

Chapter 2

The Concept of the Potential Energy Surface

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

Albert Einstein

Abstract 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. 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 Schrödinger equation to molecules by allowing us to focus on the electronic energy and add in the nuclear repulsion energy later; this third point, very important in practical molecular computations, is elaborated on in [Chapter 5](#). Geometry optimization and transition state optimization are explained.

2.1 Perspective

We begin a more detailed look at computational chemistry with the potential energy surface (PES) because this is central to the subject. Many important concepts that might appear to be mathematically challenging can be grasped intuitively with the insight provided by the idea of the PES [1].

Consider a diatomic molecule AB. In some ways a molecule behaves like balls (atoms) held together by springs (chemical bonds); in fact, this simple picture is the basis of the important method *molecular mechanics*, discussed in [Chapter 3](#). If we take a macroscopic balls-and-spring model of our diatomic molecule in its normal geometry (the equilibrium geometry), grasp the “atoms” and distort the model by stretching or compressing the “bonds”, we increase the potential energy of the molecular model (Fig. 2.1). The stretched or compressed spring possesses energy, by definition, since we moved a force through a distance to distort it. Since the

model is motionless while we hold it at the new geometry, this energy is not kinetic and so is by default *potential* (“depending on position”). The graph of potential energy against bond length is an example of a potential energy surface. A line is a one-dimensional “surface”; we will soon see an example of a more familiar two-dimensional surface rather than the line of Fig. 2.1.

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

1. They vibrate incessantly (as we would expect from Heisenberg’s uncertainty principle: a stationary molecule would have an exactly defined momentum and position) about the equilibrium bond length, so that they always possess kinetic energy (T) and/or potential energy (V): as the bond length passes through the equilibrium length, $V = 0$, while at the limit of the vibrational amplitude, $T = 0$; at all other positions both T and V are nonzero. The fact that a molecule is never actually stationary with zero kinetic energy (it always has *zero point energy*; Section 2.5) is usually shown on potential energy/bond length diagrams by drawing a series of lines above the bottom of the curve (Fig. 2.2) to indicate the possible amounts of vibrational energy the molecule can have (the *vibrational levels* it can occupy). A molecule never sits at the bottom of the curve, but rather occupies one of the vibrational levels, and in a collection of molecules the levels are populated according to their spacing and the temperature [2]. We will usually ignore the vibrational levels and consider molecules to rest on the actual potential energy curves or (see below) surfaces.
2. Near the equilibrium bond length q_e the potential energy/bond length curve for a macroscopic balls-and-spring model or a real molecule is described fairly well by a quadratic equation, that of the simple harmonic oscillator ($E = (1/2) K (q - q_e)^2$, where k is the force constant of the spring). However, the potential energy deviates from the quadratic (q^2) curve as we move away from q_e (Fig. 2.2). The deviations from molecular reality represented by this *anharmonicity* are not important to our discussion.

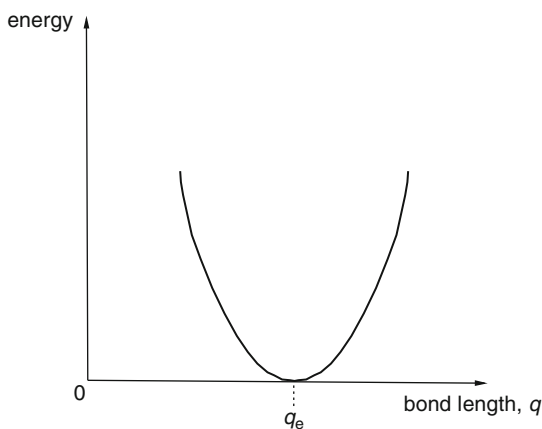


Fig. 2.1 The potential energy surface for a diatomic molecule. The potential energy increases if the bond length q is stretched or compressed away from its equilibrium value q_e . The potential energy at q_e (zero distortion of the bond length) has been chosen here as the zero of energy

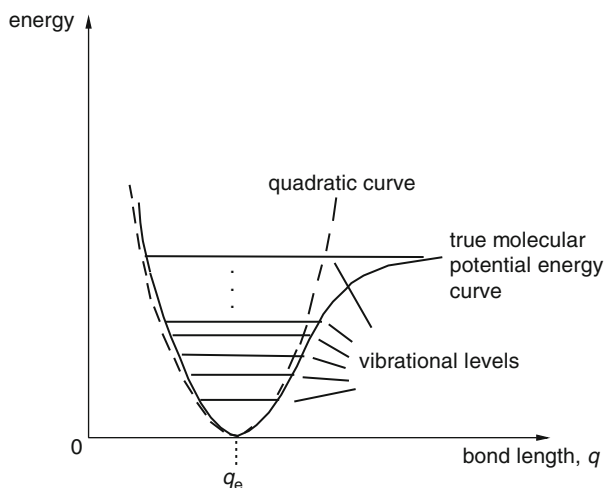


Fig. 2.2 Actual molecules do not sit still at the bottom of the potential energy curve, but instead occupy vibrational levels. Also, only near q_e , the equilibrium bond length, does the quadratic curve approximate the true potential energy curve

Figure 2.1 represents a one-dimensional PES in the two-dimensional graph of E vs. q . A diatomic molecule AB has only one geometric parameter for us to vary, the bond length q_{AB} . Suppose we have a molecule with more than one geometric parameter, for example water: the geometry is defined by two bond lengths and a bond angle. If we reasonably content ourselves with allowing the two bond lengths to be the same, i.e. if we limit ourselves to C_{2v} symmetry (two planes of symmetry and a two-fold symmetry axis; see Section 2.6) then the PES for this triatomic molecule is a graph of E versus two geometric parameters, q_1 = the O–H bond length, and q_2 = the H–O–H bond angle (Fig. 2.3). Figure 2.3 represents a two-dimensional PES (a normal surface is a 2-D object) in the three-dimensional graph; we could make an actual 3-D model of this drawing of a 3-D graph of E versus q_1 and q_2 .

We can go beyond water and consider a triatomic molecule of lower symmetry, such as HOF, hypofluorous acid. This has three geometric parameters, the H–O and O–F lengths and the H–O–F angle. To construct a Cartesian PES graph for HOF analogous to that for H₂O would require us to plot E vs. q_1 = H–O, q_2 = O–F, and q_3 = angle H–O–F. We would need four mutually perpendicular axes (for E , q_1 , q_2 , q_3 , Fig. 2.4), and since such a four-dimensional graph cannot be constructed in our three-dimensional space we cannot accurately draw it. The HOF PES is a 3-D “surface” of more than two dimensions in 4-D space: it is a hypersurface, and potential energy surfaces are sometimes called 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, where f is the function that describes how E varies with the q ’s, and treat the hypersurface mathematically. For example, in the AB diatomic molecule PES (a line) of Fig. 2.1 the minimum

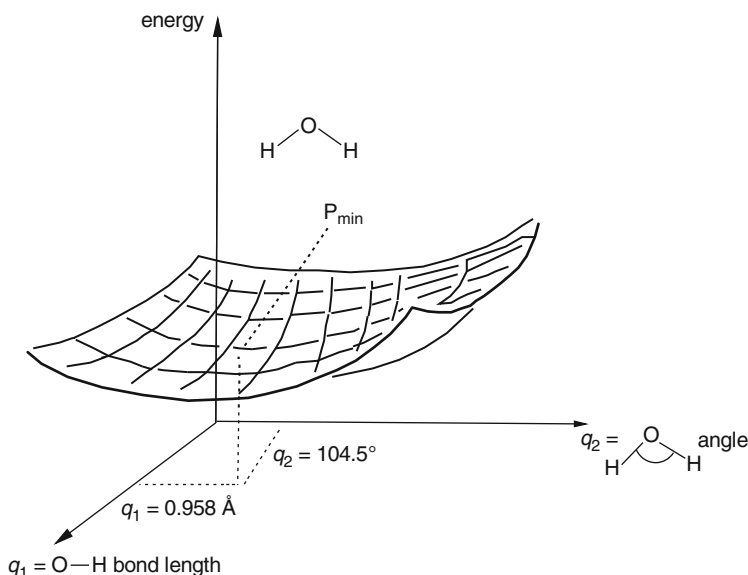
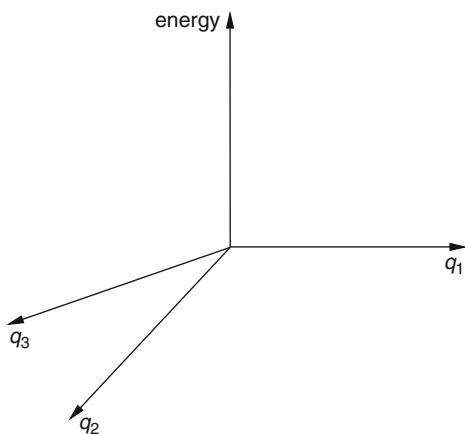


Fig. 2.3 The H_2O potential energy surface. The point P_{\min} corresponds to the minimum-energy geometry for the three atoms, i.e. to the equilibrium geometry of the water molecule

Fig. 2.4 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



potential energy geometry is the point at which $dE/dq = 0$. On the H_2O PES (Fig. 2.3) the minimum energy geometry is defined by the point P_m , corresponding to the equilibrium values of q_1 and q_2 ; at this point $dE/dq_1 = dE/dq_2 = 0$. Although hypersurfaces cannot be faithfully rendered pictorially, it is very useful to a computational chemist to develop an intuitive understanding of them. This can be gained with the aid of diagrams like Figs. 2.1 and 2.3, where we content ourselves with a line or a two-dimensional surface, in effect using a slice of a multidimensional diagram. This can be understood by analogy: Fig. 2.5 shows how 2-D slices

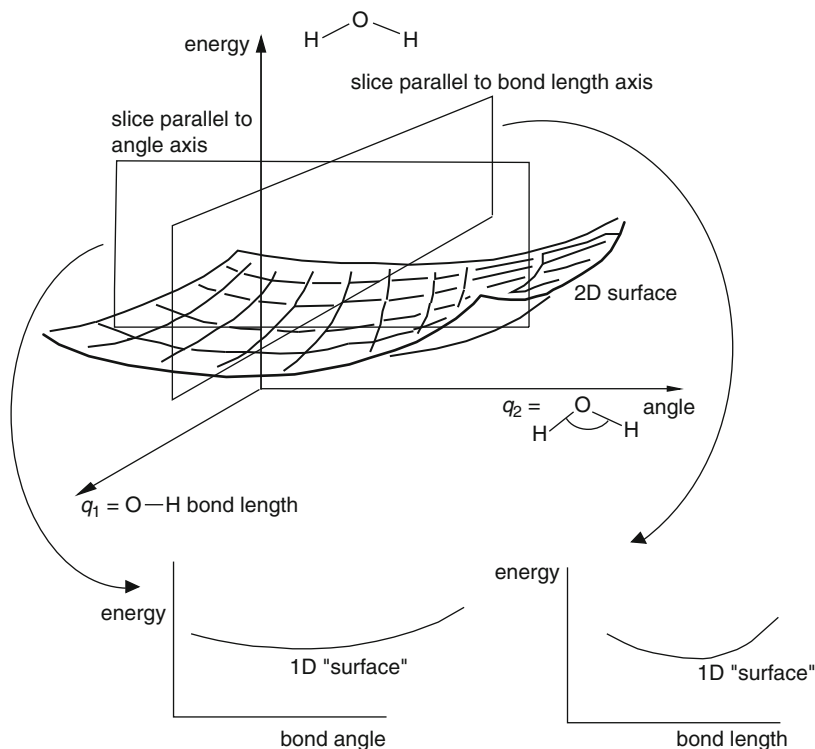


Fig. 2.5 Slices through a 2D potential energy surface give 1D surfaces. A slice that is parallel to neither axis would give a plot of geometry versus a composite of bond angle and bond length, a kind of average geometry

can be made of the 3-D diagram for water. 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. Analogously, we can take a 3-D slice of the hypersurface for HOF (Fig. 2.6) 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. We shall see that these 2D and particularly 3D graphs preserve qualitative and even quantitative features of the mathematically rigorous but unvisualizable $E = f(q_1, q_2, \dots q_n)$ n -dimensional hypersurface.

2.2 Stationary Points

Potential energy surfaces are important because they aid us in visualizing and understanding the relationship between potential energy and molecular geometry, and in understanding how computational chemistry programs locate and characterize structures

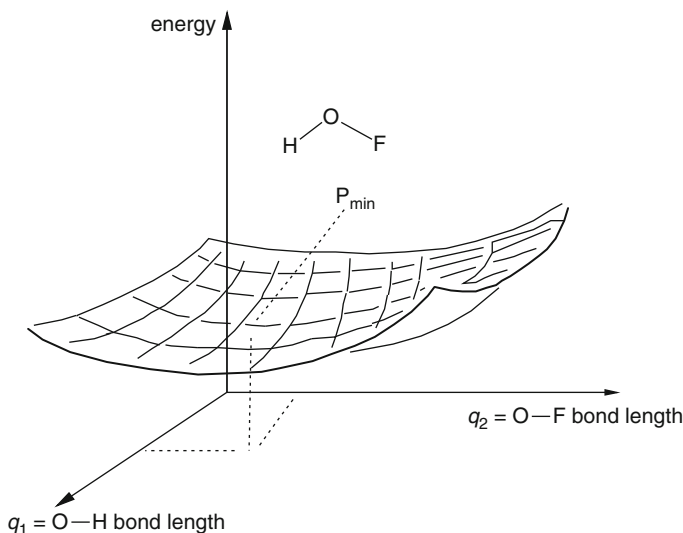
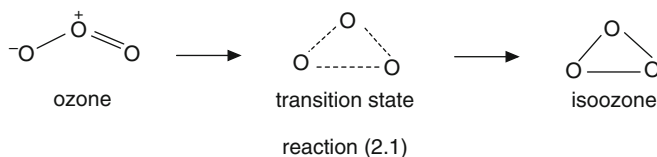


Fig. 2.6 A potential energy surface (PES) for HOF. Here the HOF angle is not shown. This picture could represent one of two possibilities: the angle might be the same (some constant, reasonable value) for every calculated point on the surface; this would be an unrelaxed or rigid PES. Alternatively, for 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 (Section 2.4); this would be a relaxed PES

of interest. 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: our “structures of interest” are molecules and the transition states linking them. Consider the reaction



A priori, 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 Reaction (2.1). We can depict this process on a PES. The potential energy E 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. Figure 2.7 shows the PES for Reaction (2.1), as calculated by the AM1 semiempirical method (Chapter 6; the AM1 method is unsuitable for *quantitative* treatment of this problem, but the potential energy surface shown makes the point), and shows how a 2D slice from

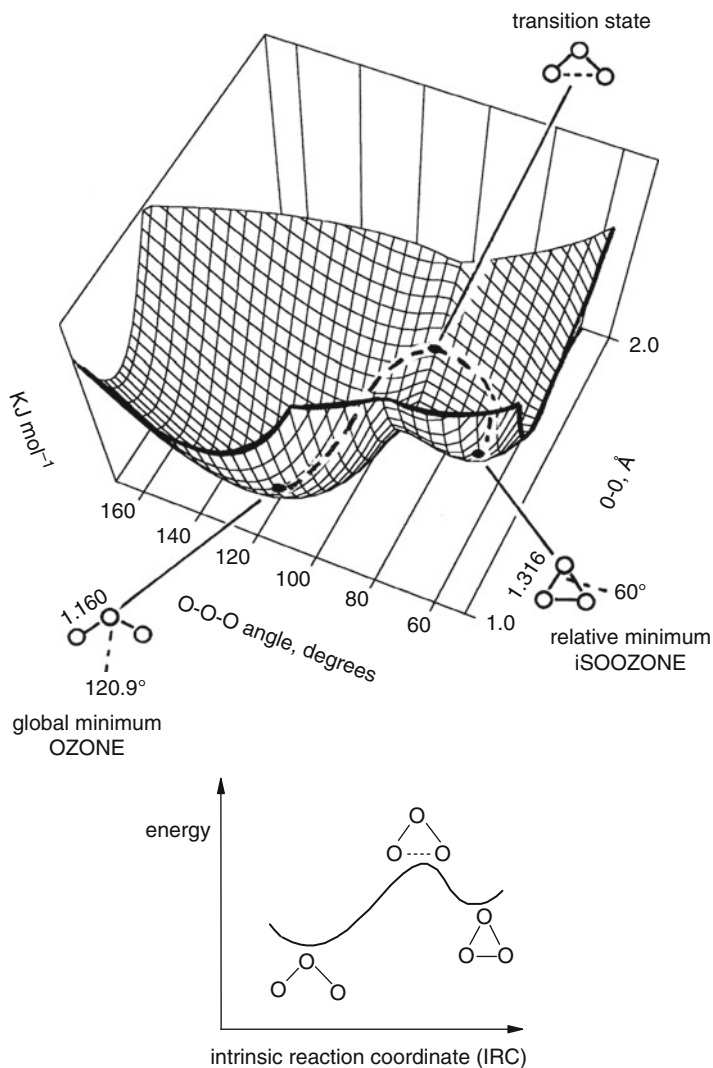


Fig. 2.7 The ozone/isoozone potential energy surface (calculated by the AM1 method; [Chapter 6](#)), a 2D surface in a 3D diagram. The *dashed line* on the surface is the reaction coordinate (intrinsic reaction coordinate, IRC). A slice through the reaction coordinate gives a 1D “surface” in a 2D diagram. The diagram is not meant to be quantitatively accurate

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 the transition state, that is, along the *reaction coordinate*, and the horizontal axis (the reaction coordinate) of the 2D diagram is a composite of O-O bond length and O-O-O angle. In most discussions this horizontal axis is left quantitatively undefined; qualitatively, the reaction coordinate represents the

progress of the reaction. The three species of interest, ozone, isoozone, and the transition state linking these two, are called *stationary points*. A stationary point 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 on a stationary point will remain balanced, i.e. stationary (in principle; for a transition state the balancing would have to be exquisite indeed). At any other point on a potential surface the marble will roll toward a region of lower potential energy.

Mathematically, a stationary point is one at which the first derivative of the potential energy with respect to each geometric parameter is zero¹:

$$\frac{\partial E}{\partial q_1} = \frac{\partial E}{\partial q_2} = \dots = 0 \quad (*2.1)$$

Partial derivatives, $\partial E/\partial q$, are written here rather than dE/dq , to emphasize that each derivative is with respect to just one of the variables q of which E is a function. Stationary points that correspond to actual molecules with a finite lifetime (in contrast to transition states, which exist only for an instant), like ozone or isoozone, are *minima*, or *energy minima*: each occupies the lowest-energy point in its region of the PES, and any small change in the geometry increases the energy, as indicated in Fig. 2.7. Ozone is a *global minimum*, since it is the lowest-energy minimum on the whole PES, while 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. 2.7) 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 [3].

Inspection of Fig. 2.7 shows that 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* (Fig. 2.8). 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; Eq. 2.1), 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 (examine Fig. 2.8). Recalling that minima and maxima can be distinguished by their second derivatives, we can write:

¹Equations marked with an asterisk are those which should be memorized.

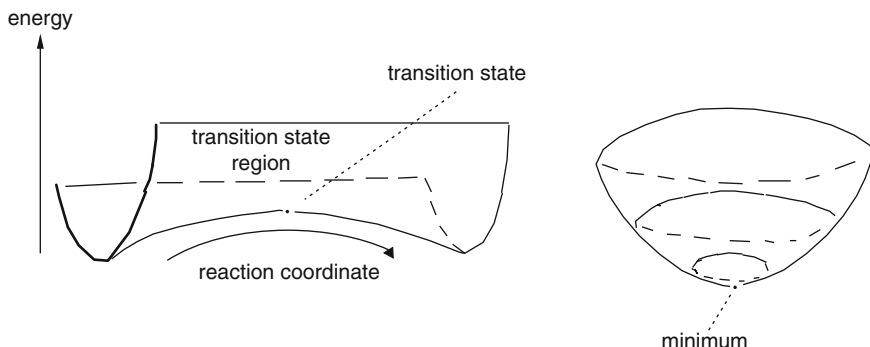


Fig. 2.8 A transition state or saddle point and a minimum. At both the transition state and the minimum $\partial E / \partial q = 0$ for all geometric coordinates q (along all directions). At the transition state $\partial^2 E / \partial q^2 < 0$ for $q =$ the reaction coordinate and > 0 for all other q (along all other directions). At a minimum $\partial^2 E / \partial q^2 > 0$ for all q (along all directions)

For a *minimum*

$$\frac{\partial^2 E}{\partial q^2} > 0 \quad (*2.2)$$

for all q .

For a *transition state*

$$\frac{\partial^2 E}{\partial q^2} > 0 \quad (*2.3)$$

for all q , except along *the reaction coordinate*, and

$$\frac{\partial^2 E}{\partial q^2} < 0 \quad (*2.4)$$

along the reaction coordinate.

The distinction is sometimes made between a *transition state* and a *transition structure* [4]. Strictly speaking, a transition state is a thermodynamic concept, the species an ensemble of which are in a kind of equilibrium with the reactants in Eyring's² transition-state theory [5]. Since equilibrium constants are determined by free energy differences, the transition structure, within the strict use of the term, is a free energy maximum along the reaction coordinate (in so far as a single species can

²Henry Eyring, American chemist. Born Colonia Juarárez, Mexico, 1901. Ph.D. University of California, Berkeley, 1927. Professor Princeton, University of Utah. Known for his work on the theory of reaction rates and on potential energy surfaces. Died Salt Lake City, Utah, 1981.

be considered representative of the ensemble). This species is also often (but not always [5]) also called an activated complex. A transition *structure*, in strict usage, is the saddle point (Fig. 2.8) on a theoretically calculated (e.g. Fig. 2.7) PES. Normally such a surface is drawn through a set of points each of which represents the enthalpy of a molecular species at a certain geometry; recall that free energy differs from enthalpy by temperature times entropy. The transition structure is thus a saddle point on an enthalpy surface. However, the energy of each of the calculated points does not normally include the vibrational energy, and even at 0 K a molecule has such energy (zero point energy: Fig. 2.2, and Section 2.5). The usual calculated PES is thus a hypothetical, physically unrealistic surface in that it neglects vibrational energy, but it should qualitatively, and even semiquantitatively, resemble the vibrationally-corrected one since in considering *relative* enthalpies ZPEs at least roughly cancel. In accurate work ZPEs are calculated for stationary points and added to the “frozen-nuclei” energy of the species at the bottom of the reaction coordinate curve in an attempt to give improved relative energies which represent enthalpy differences at 0 K (and thus, at this temperature where entropy is zero, free energy differences also; Fig. 2.19). It is also possible to calculate enthalpy and entropy differences, and thus free energy differences, at, say, room temperature (Section 5.5.2). Many chemists do not routinely distinguish between the two terms, and in this book the commoner term, transition state, is used. Unless indicated otherwise, it will mean a calculated geometry, the saddle point on a hypothetical vibrational-energy-free PES.

The geometric parameter corresponding to the reaction coordinate is usually a composite of several parameters (bond lengths, angles and dihedrals), although for some reactions one two may predominate. In Fig. 2.7, the reaction coordinate is a composite of the O–O bond length and the O–O–O bond angle.

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, corresponds to a transition state. Some PES's have points where the second derivative of energy with respect to more than one coordinate is negative; these are *higher-order saddle points* or *hilltops*: for example, a second-order saddle point is a point on the PES which is a maximum along *two* paths connecting stationary points. The propane PES, Fig. 2.9, provides examples of a minimum, a transition state and a hilltop – a second-order saddle point in this case. Figure 2.10 shows the three stationary points in more detail. The “doubly-eclipsed” conformation (Fig. 2.10a) in which there is eclipsing as viewed along the C1–C2 and the C3–C2 bonds (the dihedral angles are 0° viewed along these bonds) is a second-order saddle point because single bonds do not like to eclipse single bonds and rotation about the C1–C2 and the C3–C2 bonds will remove this eclipsing: there are *two* possible directions along the PES which lead, without a barrier, to lower-energy regions, i.e. changing the H–C1/C2–C3 dihedral and changing the H–C3/C2–C1 dihedral. Changing one of these leads to a “singly-eclipsed” conformation (Fig. 2.10b) with only one offending eclipsing CH₃–CH₂ arrangement, and this is a first-order saddle point, since there is now only one direction along the PES which leads to relief of the eclipsing interactions (rotation around C3–C2). This route

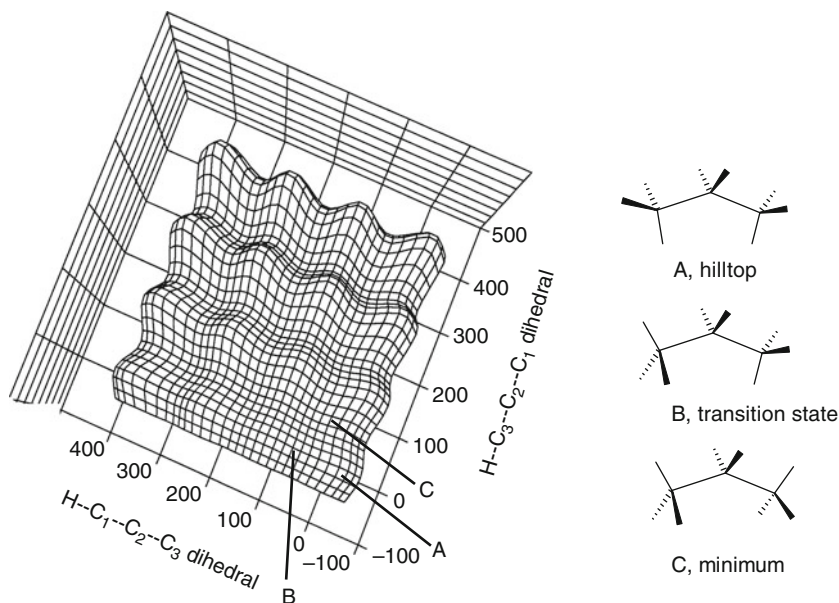


Fig. 2.9 The propane potential energy surface as the two HCCC dihedrals are varied (calculated by the AM1 method, [Chapter 6](#)). Bond lengths and angles were not optimized as the dihedrals were varied, so this is not a relaxed PES; however, changes in bond lengths and angles from one propane conformation to another are small, and the relaxed PES should be very similar to this one

gives a conformation C which has no eclipsing interactions and is therefore a minimum. There are no lower-energy structures on the C_3H_8 PES and so C is the global minimum.

The geometry of propane depends on more than just two dihedral angles, of course; there are several bond lengths and bond angles and the potential energy will vary with changes in all of them. Figure 2.9 was calculated by varying only the dihedral angles associated with the C1–C2–C3–C4 bonds, keeping the other geometrical parameters the same as they are in the all-staggered conformation. If at every point on the dihedral/dihedral grid all the other parameters (bond lengths and angles) had been optimized (adjusted to give the lowest possible energy, for that particular calculational method; [Section 2.4](#)), the result would have been a *relaxed* PES. In Fig. 2.9 this was not done, but because bond lengths and angles change only slightly with changes in dihedral angles the PES would not be altered much, while the time required for the calculation (for the *potential energy surface scan*) would have been greater. Figure 2.9 is a nonrelaxed or rigid PES, albeit not very different, in this case, from a relaxed one.

Chemistry is essentially the study of the stationary points on potential energy surfaces: in studying more or less stable molecules we focus on minima, and in investigating chemical reactions we study the passage of a molecule from a

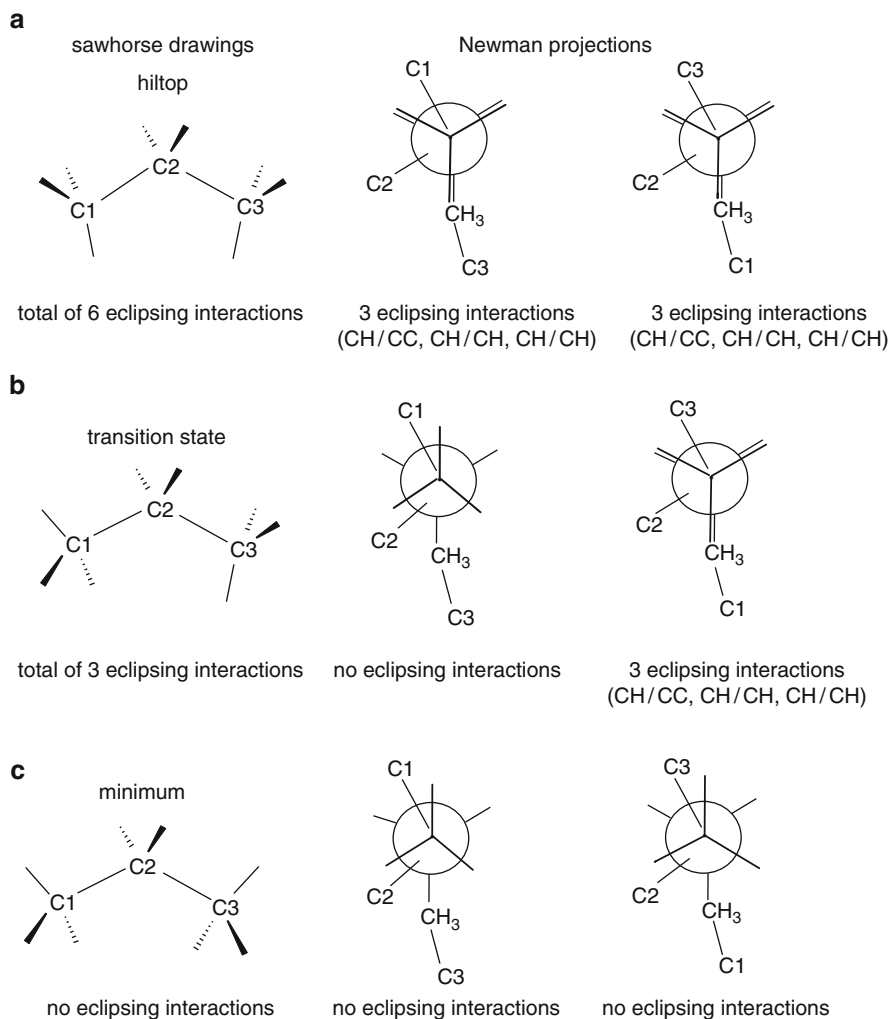


Fig. 2.10 The stationary points on the propane potential energy surface. Hydrogens at the end of CH bonds are omitted for clarity

minimum through a transition state to another minimum. There are four known forces in nature: the gravitational force, the strong and the weak nuclear forces, and the electromagnetic force. Celestial mechanics studies the motion of stars and planets under the influence of the gravitational force and nuclear physics studies the behaviour of subatomic particles subject to the nuclear forces. Chemistry is concerned with aggregates of nuclei and electrons (with molecules) held together by the electromagnetic force, and with the shuffling of nuclei, followed by their

obedient retinue of electrons, around a potential energy surface under the influence of this force (with chemical reactions).

The concept of the chemical potential energy surface apparently originated with R. Marcelin [6]: in a dissertation-long paper (111 pages) he laid the groundwork for transition-state theory 20 years before the much better-known work of Eyring [5,7]. The importance of Marcelin's work is acknowledged by Rudolph Marcus in his Nobel Prize (1992) speech, where he refers to "...Marcelin's classic 1915 theory which came within one small step of the transition state theory of 1935." The paper was published the year after the death of the author, who seems to have died in World War I, as indicated by the footnote "Tué à l'ennemi en sept 1914". The first potential energy surface was calculated in 1931 by Eyring and Polanyi,³ using a mixture of experiment and theory [8].

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) (which species we call the reactant and which the product is inconsequential here). This picture is immensely useful, and may well apply to the great majority of reactions. However, for some reactions it is deficient. Carpenter has shown that in some cases a reactive intermediate does not tarry in a PES well and then proceed to react. Rather it appears to scoot over a plateau-shaped region of the PES, retaining a memory ("dynamical information") of the atomic motions it acquired when it was formed. When this happens there are two (say) intermediates with the same crass geometry, but different atomic motions, leading to different products. The details are subtle, and the interested reader is commended to the relevant literature [9].

2.3 The Born–Oppenheimer Approximation

A potential energy surface is a plot of the energy of a collection of nuclei and electrons against the geometric coordinates of the nuclei – essentially a plot of molecular energy versus molecular geometry (or it may be regarded as the mathematical equation that gives the energy as a function of the nuclear coordinates). The nature (minimum, saddle point or neither) of each point was discussed in terms of the response of the energy (first and second derivatives) to changes in nuclear coordinates. But if a molecule is a collection of nuclei and electrons why plot energy versus *nuclear* coordinates – why not against *electron* coordinates? In other words, why are nuclear coordinates the parameters that define molecular geometry? The answer to this question lies in the Born–Oppenheimer approximation.

³Michael Polanyi, Hungarian-British chemist, economist, and philosopher. Born Budapest 1891. Doctor of medicine 1913, Ph.D. University of Budapest, 1917. Researcher Kaiser-Wilhelm Institute, Berlin, 1920–1933. Professor of chemistry, Manchester, 1933–1948; of social studies, Manchester, 1948–1958. Professor Oxford, 1958–1976. Best known for book "Personal Knowledge", 1958. Died Northampton, England, 1976.

Born⁴ and Oppenheimer⁵ showed in 1927 [10] that to a very good approximation the nuclei in a molecule are stationary with respect to the electrons. This is a qualitative expression of the principle; mathematically, the approximation states that the Schrödinger equation (Chapter 4) for a molecule may be separated into an electronic and a nuclear equation. One consequence of this is that all (!) we have to do to calculate the energy of a molecule is to solve the *electronic* Schrödinger equation and then add the electronic energy to the internuclear repulsion (this latter quantity is trivial to calculate) to get the total internal energy (see Section 4.4.1). A deeper consequence of the Born–Oppenheimer approximation is that a molecule has a shape.

The nuclei see the electrons as a smeared-out cloud of negative charge which binds them in fixed relative positions (because of the mutual attraction between electrons and nuclei in the internuclear region) and which defines the (somewhat fuzzy) surface [11] of the molecule (see Fig. 2.11). Because of the rapid motion of the electrons compared to the nuclei the “permanent” geometric parameters of the molecule are the *nuclear* coordinates. The energy (and the other properties) of a molecule is a *function* of the electron coordinates ($E = \Psi(x, y, z$ of each electron); Section 5.2), but depends only *parametrically* on the nuclear coordinates, i.e. for each geometry 1, 2, ... there is a particular energy: $E_1 = \Psi_1(x, y, z, \dots)$, $E_2 = \Psi_2(x, y, z, \dots)$; cf. x^n , which is a function of x but depends only parametrically on the particular n .

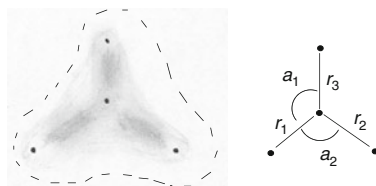


Fig. 2.11 The nuclei in a molecule see a time-averaged electron cloud. The nuclei vibrate about equilibrium points which define the molecular geometry; this geometry can be expressed simply as the nuclear Cartesian coordinates, or alternatively as bond lengths and angles r and a here) and dihedrals, i.e. as internal coordinates. As far as size goes, the experimentally determined van der Waals surface encloses about 98% of the electron density of a molecule

⁴Max Born, German-British physicist. Born in Breslau (now Wrocław, Poland), 1882, died in Göttingen, 1970. Professor Berlin, Cambridge, Edinburgh. Nobel Prize, 1954. One of the founders of quantum mechanics, originator of the probability interpretation of the (square of the) wave-function (Chapter 4).

⁵J. Robert Oppenheimer, American physicist. Born in New York, 1904, died in Princeton 1967. Professor California Institute of Technology. Fermi award for nuclear research, 1963. Important contributions to nuclear physics. Director of the Manhattan Project 1943–1945. Victimized as a security risk by senator Joseph McCarthy’s Un-American Activities Committee in 1954. Central figure of the eponymous PBS TV series (Oppenheimer: Sam Waterston).

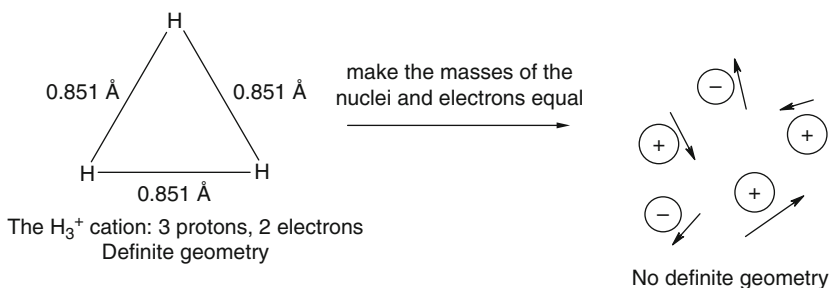


Fig. 2.12 A molecule has a definite shape because unlike the electrons, the nuclei are (relatively) stationary (since they are much more massive). If the masses of the nuclei and the electrons could be made equal, the distinction in lethargy would be lost, and the molecular geometry would dissolve

Actually, the nuclei are not stationary, but execute vibrations of small amplitude about equilibrium positions; it is these equilibrium positions that we mean by the “fixed” nuclear positions. It is only because it is meaningful to speak of (almost) fixed nuclear coordinates that the concepts of molecular geometry or shape and of the PES are valid [12]. The nuclei are much more sluggish than the electrons because they are much more massive (a hydrogen nucleus is about 2,000 more massive than an electron).

Consider the molecule H_3^+ , made up of three protons and two electrons. Ab initio calculations assign it the geometry shown in Fig. 2.12. The equilibrium positions of the nuclei (the protons) lie at the corners of an equilateral triangle and H_3^+ has a definite shape. But suppose the protons were replaced by positrons, which have the same mass as electrons. The distinction between nuclei and electrons, which in molecules rests on mass and not on some kind of charge chauvinism, would vanish. We would have a quivering cloud of flitting particles to which a shape could not be assigned on a macroscopic time scale.

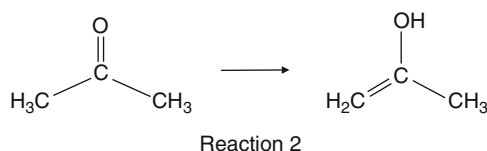
A calculated PES, which we might call a Born–Oppenheimer surface, is normally the set of points representing the geometries, and the corresponding energies, of a collection of atomic nuclei; the electrons are taken into account in the calculations as needed to assign charge and multiplicity (multiplicity is connected with the number of unpaired electrons). Each point corresponds to a set of stationary nuclei, and in this sense the surface is somewhat unrealistic (see Section 2.5).

2.4 Geometry Optimization

The characterization (the “location” or “locating”) of a stationary point on a PES, that is, demonstrating that the point in question exists and calculating its geometry and energy, is a *geometry optimization*. The stationary point of interest might be a minimum, a transition state, or, occasionally, a higher-order saddle point. Locating a minimum is often called an energy minimization or simply a minimization, and

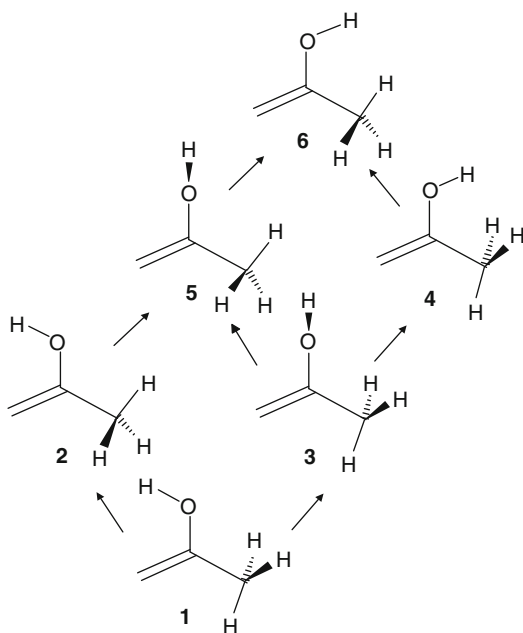
locating a transition state is often referred to specifically as a transition state optimization. Geometry optimizations are done by starting with an input structure that is believed to resemble (the closer the better) the desired stationary point and submitting this plausible structure to a computer 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 (Section 2.2) may then be determined (Section 2.5) to characterize the structure as a minimum or as some kind of saddle point.

Let us consider a problem that arose in connection with an experimental study. Propanone (acetone) was subjected to ionization followed by neutralization of the radical cation, and the products were frozen in an inert matrix and studied by IR spectroscopy [13]. The spectrum of the mixture suggested the presence of the enol isomer of propanone, 1-propen-2-ol (Reaction 2.2):



To confirm (or refute) this the IR spectrum of the enol might be calculated (see Section 2.5 and the discussions of the calculation of IR spectra in subsequent chapters). But which conformer should one choose for the calculation? Rotation about the C–O and C–C bonds creates six plausible stationary points (Fig. 2.13),

Fig. 2.13 The plausible stationary points on the propenol potential energy surface. A PES scan (Fig. 2.14) 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



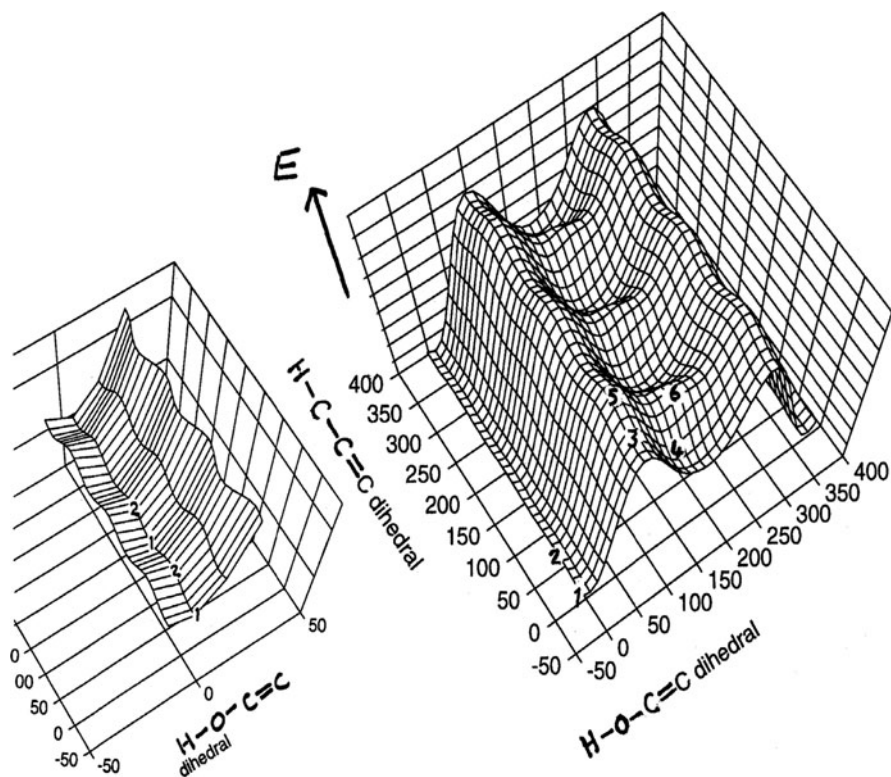


Fig. 2.14 The 1-propen-2-ol potential energy surface (calculated by the AM1 method) (see Fig. 2.13)

and a PES scan (Fig. 2.14) indicated that there are indeed six such species. Examination of this PES shows that the global minimum is structure **1** and that there is a relative minimum corresponding to structure **4**. Geometry optimization starting from an input structure resembling **1** gave a minimum corresponding to **1**, while optimization starting from a structure resembling **4** gave another, higher-energy minimum, resembling **4**. Transition-state optimizations starting from appropriate structures yielded the transition states **2** and **3**. These stationary points were all characterized as minima or transition states by second-derivative calculations (Section 2.5) (the species **5** and **6** were not located). The calculated IR spectrum of **1** (using the ab initio HF/6-31G* method – Chapter 5) was in excellent agreement with the observed spectrum of the putative propenol.

This illustrates a general principle: the optimized structure one obtains is that closest in geometry on the PES to the input structure (Fig. 2.15). 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). Of course we may not be interested in the global minimum; for example, if we wish to study the cyclic isomer of ozone (Section 2.2) we will use as

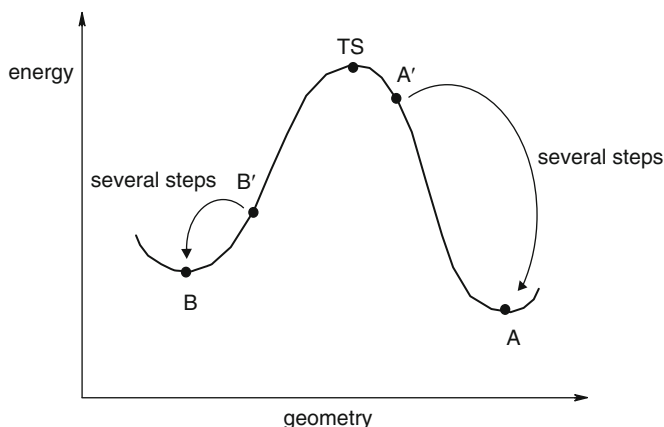


Fig. 2.15 Geometry optimization to a minimum gives the minimum closest to the input structure. The input structure A' is moved toward the minimum A , and B' toward B . To locate a transition state a special algorithm is usually used: this moves the initial structure A' toward the transition state TS . Optimization to each of the stationary points would probably actually require several steps (see Fig. 2.16)

input an equilateral triangle structure, probably with bond lengths about those of an O–O single bond.

In the propenol example, the PES scan suggested that to obtain the global minimum we should start with an input structure resembling **1**, but the exact values of the various bond lengths and angles were unknown (the exact values of even the dihedrals was not known with certainty, although general chemical knowledge made $\text{H–O–C–C} = \text{H–C–C}=\text{C} = 0^\circ$ seem plausible). The actual creation of input structures is usually done nowadays with an interactive mouse-driven program, in much the same spirit that one constructs plastic models or draws structures on paper. 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 coordinates).

To move along the PES from the input structure to the nearest minimum is obviously trivial on the one-dimensional PES of a diatomic molecule: one simply changes the bond length till that corresponding to 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 (Fig. 2.16). It is not possible, in general, 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, given a reasonable input geometry. The most widely-used algorithms for geometry optimization [14] use the first and second derivatives of the energy with respect to the geometric parameters. To get a feel for how this works, consider the simple case of a one-dimensional PES, as for a diatomic molecule (Fig. 2.17). The input structure is at the point $P_i(E_i, q_i)$ and the proximate minimum, corresponding to the optimized structure being sought, is at the point $P_o(E_o, q_o)$. Before the optimization

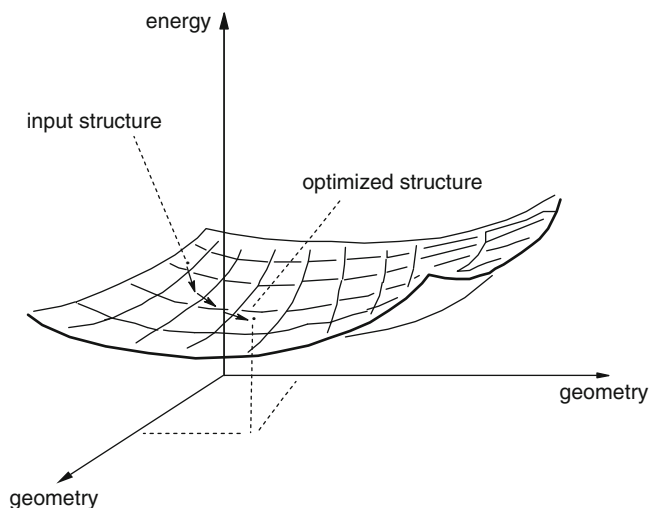


Fig. 2.16 An efficient optimization algorithm knows approximately in which direction to move and how far to step, in an attempt to reach the optimized structure in relatively few (commonly about five to ten) steps

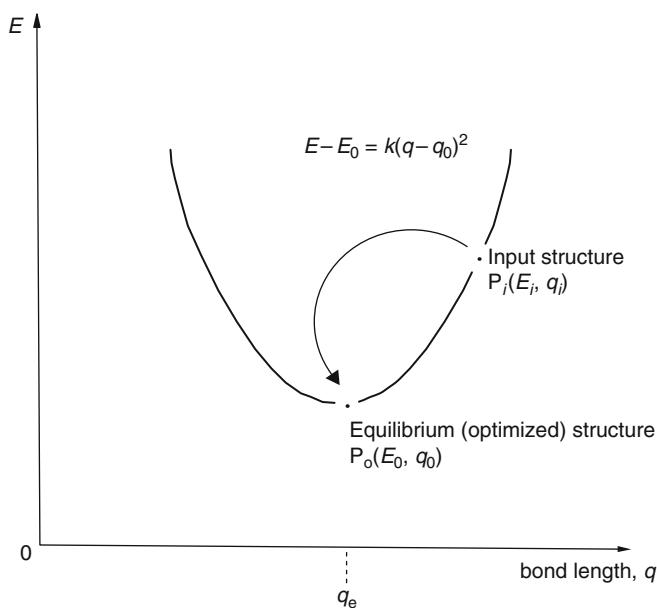


Fig. 2.17 The potential energy of a diatomic molecule near the equilibrium geometry is approximately a quadratic function of the bond length. Given an input structure (i.e. given the bond length q_i), a simple algorithm would enable the bond length of the optimized structure to be found in one step, if the function were strictly quadratic

has been carried out the values of E_o and q_o are of course unknown. If we assume that near a minimum the potential energy is a quadratic function of q , which is a fairly good approximation, then

$$E - E_o = k(q - q_o)^2 \quad (2.5)$$

$$\text{At the input point} \quad (dE/dq)_i = 2k(q_i - q_o) \quad (2.6)$$

$$\text{At all points} \quad d^2E/dq^2 = 2k (= \text{force constant}) \quad (2.7)$$

$$\text{From Eqs. (2.6) and (2.7),} \quad (dE/dq)_i = (d^2E/dq^2)(q_i - q_o) \quad (2.8)$$

$$\text{and} \quad q_o = q_i - (dE/dq)_i / (d^2E/dq^2) \quad (2.9)$$

Equation 2.9 shows that if we know $(dE/dq)_i$, the slope or gradient of the PES at the point of the initial structure, (d^2E/dq^2) , the curvature of the PES (which for a quadratic curve $E(q)$ is independent of q) and q_i , the initial geometry, we can calculate q_o , the optimized geometry. The second derivative of potential energy with respect to geometric displacement is the force constant for motion along that geometric coordinate; as we will see later, this is an important concept in connection with calculating vibrational spectra.

For multidimensional PES's, i.e. for almost all real cases, far more sophisticated algorithms are used, and several steps are needed since the curvature is not exactly quadratic. The first step results in a new point on the PES that is (probably) closer to the minimum than was the initial structure. This new point then serves as the initial point for a second step toward the minimum, etc. Nevertheless, most modern geometry optimization methods do depend on calculating the first and second derivatives of the energy at the point on the PES corresponding to the input structure. Since the PES is not strictly quadratic, the second derivatives vary from point to point and are updated as the optimization proceeds.

In the illustration of an optimization algorithm using a diatomic molecule, Eq. 2.9 referred to the calculation of first and second derivatives with respect to bond length, which latter is an internal coordinate (inside the molecule). Optimizations are actually commonly done using Cartesian coordinates x , y , z . Consider the optimization of a triatomic molecule like HOF in a Cartesian coordinate system. Each of the three atoms has an x , y and z coordinate, giving nine geometric parameters, q_1, q_2, \dots, q_9 ; the PES would be a nine-dimensional hypersurface on a 10D graph. We need the first and second derivatives of E with respect to each of the nine q 's, and these derivatives are manipulated as matrices. Matrices are discussed in Section 4.3.3; here we need only know that a matrix is a rectangular array of numbers that can be manipulated mathematically, and that they provide a convenient way of handling sets of linear equations. The first-derivative matrix, the gradient matrix, for the input structure can be written as a column matrix

$$\mathbf{g}_i = \begin{pmatrix} (\partial E / \partial \mathbf{q}_1)_i \\ (\partial E / \partial \mathbf{q}_2)_i \\ \vdots \\ (\partial E / \partial \mathbf{q}_9)_i \end{pmatrix} \quad (2.10)$$

and the second-derivative matrix, the force constant matrix, is

$$\mathbf{H} = \begin{pmatrix} \partial^2 E / \partial \mathbf{q}_1 \mathbf{q}_1 & \partial^2 E / \partial \mathbf{q}_1 \mathbf{q}_2 \cdots & \partial^2 E / \partial \mathbf{q}_1 \mathbf{q}_9 \\ \partial^2 E / \partial \mathbf{q}_2 \mathbf{q}_1 & \partial^2 E / \partial \mathbf{q}_2 \mathbf{q}_2 \cdots & \partial^2 E / \partial \mathbf{q}_2 \mathbf{q}_9 \\ \vdots & \vdots & \vdots \\ \partial^2 E / \partial \mathbf{q}_9 \mathbf{q}_1 & \partial^2 E / \partial \mathbf{q}_9 \mathbf{q}_2 \cdots & \partial^2 E / \partial \mathbf{q}_9 \mathbf{q}_9 \end{pmatrix} \quad (2.11)$$

The force constant matrix is called the Hessian.⁶ The Hessian is particularly important, not only for geometry optimization, but also for the characterization of stationary points as minima, transition states or hilltops, and for the calculation of IR spectra (Section 2.5). In the Hessian $\partial^2 E / \partial q_1 q_2 = \partial^2 E / \partial q_2 q_1$, as is true for all well-behaved functions, but this systematic notation is preferable: the first subscript refers to the row and the second to the column. The geometry coordinate matrices for the initial and optimized structures are

$$\mathbf{q}_i = \begin{pmatrix} q_{i1} \\ q_{i2} \\ \vdots \\ q_{i9} \end{pmatrix} \quad (2.12)$$

and

$$\mathbf{q}_o = \begin{pmatrix} q_{o1} \\ q_{o2} \\ \vdots \\ q_{o9} \end{pmatrix} \quad (2.13)$$

The matrix equation for the general case can be shown to be:

$$\mathbf{q}_o = \mathbf{q}_i - \mathbf{H}^{-1} \mathbf{g}_i \quad (2.14)$$

which is analogous to Eq. 2.9 for the optimization of a diatomic molecule, which could be written

$$q_o = q_i - (d^2 E / dq^2)^{-1} (dE / dq)_i$$

⁶Ludwig Otto Hesse, 1811–1874, German mathematician.

For n atoms we have $3n$ Cartesians; \mathbf{q}_0 , \mathbf{q}_i and \mathbf{g}_i are $3n \times 1$ column matrices and \mathbf{H} is a $3n \times 3n$ square matrix; multiplication by the inverse of \mathbf{H} rather than division by \mathbf{H} is used because matrix division is not defined. Equation 2.14 shows that for an efficient geometry optimization we need an initial structure (for \mathbf{q}_i), initial gradients (for \mathbf{g}_i) and second derivatives (for \mathbf{H}). With an initial “guess” for the geometry (for example from a model-building program followed by molecular mechanics) as input, gradients can be readily calculated analytically (from the derivatives of the molecular orbitals and the derivatives of certain integrals). An approximate initial Hessian is often calculated from molecular mechanics (Chapter 3). Since the PES is not really exactly quadratic, the first step does not take us all the way to the optimized geometry, corresponding to the matrix \mathbf{q}_0 . Rather, we arrive at \mathbf{q}_1 , the first calculated geometry; using this geometry a new gradient matrix and a new Hessian are calculated (the gradients are calculated analytically and the second derivatives are updated using the changes in the gradients – see below). Using \mathbf{q}_1 and the new gradient and Hessian matrices a new approximate geometry matrix \mathbf{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.

As the optimization proceeds the Hessian is updated by approximating each second derivative as a ratio of finite increments:

$$\frac{\partial^2 E}{\partial q_i \partial q_j} \approx \frac{\Delta(\partial E / \partial q_j)}{\Delta q_i} \quad (2.15)$$

i.e. as the change in the gradient divided by the change in geometry, on going from the previous structure to the latest one. 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, for a minimum or a transition state, usually provides a good Hessian and geometry for input to a higher-level optimization [15]. Finding a transition state (i.e. optimizing an input structure to a transition state structure) is a more challenging computational problem than finding a minimum, as the characteristics of the PES at the former are more complicated than at 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. Nevertheless, modifications of the minimum-search algorithm enable transition states to be located, albeit often with less ease than minima.

2.5 Stationary Points and Normal-Mode Vibrations – Zero Point Energy

Once a stationary point has been found by geometry optimization, it is usually desirable to check whether it is a minimum, a transition state, or a hilltop. This is done by calculating the vibrational frequencies. Such a calculation involves finding the *normal-mode* frequencies; these 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. In a normal-mode vibration all the atoms move in phase with the same frequency: they all reach their maximum and minimum displacements and their equilibrium positions at the same moment. The other vibrations of the molecule are combinations of these simple vibrations. 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: the motion of each atom can be described by three vectors, along the x , y , and z axes of a Cartesian coordinate system; after removing the 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), we are left with $3n - 6$ independent vibrational motions. Arranging these in appropriate combinations gives $3n - 6$ normal modes. A linear molecule has $3n - 5$ normal modes, since we need subtract only 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, and HCN has $3n - 5 = 3(3) - 5 = 4$ normal modes. For water (Fig. 2.18) mode 1 is a bending mode (the H–O–H angle decreases and increases), mode 2 is a symmetric stretching mode (both O–H bonds stretch and contract simultaneously) and mode 3 is an asymmetric stretching mode (as the O–H₁ bond stretches the O–H₂ bond contracts, and vice versa). 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; the normal-mode frequency (there is only one for a diatomic, of course) is given by [16]:

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \quad (*2.16)$$

where $\tilde{\nu}$ = vibrational “frequency”, actually wavenumber, in cm^{-1} ; from deference to convention we use cm^{-1} although the cm is not an SI unit, and so the other units will also be non-SI; $\tilde{\nu}$ signifies the number of wavelengths that will fit into one cm. The symbol ν is the Greek letter nu, which resembles an angular vee; $\tilde{\nu}$ could be

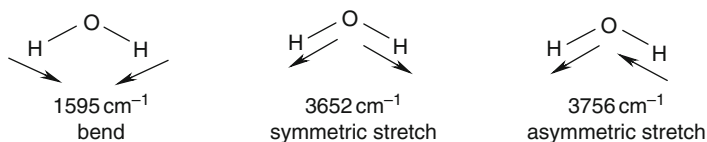


Fig. 2.18 The normal-mode vibrations of water. The *arrows* indicate the directions in which the atoms move; on reaching the maximum amplitude these directions are reversed

read “nu tilde”; $\bar{\nu}$, “nu bar”, has been used less frequently. c = velocity of light, k = force constant for the vibration, μ = reduced mass of the molecule = $(m_A m_B)/(m_A + m_B)$; m_A and m_B are the masses of A and B.

The force constant k of a vibrational mode is a measure of the “stiffness” of the molecule toward that vibrational mode – the harder it is to stretch or bend the molecule in the manner of that mode, the bigger is that force constant (for a diatomic molecule k simply corresponds to the stiffness of the one bond). The fact that the frequency of a vibrational mode is related to the force constant for the mode suggests that it might be 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). This is indeed possible: *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 (Section 4.3.3) is a process in which a square matrix \mathbf{A} is decomposed into three square matrices, \mathbf{P} , \mathbf{D} , and \mathbf{P}^{-1} : $\mathbf{A} = \mathbf{P}\mathbf{D}\mathbf{P}^{-1}$. \mathbf{D} is a diagonal matrix: as with \mathbf{k} in Eq. 2.17 all its off-diagonal elements are zero. \mathbf{P} is a premultiplying matrix and \mathbf{P}^{-1} is the inverse of \mathbf{P} . When matrix algebra is applied to physical problems, the diagonal row elements of \mathbf{D} are the magnitudes of some physical quantity, and each column of \mathbf{P} is a set of coordinates which give a direction associated with that physical quantity. These ideas are made more concrete in the discussion accompanying Eq. 2.17, which shows the diagonalization of the Hessian matrix for a triatomic molecule, e.g. H_2O .

$$\begin{aligned} \mathbf{H} &= \begin{pmatrix} \partial^2 E / \partial q_1 q_1 & \partial^2 E / \partial q_1 q_2 & \cdots & \partial^2 E / \partial q_1 q_9 \\ \partial^2 E / \partial q_2 q_1 & \partial^2 E / \partial q_2 q_2 & \cdots & \partial^2 E / \partial q_2 q_9 \\ \vdots & \vdots & \cdots & \vdots \\ \partial^2 E / \partial q_9 q_1 & \partial^2 E / \partial q_9 q_2 & \cdots & \partial^2 E / \partial q_9 q_9 \end{pmatrix} \\ &= \begin{pmatrix} q_{11} & q_{12} & \cdots & q_{19} \\ q_{21} & q_{22} & \cdots & q_{29} \\ \vdots & \vdots & \cdots & \vdots \\ q_{91} & q_{92} & \cdots & q_{99} \end{pmatrix} \begin{pmatrix} k_1 & 0 & \cdots & 0 \\ 0 & k_2 & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & k_9 \end{pmatrix} \mathbf{P}^{-1} \quad (2.17) \\ &\quad \mathbf{P} \qquad \mathbf{k} \end{aligned}$$

Equation 2.17 is of the form $\mathbf{A} = \mathbf{P}\mathbf{D}\mathbf{P}^{-1}$. The 9×9 Hessian for a triatomic molecule (three Cartesian coordinates for each atom) is decomposed by diagonalization into a \mathbf{P} matrix whose columns are “direction vectors” for the vibrations whose force constants are given by the \mathbf{k} matrix. Actually, columns 1, 2 and 3 of \mathbf{P} and the corresponding k_1 , k_2 and k_3 of \mathbf{k} refer to *translational* motion of the molecule (motion of the whole molecule from one place to another in space); these three “force constants” are nearly zero. Columns 4, 5 and 6 of \mathbf{P} and the corresponding k_4 , k_5 and k_6 of \mathbf{k} refer to rotational motion about the three principal

axes of rotation, and are also nearly zero. Columns 7, 8 and 9 of \mathbf{P} and the corresponding k_7 , k_8 and k_9 of \mathbf{k} are the direction vectors and force constants, respectively, for the normal-mode vibrations: k_7 , k_8 and k_9 refer to vibrational modes 1, 2 and 3, while the seventh, eighth, and ninth columns of \mathbf{P} are composed of the x, y and z components of vectors for motion of the three atoms in mode 1 (column 7), mode 2 (column 8), and mode 3 (column 9). “Mass-weighting” the force constants, i.e. taking into account the effect of the masses of the atoms (cf. Eq. 2.16 for the simple case of a diatomic molecule), gives the vibrational frequencies. The \mathbf{P} matrix is the *eigenvector* matrix and the \mathbf{k} matrix is the *eigenvalue* matrix from diagonalization of the Hessian \mathbf{H} . “Eigen” is a German prefix meaning “appropriate, suitable, actual” and is used in this context to denote mathematically appropriate entities for the solution of a matrix equation. Thus the directions of the normal-mode frequencies are the eigenvectors, and their magnitudes are the mass-weighted eigenvalues, of the Hessian.

Vibrational frequencies are calculated to obtain IR spectra, to characterize stationary points, and to obtain zero point energies (below). 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 (for example an ab initio method with a particular correlation level and basis set – see Chapter 5). This is because (1) the use of second derivatives as force constants presupposes that the PES is quadratically curved along each geometric coordinate q (Fig. 2.2) but it is only near a stationary point that this is true, and (2) use of a method other than that used to obtain the stationary point presupposes that the PES’s of the two methods are parallel (that they have the same curvature) at the stationary point. Of course, “provisional” force constants at nonstationary points are used in the optimization process, as the Hessian is updated from step to step. Calculated IR frequencies are usually somewhat too high, but (at least for ab initio and density functional calculations) can be brought into reasonable agreement with experiment by multiplying them by an empirically determined factor, commonly about 0.9 [17] (see the discussion of frequencies in Chapters 5–7).

A minimum on the PES has all the normal-mode force constants (all the eigenvalues of the Hessian) positive: for each vibrational mode there is a restoring force, like that of a spring. As the atoms execute the motion, the force pulls and slows them till they move in the opposite direction; each vibration is periodic, over and over. The species corresponding to the minimum sits in a well and vibrates forever (or until it acquires enough energy to react). For a transition state, however, one of the vibrations, that along the reaction coordinate, is different: motion of the atoms corresponding to *this* mode takes the transition state toward the product or toward the reactant, without a restoring force. This one “vibration” is not a periodic motion but rather takes the species through the transition state geometry on a one-way journey. Now, the force constant is the first derivative of the gradient or slope (the derivative of the first derivative); examination of Fig. 2.8 shows that along the reaction coordinate the surface slopes downward, so the force constant for this mode is *negative*. A transition state (a first-order saddle point) has one and only one negative normal-mode force constant (one negative eigenvalue of the Hessian).

Since a frequency calculation involves taking the square root of a force constant (Eq. 2.16), and the square root of a negative number is an imaginary number, a transition state has one imaginary frequency, corresponding to the reaction coordinate. In general an n th-order saddle point (an n th-order hilltop) has n negative normal-mode force constants and so n imaginary frequencies, corresponding to motion from one stationary point of some kind to another.

A stationary point could of course 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 checks the nature of a stationary point by calculating the frequencies and seeing how many imaginary frequencies are present; a minimum has none, a transition state one, and a hilltop more than one. 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 example, the transition state for the unimolecular isomerization of HCN to HNC shows an H bonded to both C and N by an unusually long bond, and the CN bond length is in-between that of HCN and HNC.
2. It must have one and only one imaginary frequency (some programs indicate this as a negative frequency, e.g. $-1,900\text{ cm}^{-1}$ instead of the correct $1,900i$ ($i = \sqrt{-1}$)).
3. The imaginary frequency must correspond to the reaction coordinate. This is usually clear from animation of the frequency (the motion, stretching, bending, twisting, corresponding to a frequency may be visualized with a variety of programs). For example, the transition state for the unimolecular isomerization of HCN to HNC shows an imaginary frequency which when animated clearly shows the H migrating between the C and the N. Should it not be clear from animation which two species the transition state connects, one may resort to an *intrinsic reaction coordinate* (IRC) calculation [18]. This procedure follows the transition state downhill along the IRC (Section 2.2), generating a series of structures along the path to the reactant or product. Usually it is clear where the transition state is going without following it all the way to a stationary point.
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; most programs will calculate this automatically as part of a frequency job). The ZPE is the energy a molecule has even at absolute zero (Fig. 2.2), as a consequence of the fact that even at this temperature it still vibrates [2]. 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 (by subtraction), since for a given reaction the ZPE of the reactant, transition state and product tend to be roughly the same. However, for accurate work the ZPE

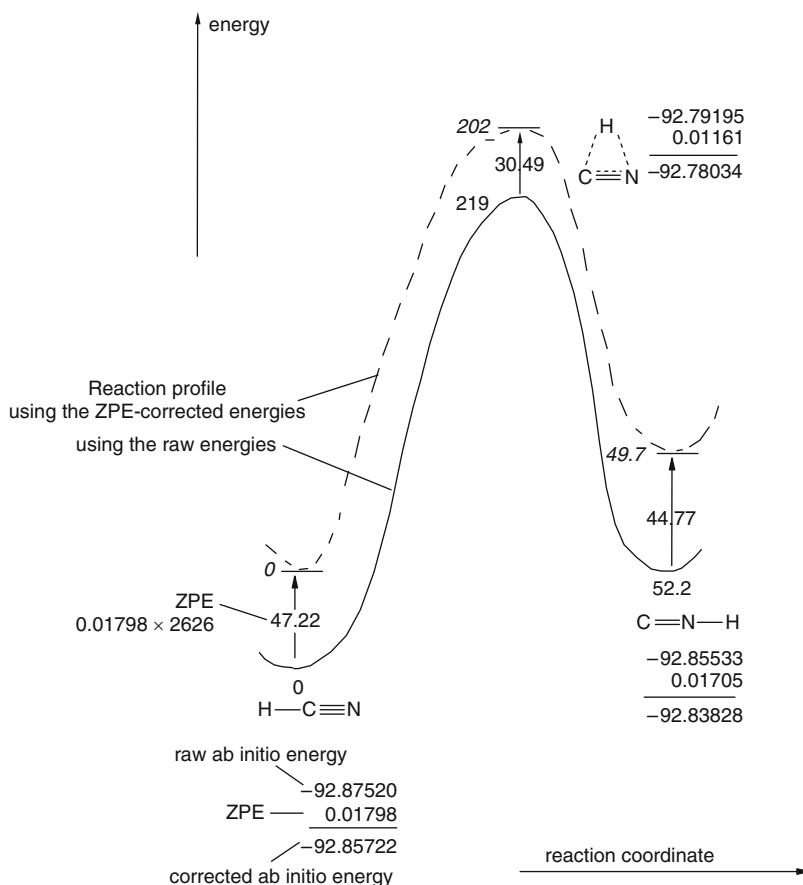


Fig. 2.19 Correcting relative energies for zero-point energy (ZPE). These are ab initio HF/6-31G* (Chapter 5) results for the $\text{HCN} \rightarrow \text{HNC}$ reaction. The corrections are most simply made by adding the ZPE to the raw energy (in energy units called Hartrees or atomic units), to get the corrected energies. Using corrected or uncorrected energies, relative energies are obtained by setting the energy of one species (usually that of lowest energy) equal to zero. Finally, energy differences in Hartrees were multiplied by 2,626 to get kJ mol^{-1} . The ZPEs are also shown here in kJ mol^{-1} , just to emphasize that they are not small compared to reaction energies or activation energies, but tend to cancel; for accurate work ZPE-corrected energies should be used

should be added to the “total” (electronic + nuclear repulsion) energies of species and the ZPE-corrected energies should then be compared (Fig. 2.19). Like the frequencies, 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 [17].

The Hessian that results from a geometry optimization was built up in steps from one geometry to the next, approximating second derivatives from the changes in gradients (Eq. 2.15). This Hessian is not accurate enough for the calculation of

frequencies and ZPE's. The calculation of an accurate Hessian for a stationary point can be done analytically or numerically. Accurate numerical evaluation approximates the second derivative as in Eq. 2.15, but instead of $\Delta(\partial V/\partial q)$ and Δq being taken from optimization iteration steps, they are obtained by changing the position of each atom of the optimized structure slightly ($\Delta q = \text{about } 0.01 \text{ \AA}$) and calculating analytically the change in the gradient at each geometry; subtraction gives $\Delta(\partial V/\partial q)$. This can be done for a change in one direction only for each atom (method of forward differences) or more accurately by going in two directions around the equilibrium position and averaging the gradient change (method of central differences). Analytical calculation of ab initio frequencies is much faster than numerical evaluation, but demands on computer hard drive space may make numerical calculation the only recourse at high ab initio levels (Chapter 5).

2.6 Symmetry

Symmetry is important in theoretical chemistry (and even more so in theoretical physics), but our interest in it here is bounded by modest considerations: we want to see why symmetry is relevant to setting up a calculation and interpreting the results, and to make sense of terms like C_{2v} , C_s , etc., which are used in various places in this book. Excellent expositions of symmetry are given by, for example, Atkins [19] and Levine [20].

The symmetry of a molecule is most easily described by using one of the standard designations like C_{2v} , C_s . These are called point groups (Schoenflies point groups) because when symmetry operations (below) are carried out on a molecule (on any object) with symmetry, at least one point is left unchanged. The classification is according to the presence of symmetry elements and corresponding symmetry operations. The main symmetry elements are mirror planes (symmetry planes), symmetry axes, and an inversion center; other symmetry elements are the entire object, and an improper rotation axis. The operation corresponding to a mirror plane is reflection in that plane, the operation corresponding to a symmetry axis is rotation about that axis, and the operation corresponding to an inversion center is moving each point in the molecule along a straight line to that center then moving it further, along the line, an equal distance beyond the center. The "entire object" element corresponds to doing nothing (a null operation); in common parlance an object with only this symmetry element would be said to have no symmetry. The improper rotation axis corresponds to rotation followed by a reflection through a plane perpendicular to that rotation axis. We are concerned mainly with the first three symmetry elements. The examples below are shown in Fig. 2.20.

C₁ A molecule with no symmetry elements at all is said to belong to the group C_1 (to have " C_1 symmetry"). The only symmetry operation such a molecule permits is the null operation – this is the only operation that leaves it unmoved. An example is CHBrClF, with a so-called asymmetric atom; in fact, *most* molecules have no

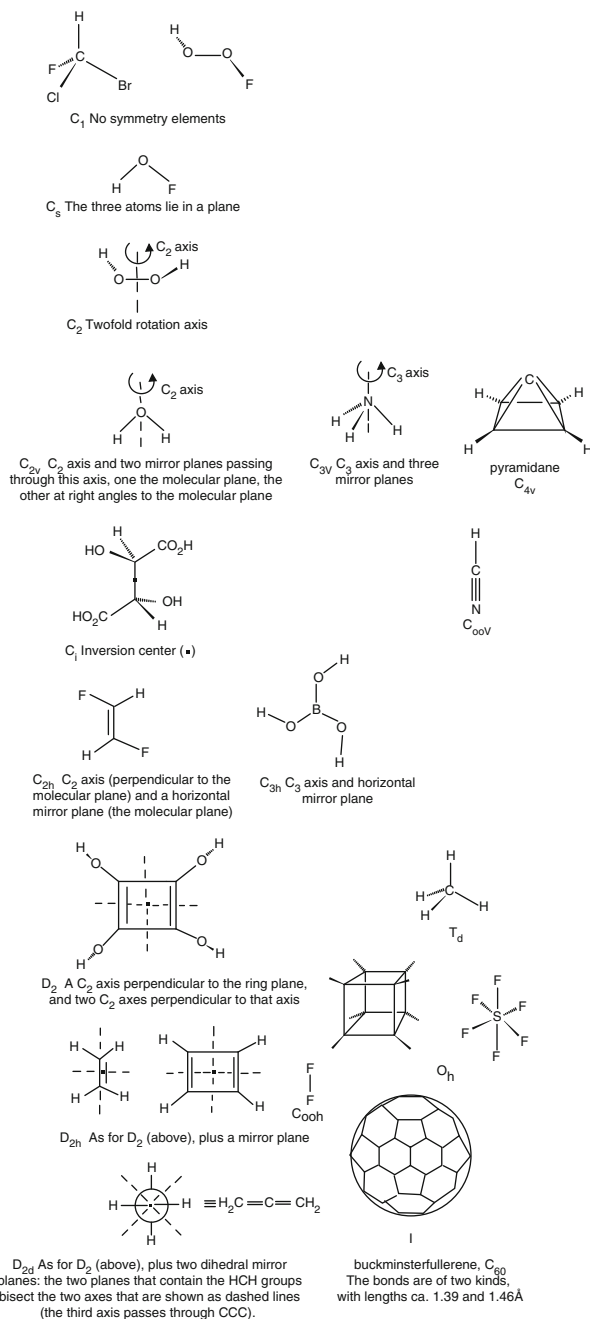


Fig. 2.20 Examples of molecules with various symmetry elements (belonging to various point groups)

symmetry – just think of steroids, alkaloids, proteins, most drugs. Note that a molecule does not need an “asymmetric atom” to have C_1 symmetry: HOOH in the conformation shown is C_1 (has no symmetry).

C_s A molecule with only a mirror plane belongs to the group C_s . Example: HOF. Reflection in this plane leaves the molecule apparently unmoved.

C_2 A molecule with only a C_2 axis belongs to the group C_2 . Example: H_2O_2 in the conformation shown. Rotation about this axis through 360° gives the same orientation twice. Similarly C_3 , C_4 , etc. are possible.

C_{2v} A molecule with two mirror planes whose intersection forms a C_2 axis belongs to the C_{2v} group. Example: H_2O . Similarly NH_3 is C_{3v} , pyramidine is C_{4v} , and HCN is $C_{\infty v}$.

C_i A molecule with only an inversion center (center of symmetry) belongs to the group C_i . Example: *meso*-tartaric acid in the conformation shown. Moving any point in the molecule along a straight line to this center, then continuing on an equal distance leaves the molecule apparently unchanged.

C_{2h} A molecule with a C_2 axis and a mirror plane horizontal to this axis is C_{2h} (a C_{2h} object will also perform have an inversion center). Example: (*E*)-1,2-difluoroethene. Similarly $B(OH)_3$ is C_{3h} .

D_2 A molecule with a C_2 axis and two more C_2 axes, perpendicular to that axis, has D_2 symmetry. Example: the tetrahydroxycyclobutadiene shown. Similarly, a molecule with a C_3 axis (the *principal axis*) and three other perpendicular C_2 axes is D_3 .

D_{2h} A molecule with a C_2 axis and two perpendicular C_2 axes (as for D_2 above), plus a mirror plane is D_{2h} . Examples: ethene, cyclobutadiene. Similarly, a C_3 axis (the principal axis), three perpendicular C_2 axes and a mirror plane horizontal to the principal axis confer D_{3h} symmetry, as in the cyclopropenyl cation. Similarly, benzene is D_{6h} , and F_2 is $D_{\infty h}$.

D_{2d} A molecule is D_{2d} if it has a C_2 axis and two perpendicular C_2 axes (as for D_2 above), plus two “dihedral” mirror planes; these are mirror planes that bisect two C_2 axes (in general, that bisect the C_2 axes perpendicular to the principal axis). Example: allene (propadiene). Staggered ethane is D_{3d} (it has D_3 symmetry elements plus three dihedral mirror planes. D_{nd} symmetry can be hard to spot).

Molecules belonging to the cubic point groups can, in some sense, be fitted symmetrically inside a cube. The commonest of these are T_d , O_h and I ; they will be simply exemplified:

T_d This is tetrahedral symmetry. Example: CH_4 .

O_h This might be considered “cubic symmetry”. Example: cubane, SF_6 .

I Also called icosahedral symmetry. Example: buckminsterfullerene.

Less-common groups are S_4 , and the cubic groups T , T_h (dodecahedrane is T_h) and O (see [19,20]). Atkins [19] and Levine [20] give flow charts which make it relatively simple to assign a molecule to its point group, and Atkins provides pictures of objects of various symmetries which often make it possible to assign a point group without having to examine the molecule for its symmetry elements.

We saw above that most molecules have no symmetry. So why is a knowledge of symmetry important in chemistry? Symmetry considerations are essential in the theory of molecular electronic (UV) spectroscopy and sometimes in analyzing in detail molecular wavefunctions (Chapter 4), but for us the reasons are more pragmatic. A calculation run on a molecule whose input structure has the exact symmetry that the molecule should have 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. Input molecular structures for a calculation are usually created with an interactive graphical program and a computer mouse: atoms are assembled into molecules much as with a model kit, or the molecule might be drawn on the computer screen. If the molecule has symmetry (if it is not C_1) this can be imposed by optimizing the geometry with molecular mechanics (Chapter 3). Now consider water: we would of course normally input the H_2O molecule with its exact equilibrium C_{2v} symmetry, but we could also alter the input structure slightly making the symmetry C_s (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 C_s 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? Although a successful geometry optimization will give essentially the same geometry from a slightly distorted input structure as from one with the perfect symmetry of the molecule in question, 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. This can confuse an analysis of the geometry, and carries over into the calculation of other properties like, say, charges on atoms – corresponding atoms should have exactly the same charges. Thus both esthetic and practical considerations encourage us to aim for the exact symmetry that the molecule should possess.

2.7 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 ($\partial^2 E/\partial q_i \partial q_j > 0$ for all q) and transition states or first-order saddle points; $\partial^2 E/\partial q_i \partial q_j < 0$ 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 Schrödinger equation to molecules by allowing us to focus on the electronic energy and add in the nuclear repulsion energy later; this third point, very important in practical molecular computations, is elaborated on in [Chapter 5](#).

Geometry optimization is the process of starting with an input structure “guess” and finding a stationary point on the PES. The stationary point found will normally be the one closest to the input structure, not necessarily the global minimum. A transition state optimization usually requires a special algorithm, since it is more demanding than that required to find a minimum. Modern optimization algorithms use analytic first derivatives and (usually numerical) 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. A procedure of “mass-weighting” the force constants gives the normal-mode vibrational frequencies. For a minimum all the vibrations are real, while a transition state has one imaginary vibration, corresponding to motion along the reaction coordinate. The criteria for a transition state 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 zero-point energy (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).

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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 transition state is a maximum on a PES.
6. What is the Born–Oppenheimer approximation, and why is it important?
7. Explain, for a reaction $A \rightarrow B$, 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?

Harder Questions

1. The Born–Oppenheimer principle is often said to be a prerequisite for the concept of a potential energy surface. Yet the idea of a potential energy surface (Marcelin 1915) predates the Born–Oppenheimer principle (1927). Discuss.
2. How high would you have to lift a mole of water for its gravitational potential energy to be equivalent to the energy needed to dissociate it completely into hydroxyl radicals and hydrogen atoms? The strength of the O–H bond is about 400 kJ mol^{-1} ; the gravitational acceleration g at the Earth's surface (and out to hundreds of kilometres) is about 10 m s^{-2} . What does this indicate about the role of gravity in chemistry?
3. If gravity plays no role in chemistry, why are vibrational frequencies different for, say, C–H and C–D bonds?
4. We assumed that the two bond lengths of water are equal. Must an acyclic molecule AB_2 have equal A–B bond lengths? What about a cyclic molecule AB_2 ?
5. Why are chemists but rarely interested in finding and characterizing second-order and higher saddle points (hilltops)?
6. What kind(s) of stationary points do you think a second-order saddle point connects?

7. If a species has one calculated frequency very close to 0 cm^{-1} what does that tell you about the (calculated) potential energy surface in that region?
8. The ZPE of many molecules is greater than the energy needed to break a bond; for example, the ZPE of hexane is about 530 kJ mol^{-1} , while the strength of a C–C or a C–H bond is only about 400 kJ mol^{-1} . Why then do such molecules not spontaneously decompose?
9. Only certain parts of a potential energy surface are chemically interesting: some regions are flat and featureless, while yet other parts rise steeply and are thus energetically inaccessible. Explain.
10. Consider two potential energy surfaces for the $\text{HCN} \rightleftharpoons \text{HNC}$ reaction: *A*, a plot of energy versus the H–C bond length, and *B*, a plot of energy versus the HNC angle. Recalling that HNC is the higher-energy species, sketch qualitatively the diagrams for *A* and *B*.

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