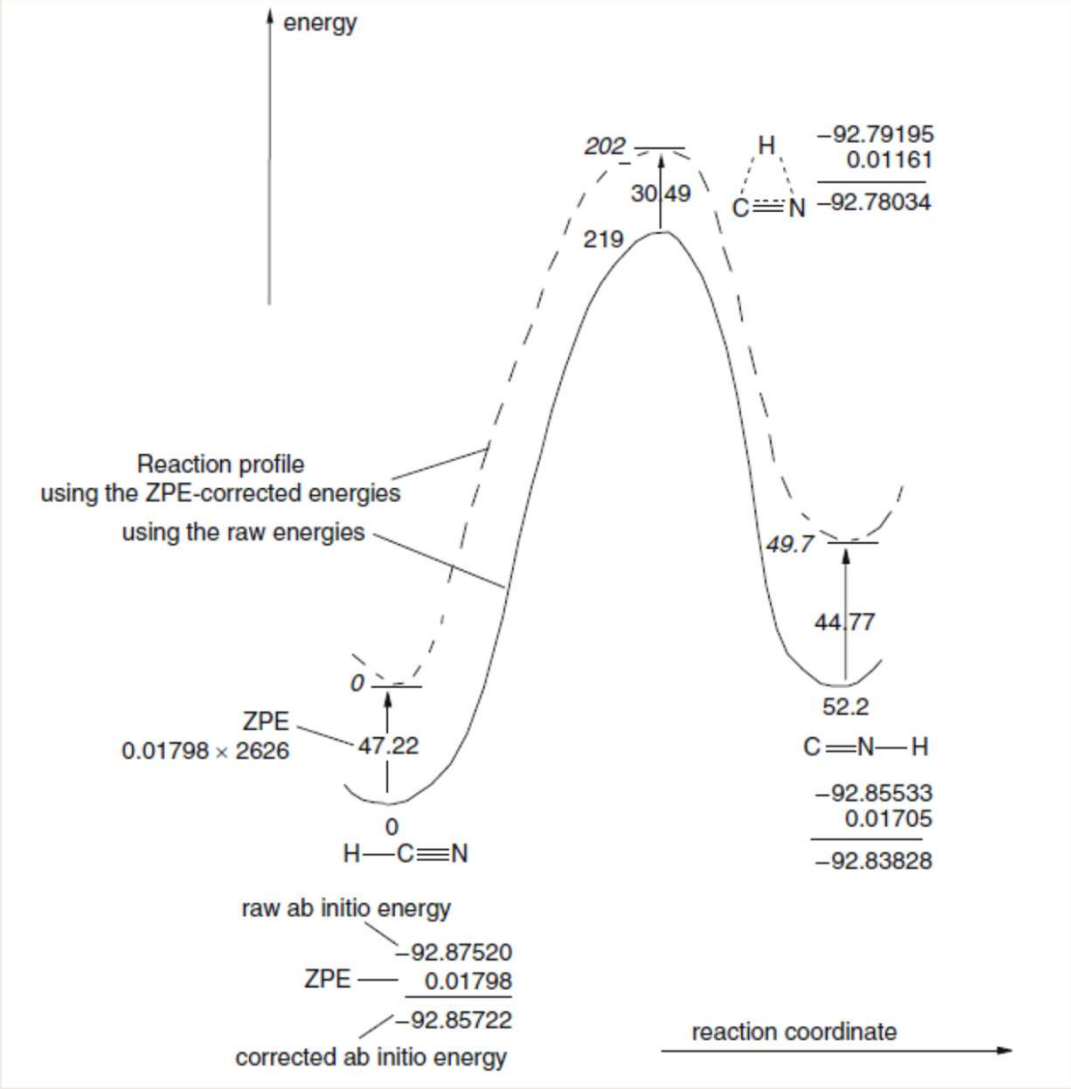
- Vibrational frequencies are calculated to obtain IR spectra, to characterize stationary points, and to obtain zero point energies.
- The calculation of meaningful frequencies is valid only at a stationary point and only using the same method that was used to optimize to that stationary point.
- This is because: second derivatives ≅ force constants (presupposes that the PES is quadratically curved along each geometric coordinate q; it is only near a stationary point that this is true,
- Calculated IR frequencies are usually somewhat too high → scalling (by multiplying them by an empirically determined factor, commonly about 0.9 for ab initio and density functional calculations)

- A minimum on the PES: all the normal-mode force constants (all the eigenvalues of the Hessian) are positive.
- The species corresponding to the minimum sits in a well and vibrates (periodic) forever (or until it acquires enough energy to react).
- A transition state (a first-order saddle point) has one and only one negative normal-mode force constant (one negative eigenvalue of the Hessian).
- That is along the reaction coordinate: motion of the atoms corresponding to this mode takes the transition state toward the product or toward the reactant, without a restoring force. This is not a periodic motion but rather takes the species through the transition state geometry on a oneway journey.
- The force constant is the first derivative of the gradient or slope (the derivative of the first derivative); along the reaction coordinate the surface slopes downward, so the force constant for this mode is negative.

- frequency $\propto$ the square root of a force constant (a negative number) → is an imaginary number.
- a transition state has one imaginary frequency, corresponding to the reaction coordinate.
- In general an nth-order saddle point (an nth-order hilltop) has n negative normal-mode force constants and so n imaginary frequencies.
- A stationary point could be characterized just from the number of negative force constants, but the mass-weighting requires much less time than calculating the force constants, and the frequencies themselves are often wanted anyway, for example for comparison with experiment. In practice one usually
- checking the nature of a stationary point: a minimum has none, a transition state one, and a hilltop more than one imaginary frequencies.

- If one is seeking a particular transition state the criteria to be satisfied are:
- 1. It should look right. The structure of a transition state should lie somewhere between that of the reactants and the products; for HCN → HNC, H bonded to both C and N by an unusually long bond in TS.
- 2. It must have one and only one imaginary frequency.
- 3. The imaginary frequency must correspond to the reaction coordinate. (animation of the motion, stretching, bending, and twisting can be visualized with a variety of programs). Reactant and product may not be clear from animation; one may resort to an intrinsic reaction coordinate (IRC) calculation.
- 4. The energy of the transition state must be higher than that of the two species it connects.

- Besides indicating the IR spectrum and providing a check on the nature of stationary points, the calculation of vibrational frequencies also provides the zero-point energy (ZPE).
- The ZPE is the energy a molecule has even at absolute zero (still vibrates).
- The ZPE of a species is usually not small compared to activation energies or reaction energies, but ZPEs tend to cancel out when these energies are calculated (the ZPE of reactant, transition state and product tend to be roughly the same).
- for accurate works, the ZPE-corrected energies should be compared.
- the ZPE is usually corrected by multiplying it by an empirical factor; this is sometimes the same as the frequency correction factor, but slightly different factors have been recommended.



Correcting relative energies for zero-point energy (ZPE). These are ab initio HF/6-31G* results for the HCN→HNC reaction. Finally, energy differences in Hartrees were multiplied by 2,626 to get kJ mol^{-1}.

- This Hessian that is used in optimization is not accurate enough for the calculation of frequencies and ZPE's.

$$\frac{\partial^2 E}{\partial q_i \partial q_j} \approx \frac{\Delta(\partial E/\partial q_j)}{\Delta q_i}$$

- The calculation of an accurate Hessian for a stationary point can be done analytically or numerically.
- Analytical calculation of ab initio frequencies is much faster than numerical evaluation,
- Demands on computer hard drive space may make numerical calculation the only recourse at high ab initio levels.

Symmetry

- why is a knowledge of symmetry important in chemistry?
- Symmetry considerations are essential in UV/Vis spectroscopy and sometimes in analyzing the molecular wavefunctions, but for us the reasons are more pragmatic.
- A calculation, with imposing the symmetry, will tend to be faster and will yield a "better" (see below) geometry than one run on an approximate structure, however close this may be to the exact one.
- Water: (1) input the H_2O molecule with the C_{2v} symmetry; (2) input it with the C_s symmetry (three atoms must lie in a plane).
- The C_{2v} structure has two degrees of freedom: a bond length (the two bonds are the same length) and a bond angle.
- The Cs structure has three degrees of freedom: two bond lengths and a bond angle.
- The optimization algorithm has more variables to cope with in the case of the lower-symmetry structure.
- What do we mean by a better geometry? The successful geometry optimization will give essentially the same geometries, but corresponding bond lengths and angles (e.g. the four C–H bonds and the two HCH angles of ethene) will not be exactly the same → the other calculated properties (charges on atoms) are not exactly the same.

Summary

- The potential energy surface (PES) is a central concept in computational chemistry.
- A PES is the relationship – mathematical or graphical – between the energy of a molecule (or a collection of molecules) and its geometry.
- Stationary points on a PES are points where $\partial E/\partial q = 0$ for all q, where q is a geometric parameter.
- The stationary points of chemical interest are minima ($\partial^2 E/\partial qiqj > 0$ for all q) and transition states or first-order saddle points; $\partial 2E/\partial qiqj < 0$ for one q, along the reaction coordinate (intrinsic reaction coordinate, IRC), and > 0 for all other q.
- Chemistry is the study of PES stationary points and the pathways connecting them.
- The Born–Oppenheimer approximation says that in a molecule the nuclei are essentially stationary compared to the electrons.
- This is one of the cornerstones of computational chemistry because it makes the concept of molecular shape (geometry) meaningful, makes possible the concept of a PES, and simplifies the application of the Schrodinger equation to molecules by allowing us to focus on the electronic energy and add in the nuclear repulsion energy later.

- Geometry optimization is the process of guessing an input structure and finding a SP on the PES.
- The SP found will be the one closest to the input structure, not necessarily the global min.
- Modern optimization algorithms use analytic first derivatives and second derivatives.
- It is usually wise to check that a stationary point is the desired species (a minimum or a transition state) by calculating its vibrational spectrum (its normal-mode vibrations). The algorithm for this works by calculating an accurate Hessian (force constant matrix) and diagonalizing it to give a matrix with the "direction vectors" of the normal modes, and a diagonal matrix with the force constants of these modes.
- "mass-weighting" the force constants gives the normal-mode vibrational frequencies.
- For a minimum all the vibrations are real, while a TS has one imaginary vibration, corresponding to motion along the reaction coordinate.
- The criteria for a TS are appearance, the presence of one imaginary frequency corresponding to the reaction coordinate, and an energy above that of the reactant and the product.
- Besides serving to characterize the stationary point, calculation of the vibrational frequencies enables one to predict an IR spectrum and provides the ZPE.
- The ZPE is needed for accurate comparisons of the energies of isomeric species.
- The accurate Hessian required for calculation of frequencies and ZPE's can be obtained either numerically or analytically (faster, but much more demanding of hard drive space).

Easier Questions

- 1. What is a potential energy surface (give the two viewpoints)?
- 2. Explain the difference between a relaxed PES and a rigid PES.
- 3. What is a stationary point? What kinds of stationary points are of interest to chemists, and how do they differ?
- 4. What is a reaction coordinate?
- 5. Show with a sketch why it is not correct to say that a TS is a maximum on a PES.
- 6. What is the Born–Oppenheimer approximation, and why is it important?
- 7. Explain, for a reaction A → B, how the potential energy change on a PES is related to the enthalpy change of the reaction. What would be the problem with calculating a free energy/geometry surface? Hint: Vibrational frequencies are normally calculated only for stationary points.
- 8. What is geometry optimization? Why is this process for transition states (often called transition state optimization) more challenging than for minima?
- 9. What is a Hessian? What uses does it have in computational chemistry?
- 10. Why is it usually good practice to calculate vibrational frequencies where practical, although this often takes considerably longer than geometry optimization?