Module – 04

Potential Energy Surfaces

Chemical Bonds

Syllabus

Name of Module	Syllabus
Module – 04 Potential Energy Surfaces	Chemical bonds and intermolecular interactions, Types of intermolecular interactions (charge distribution of isolated molecules, electrostatic interaction, induction interaction, London or dispersion forces, hydrogen bonding, repulsive interaction, relative contribution of different terms), representing the potential energy surfaces (pair additivity, rare gas), intramolecular interactions (bond stretching, angle bending, torsional and improper terms).

Why do the atoms combine together?

What type of force act between the two atoms which held them together?

✓ **Any unstable system has basic urge to acquire stability.**

✓ **Except Inert gases, the atoms of all other elements lacks stability. Therefore they somehow try to acquire stability in their electronic configuration.**

✓ **This tendency compel the atoms to enter into chemical combination.**

✓ **When two atoms combine together they try to acquire stable electronic configuration by giving or taking or sharing electrons and thus establish some sort of binding force or chemical bonding between them.**

Chemical bonding refers to the formation of a chemical bond between two or more atoms, molecules, ions to give rise to a chemical compound. These chemical bonds keeps the atoms together in the chemical compound.

Chemical bonds are made due to the linkage between atoms present in a molecule. The bonds present are both strong intramolecular interactions such as covalent and ionic bonds.

There are other bonds which form due to weaker intermolecular forces which are present between atoms and these are dipole-dipole interactions, hydrogen bonding and the London dispersion forces.

An atom contains a nucleus composed of protons and neutrons, with electrons revolving around the nucleus in certain energy levels. Elements are different from each other due to their "electron cloud," or the area where electrons move around the nucleus of an atom.

Each element has a distinct electron cloud, which determines their chemical properties as well as the extent of their reactivity.

In chemical bonding, only valence electrons of an element are involved.

## Types of Chemical Bonds or Intramolecular force of attraction

✓ **Ionic Bond**
✓ **Covalent Bond**
✓ **Metallic Bond**

Ionic Bond

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge.

Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged and an atom that gains one or more electrons becomes negatively charged.

Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form **ionic networks (or lattices)**.
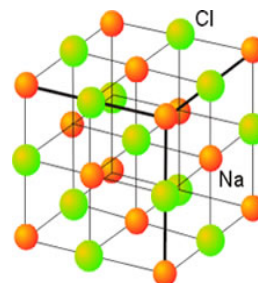
The opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge.

When metals react with non-metals, electrons are transferred from the metals to the non-metals. A metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Similarly, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. Consequently an ionic bond is formed.
For e.g. – NaCl, KCl, MgO

The formation of ionic compounds are usually ***extremely exothermic***. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the inter-nuclear distance.

Covalent Bond

A covalent bond is formed when the valence electrons from one atom are shared between two or more particular atoms. This sharing of electron between the atoms happens because atoms must satisfy octet rule.

The electron is an essential component of a chemical bond, but that it must be in the right place: between the two nuclei.

Coulomb's law can be used to calculate the forces experienced by the two nuclei for various positions of the electron. This is useful to define two regions of space about the nuclei. One region, the **binding region**, shows locations at which the electron exerts a net binding effect on the new nuclei. Outside this region, is the **anti-binding region**, the electron will actually work against binding.

A covalent bonding is the strongest bond which takes place between two non-metals.

Covalent bonds are of two types
1) *Non polar covalent bond*
2) *Polar covalent bond*

In the case of a nonpolar covalent bond, the electrons are equally shared between the two atoms. On the contrary, in polar covalent bonds, the electrons are unequally distributed between the atoms.

Covalent compounds are known to have lower melting and boiling points than ionic compounds

Metallic Bond

A metallic bond is a force that holds atoms together in a metallic substance. Such solid consists of tightly packed atoms where the outermost electron shell of each metal atom overlaps with a large number of neighboring atoms. As a consequence, the valence electrons move freely from one atom to another. They are not associated with any specific pair of atoms. This behavior is called non-localization.

Metallic bonding is sort of covalent bonding, because it involves sharing electrons.

Hydrogen Bond

A hydrogen bond is a chemical bond between a hydrogen atom and an electronegative atom. It is not an ionic or covalent bond but is a particular type of dipole-dipole attraction between molecules.

Hydrogen bonding is the weaker form of chemical bonding.

Intermolecular Interactions

Chemical Bonding means the formation of a chemical bond between two or more atoms, molecules or ions to give rise to a chemical compound. These chemical bonds keep the atoms together in the resulting compound.

Intermolecular forces (IMF) are the attractive and repulsive forces that arise between the molecules of a substance. These forces facilitate the interactions between individual molecules of a substance.

Intermolecular forces doesn't include electrostatic force that exist between two oppositely charged ions (Ionic Bond) and the force which holds the two atoms of a molecule together (Covalent Bond).

The atoms or molecules forming the solids or liquids are held together by Intermolecular forces which are responsible for most of the physical and chemical properties of matter in these states.

A **van der Waals interaction** is the attractive interaction between closed-shell molecules that depends on the distance between the molecules as $1/r^6$.

In addition, there are interactions between ions and the partial charges of polar molecules and repulsive interactions that prevent the complete collapse of matter to nuclear densities.

The repulsive interactions arise from Coulombic repulsions and indirectly from the Pauli principle (No two electron in an atom will have same set of quantum numbers) and the exclusion of electrons from regions of space where the orbitals of neighboring species overlap.

Intermolecular forces also explains why any substance exist as solid, liquid and gas at room temperature.

Types of Intermolecular Interactions

1) *Dipole-dipole interaction*
2) *Ion-dipole interaction*   *Week Van der Waals Forces*
3) *Dispersion Forces*
4) *Hydrogen bonding*   -   *Dipole-Dipole interaction*

Attractive intermolecular forces are known as van der Waals forces. These forces vary considerably in magnitude and include **dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces.** Hydrogen bonding is a particularly strong type of dipole-dipole interaction. Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category.

Dipole-Dipole Interactions

A pair of equal and opposite charges separated by a small distance is called as dipole. Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess "partial charges".
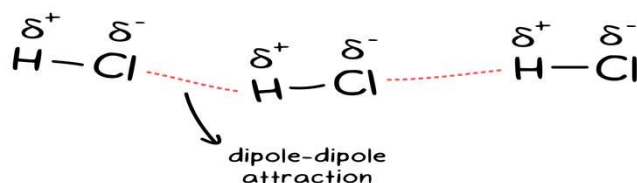
Partial charges are always less than the unit electronic charge **(1.6×10^{-19} C)**. The polar molecules interact with neighboring molecules.

This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles.

Besides dipole-dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that **the total of intermolecular forces in polar molecules increase.**

Ion-Dipole Interactions or Dipole-Induced Dipole Interactions

This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole.

Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Thus an induced dipole is developed in the other molecule.

Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarizability of the electrically neutral molecule. High polarizability increases the strength of attractive interactions.

In Ion-Dipole interaction also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.

A polar molecule with dipole moment μ_1 can induce a dipole $\mu_2{*}$ in a neighboring polarizable molecule. The induced dipole interacts with the permanent dipole of the first molecule and the two are attracted together. The average interaction energy when the separation of the molecules is r is

$$V = \frac{C}{r^6} \qquad\qquad C = \frac{\mu_1{}^2 \alpha_2}{4\pi\varepsilon_0}$$

where $\dot{\alpha}_2$ is the polarizability volume of molecule 2 and μ_1 is the permanent dipole moment of molecule 1.

The dipole–induced dipole interaction energy is independent of the temperature because thermal motion has no effect on the averaging process.

(a)

(b)
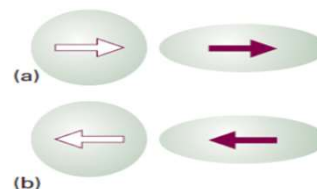
(a) A polar molecule (purple arrow) can induce a dipole (white arrow) in a nonpolar molecule, and (b) the latter's orientation follows the former's, so the interaction does not average to zero.

Dispersion Forces or London Forces or Induced dipole – Induced dipole Interaction

Atoms and non-polar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules.

These forces are always attractive and interaction energy is inversely proportional to $1/r^6$ (where r is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarizability of the particle.

Nonpolar molecules attract one another even though neither has a permanent dipole moment.

The interaction between nonpolar molecules arises from the momentary dipoles that all molecules possess as a result of fluctuations in the instantaneous positions of electrons.
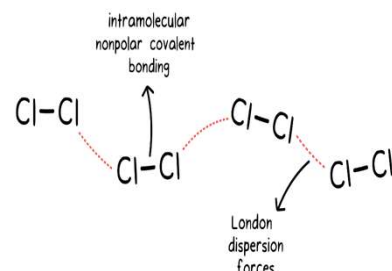
The electrons in one molecule flicker into an arrangement that gives the molecule an instantaneous dipole moment μ_1^*. This dipole generates an electric field that polarizes the other molecule and induces in that molecule an instantaneous dipole moment μ_2^*.

The two dipoles attract each other and the potential energy of the pair is lowered. Although the first molecule will go on to change the size and direction of its instantaneous dipole, the electron distribution of the second molecule will follow i.e. the two dipoles are correlated in direction.

Due to this correlation, the attraction between the two instantaneous dipoles does not average to zero and gives rise to an induced-dipole–induced-dipole interaction. This interaction is called either the **dispersion interaction** or the **London interaction**
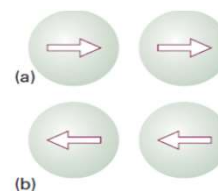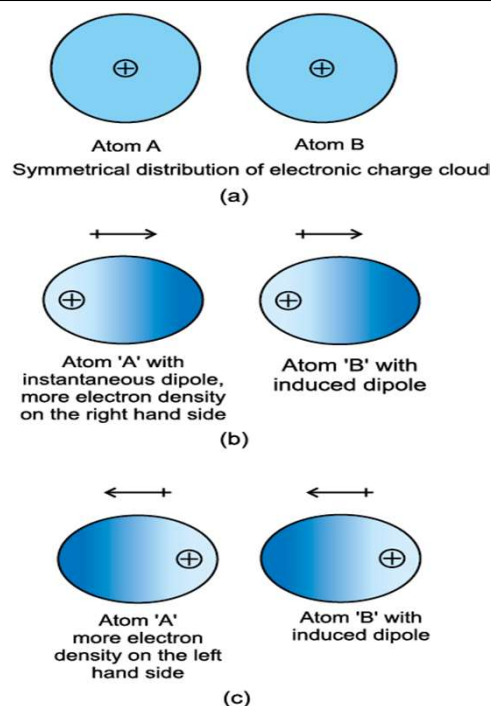

(a) In the dispersion interaction, an instantaneous dipole on one molecule induces a dipole on another molecule, and the two dipoles then interact to lower the energy. (b) The two instantaneous dipoles are correlated and, although they occur in different orientations at different instants, the interaction does not average to zero.

Illustration of Dispersion Forces

Two atoms 'A' and 'B' in the close vicinity of each other. It may happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.,* the charge cloud is more on one side than the other. This results in the development of instantaneous dipole on the atom 'A' for a very short time.

This instantaneous dipole of atom 'A' distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also.


Atom A   Atom B
Symmetrical distribution of electronic charge cloud
(a)

Atom 'A' with instantaneous dipole, more electron density on the right hand side   Atom 'B' with induced dipole
(b)

Atom 'A' more electron density on the left hand side   Atom 'B' with induced dipole
(c)

Hydrogen Bonding

Hydrogen Bonding is a special kind of dipole-dipole interaction that occurs specifically between a hydrogen atom bonded to either an oxygen, nitrogen, or fluorine atom. The partially positive end of hydrogen is attracted to the partially negative end of the oxygen, nitrogen, or fluorine of another molecule.

Hydrogen bonding is a relatively strong force of attraction between molecules and considerable energy is required to break hydrogen bonds.

Compounds with hydrogen bonding will have high boiling point, melting point and high enthalpy of vaporization. For e.g. H_2O, HF, HCl

Hydrogen bonding is conventionally regarded as being limited to N, O, and F but if B is an anionic species (such as Cl^-) it may also participate in hydrogen bonding.

Effect of hydrogen bonding on Boiling point
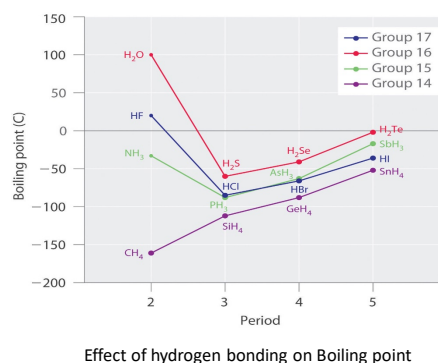
No strict cutoff for an ability to participate in hydrogen bonding but N, O, and F participate most effectively.

Repulsive and Total Interaction

Van der Waals forces may be attractive or repulsive, depending on the distance between the molecules involved.

When molecules are squeezed together the nuclear and electronic repulsions and the rising electronic kinetic energy begin to dominate the attractive forces.

The repulsions increase abruptly with decreasing separation.

At extremely high pressures the molecules are so close to each other that their atom's positive nuclei will repel and this repulsive force will exceed the attractive force from the dipole, dispersion or H-bond attraction.
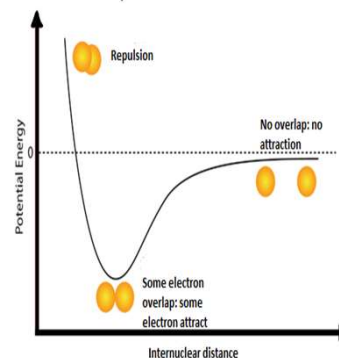
Whether the force is attractive, repulsive or non-existent (ideal gases) will depend on the sum of the attractive forces v/s the repulsive forces. If the sum of the attractive forces exceeds the sum of the repulsive forces, the molecules will attract. If the opposite is true, the molecules will repel.

The repulsive part of the intermolecular potential is essentially a display of the overlap of the wave functions of the two species in conjunction with the Pauli exclusion principle. It reflects the impossibility for electrons with the same spin to occupy the same region of space.

Potential Energy Surfaces

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.**

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).

A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms.

The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a **potential energy curve or energy profile.**

The Potential Energy Surface represents the concepts that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction is associated with a unique potential energy. This creates a smooth energy "landscape" and chemistry can be viewed from a topology **(a way of describing and predicting the molecular structure within the constraints of three-dimensional (3-D) space)** perspective (of particles evolving over "valleys" and "passes").

It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (e.g. two bond lengths) the value of the energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground).

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.

The Born–Oppenheimer approximation says that in a molecule the nuclei are essentially stationary compared to the electrons.

This concept is important in 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 to focus on the electronic energy and add in the nuclear repulsion energy.
✓ Geometry optimization and transition state optimization are explained.

The energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, or sometimes called a reaction progress curve.

A potential energy diagram shows the change in potential energy of a system as reactants are converted into products.

The enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction.

The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings.
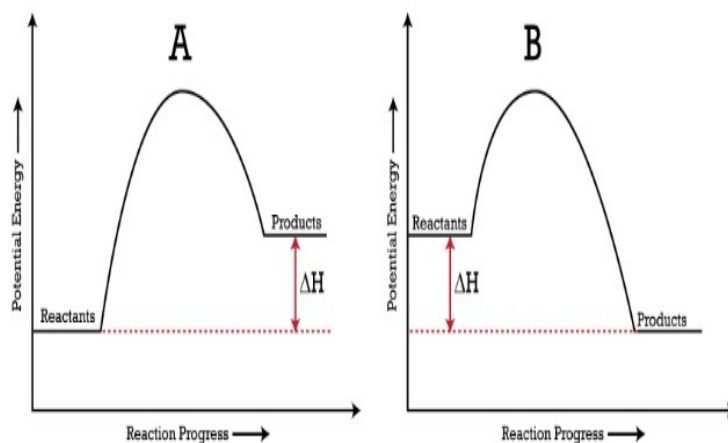
The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

The activation energy for a reaction is the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the **activation energy** of a reaction is sometimes referred to as the **activation energy barrier**. Reacting particles must have enough energy so that when they collide, they can overcome that barrier.
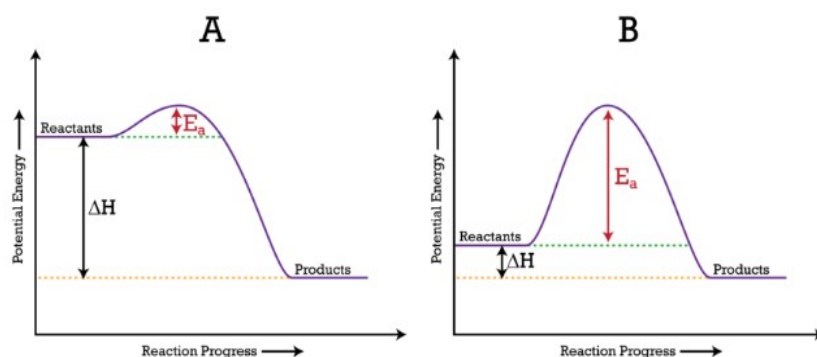
(A) The activation energy is low, meaning that the reaction is likely to be fast.

(B) The activation energy is high, meaning that the reaction is likely to be slow.

Potential Energy Diagram of Di-atomic Molecule

Consider a **diatomic molecule AB.** In some ways a molecule behaves like balls (atoms) held together by springs (chemical bonds); this is the basis of the molecular mechanics.

If we take a macroscopic balls-and-spring model of a diatomic molecule in its normal geometry (the equilibrium geometry) and hold the "atoms" and distort the model by stretching or compressing the "bonds", then there is increase the potential energy of the molecular model (Fig. 01).

The stretched or compressed spring possesses energy, since we moved a force through a distance to distort the geometry. As 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".
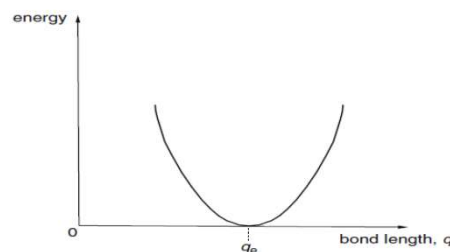

Figure – 01: The potential energy surface for a diatomic molecule. The potential energy increases if the bond length q is stretched or compressed away from its equilibrium value qe. The potential energy at qe (zero distortion of the bond length) has been chosen here as the zero of energy.

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

Point No. 01

The molecule vibrate nonstop (By Heisenberg's uncertainty principle: a stationary molecule would have 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; shown on potential energy / bond length diagrams by drawing a series of lines above the bottom of the curve to **indicate the possible amounts of vibrational energy the molecule can have (the vibrational levels it can occupy).**
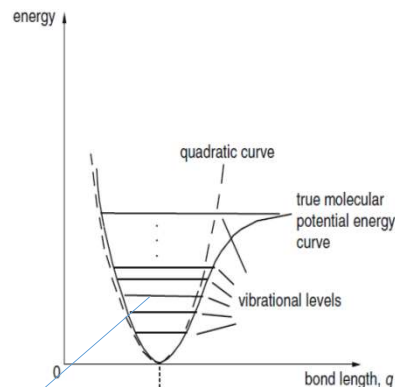
Figure – 02: Actual molecules do not sit still at the bottom of the potential energy curve, but instead occupy vibrational levels. Also, only near qe, the equilibrium bond length, does the quadratic curve approximate the true potential energy curve

A molecule never sits at the bottom of the curve but rather occupies one of the vibrational levels.

In a collection of molecules the levels are populated according to their spacing and the temperature. We usually ignore the vibrational levels and consider molecules to rest on the actual potential energy curves or surfaces.

Point No. 02

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 by a quadratic equation of the simple harmonic oscillator [$E = (\frac{1}{2})$ K $(q - q_e)^2$], where k is the force constant of the spring. The potential energy deviates from the quadratic (q^2) curve as we move away from qe.

Figure – 01: represents a one-dimensional PES in the two-dimensional graph of E v/s q. A diatomic molecule 'AB' has only one geometric parameter to vary i.e the bond length q_{AB}.

Potential Energy Diagram of Tri-atomic Molecule

Suppose we have a molecule with more than one geometric parameter, for e.g. water - the geometry is defined by two bond lengths and a bond angle.

If we restrict ourselves by 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) 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.
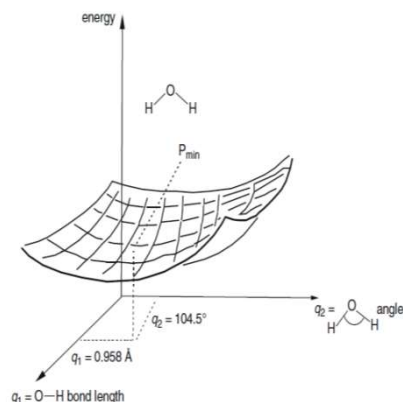
Figure 03 represents a two dimensional PES (a normal surface is a 2-D object) in the three-dimensional graph;

Figure – 03: The H2O potential energy surface. The point Pmin corresponds to the minimum-energy geometry for the three atoms, i.e. to the equilibrium geometry of the water molecule

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Potential Energy Diagram of Tri-atomic Molecule

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 similar to that for H_2O would require to plot E v/s 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. 04), and since such a four-dimensional graph cannot be constructed in three-dimensional space and hence 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 e.g. - In the AB diatomic molecule PES (a line) of Fig. 01 the minimum potential energy geometry is the point at which $\frac{dE}{dq}$ = 0. On the H_2O PES (Fig. 03) the minimum energy geometry is defined by the point P_{min}, corresponding to the equilibrium values of q_1 and q_2; at this point $\frac{dE}{dq_1} = \frac{dE}{dq_2} = 0$.

Hypersurfaces cannot be depicted pictorially, This can be obtained with the help of diagrams like Figs. 01 and 04, where we content ourselves with a line or a two-dimensional surface in effect using a slice of a multidimensional diagram.

Fig. 05 shows how 2-D slices can be made of the 3-D diagram for water.
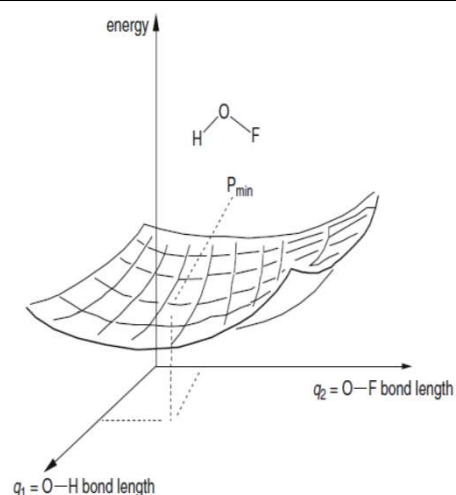
Figure – 04: A potential energy surface (PES) for HOF. Here the HOF angle is not shown. This picture could represent one of two possibilities: the angle might be the same (some constant, reasonable value) for every calculated point on the surface; this would be an unrelaxed or rigid PES. Alternatively, 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; this would be a relaxed PES

We can take a 3-D slice of the hypersurface for HOF (Fig. 05) 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.

Stationary Points

Potential energy surfaces are important because they help us in visualizing and understanding the relationship between potential energy and molecular geometry and in understanding how computational chemistry programs locate and characterize structures of interest.
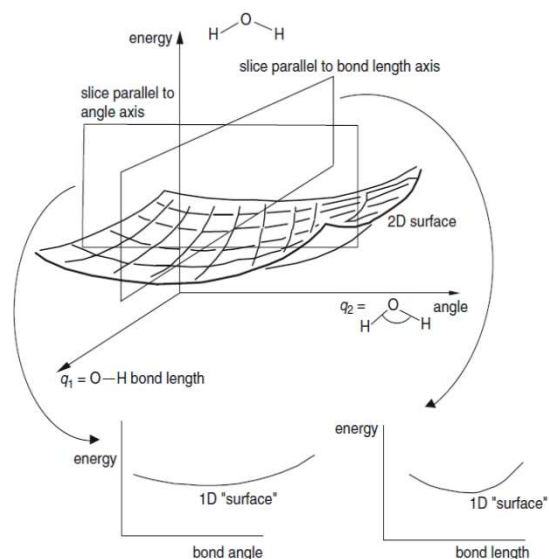
Figure – 05: Slices through a 2D potential energy surface give 1D surfaces. A slice that is parallel to neither axis would give a plot of geometry versus a composite of bond angle and bond length, a kind of average geometry

The main tasks of computational chemistry is to determine the structure and energy of molecules and of the transition states involved in chemical reactions i.e. **"structures of interest"** are molecules and the transition states linking them 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).

Stationary points on a PES are points at which the first derivative of potential energy with respect to each geometric parameter is zero.

$$\frac{\partial E}{q_1} = \frac{\partial E}{q_2} = \;....= 0.$$

Stationary points that correspond to actual molecules with a finite lifetime (in contrast to transition states, which exist only for an instant) 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.
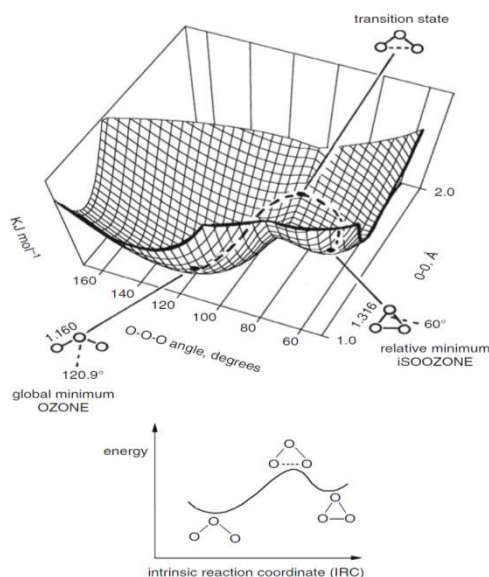
Figure – 06: The ozone/isoozone potential energy surface (calculated by the AM1 method; a 2D surface in a 3D diagram. The dashed line on the surface is the reaction coordinate (intrinsic reaction coordinate, IRC). A slice through the reaction coordinate gives a 1D "surface" in a 2D diagram.

The lowest-energy pathway linking the two minima, the reaction coordinate or intrinsic reaction coordinate (IRC; dashed line in Fig. 06) 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.
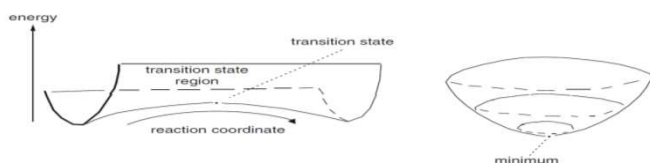
Figure – 07: A transition state or saddle point and a minimum. At both the transition state and the minimum $\partial E/\partial q$ ¼ 0 for all geometric coordinates q (along all directions). At the transition state $\partial E2/\partial q2 < 0$ for q ¼ the reaction coordinate and > 0 for all other q (along all other directions). At a minimum $\partial E2/\partial q2 > 0$ for all q (along all directions).

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. 07). 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:

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 (examine Fig. 07). Recalling that minima and maxima can be distinguished by their second derivatives, we can write:

For Minimum for all the values of 'q' $\dfrac{\partial^2 E}{q^2} > 0.$

For a transition state; for all the values of 'q' except along the $\dfrac{\partial^2 E}{q^2} > 0.$
reaction coordinates

Along the reaction coordinates $\dfrac{\partial^2 E}{q^2} < 0.$

The PES concept finds application in fields such as chemistry and physics, especially in the theoretical sub-branches of these subjects.

It can be used to theoretically explore properties of structures composed of atoms, for e.g.- finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

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Potential Energy Diagram of Ethane

Stereoisomers

Stereochemistry, Stereoisomerism or Spatial isomerism, is **a form of isomerism in which molecules have the same molecular formula and sequence of bonded atoms (constitution) but differ in the three-dimensional orientations of their atoms in space**.

Stereoisomer are of 02 types:
- ✓ Conformational Isomer
- ✓ Configurational Isomer

Configurational Isomer

Configurational isomers differ in the spatial arrangement of their atoms and can only be interconverted by *breaking* bonds and not by free rotation about single bonds. In the case of carbon compounds they do not interconvert at room temperature and *can be separated* using physical methods.

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Configurational isomers fall into two categories:
Enantiomers
Diastereoisomers.

cis-1,2-dimethylcyclopentane   *trans*-1,2-dimethylcyclopentane

Conformation

Conformation is a property of atoms in which rotation of groups about a carbon-carbon single bond takes place. The rotation usually results in different spatial arrangements of the atoms.

Conformational isomers are a type of stereoisomers where we can convert one isomer to another one just by rotating it around a single bond. These isomers are termed as conformational isomers.

Rotational energy acts as a barrier in case of single bond rotation. It has to be overcome to interconvert one conformer to another

The study of the relation between the rotation of single bonds and the molecular structure and that with the molecular energy is called conformational analysis.

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Conformations of Ethane

Ethane is a colourless and odourless gas at standard temperature. Ethane molecule consists of **07** sigma bonds. The rotation of about **06** carbon-hydrogen bonds does not result in any change of the shape of molecule because hydrogen atoms are spherical . But rotation about the carbon-carbon (C-C) bond result in many different possible molecular conformations.
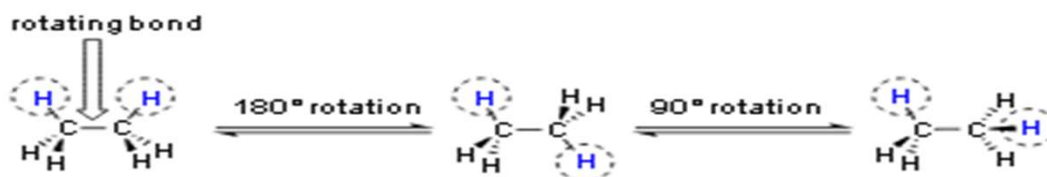
Due to the rotation about the carbon-carbon (C-C) bond the possible molecular conformations can be of following types.
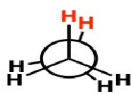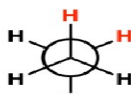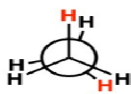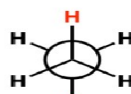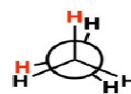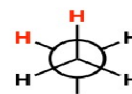
Among all the possible molecular conformations the most stable (low energy) conformation is the one in which all six C–H bonds are as far away from each other as possible (**staggered** when viewed end-on in a Newman projection).

The least stable (high energy) conformation is the one in which the six carbon-hydrogen bonds are as close as possible (**eclipsed** in a Newman projection). All other conformations lie between these two limits.

The barrier to rotation is the result of three equal C–H bond-eclipsing interactions, so we can assign a value of about 4.0 kJ/mol (1.0 kcal/mol) to each of these interactions.
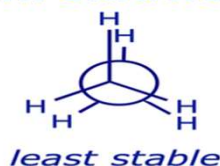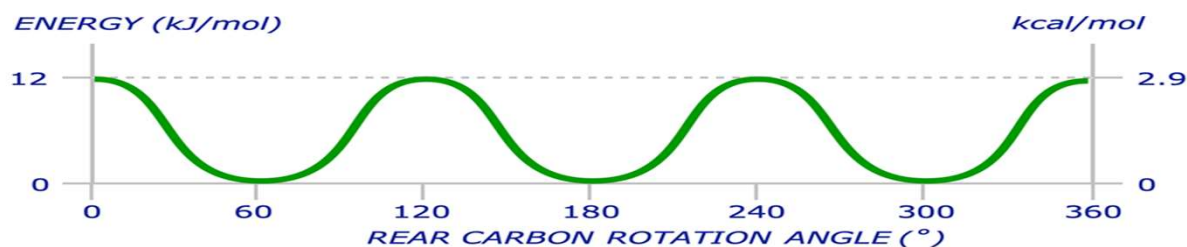
Energetically, not all conformations are equally favoured. The eclipsed conformation of ethane is less stable than the staggered conformation by 3 kcal/mol.

The staggered conformation is the most stable of all possible conformations of ethane, since the angles between C-H bonds on the front and rear carbons are maximized at 60 degrees.

In the eclipsed form, the electron densities on the C-H bonds are closer together than they are in the staggered form. When two C-H bonds are brought into a dihedral angle of zero degrees, their electron clouds experience repulsion, which raises the energy of the molecule.
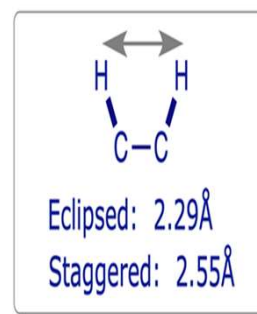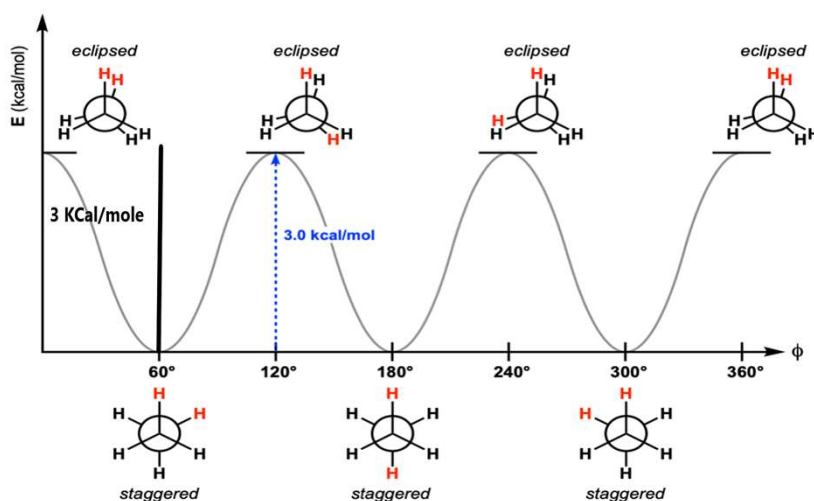
The eclipsed conformation of ethane has three such C-H eclipsing interactions, so we can infer that each eclipsed C-H "costs" roughly 1 kcal/mol.

Steric Hindrance

Eclipsing interactions are an example of a general phenomenon called steric hindrance, which occurs whenever bulky portions of a molecule repel other molecules or other parts of the same molecule.

Due to such hindrance causes resistance to rotation, it is also called **torsional strain**. The **3 kcal/mol** needed to overcome this resistance is the torsional energy.
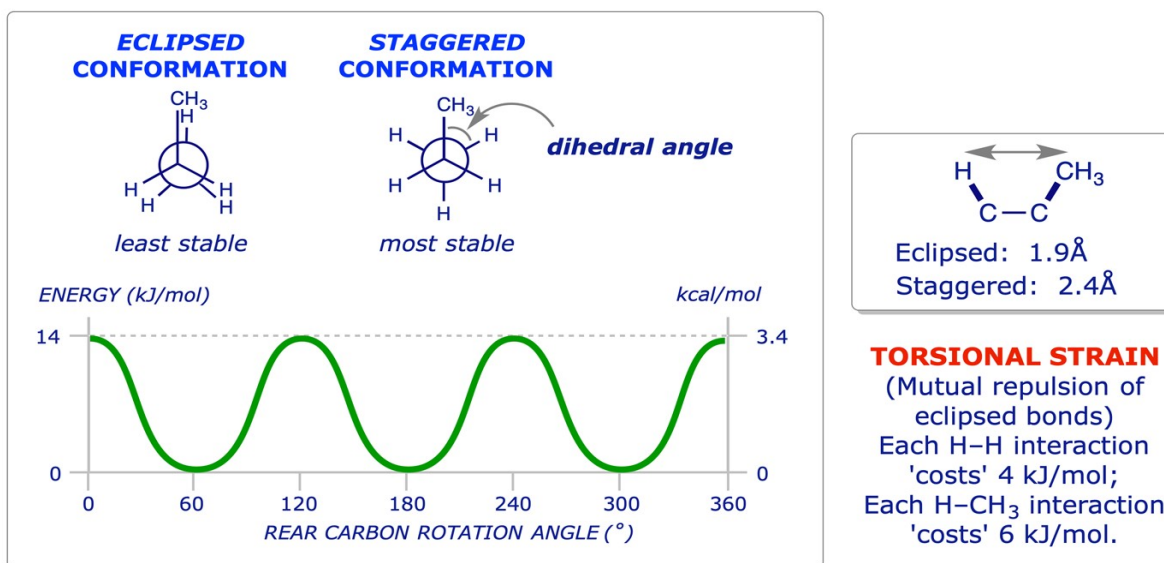
At room temperature, ethane molecules have enough energy to be in a constant state of rotation. Due to this rapid rotation, it is impossible to isolate any particular conformation in the way that *cis*- and *trans*- alkenes can be individually isolated.

Rotational barrier in ethane as a function of dihedral angle.
The barrier to rotation in ethane is about 3 Kcal/mole.

Example: Conformations of Propane

ECLIPSED CONFORMATION

least stable

STAGGERED CONFORMATION

dihedral angle

most stable

ENERGY (kJ/mol)

kcal/mol

REAR CARBON ROTATION ANGLE (°)

Eclipsed: 1.9Å
Staggered: 2.4Å

TORSIONAL STRAIN
(Mutual repulsion of eclipsed bonds)
Each H–H interaction 'costs' 4 kJ/mol;
Each H–CH$_3$ interaction 'costs' 6 kJ/mol.

Conformations of Butane

Conformational analysis is the examination of the various energy levels associated with different molecular conformations. Conformations are also the three-dimensional configurations that a molecule can achieve by freely spinning around its -bonds. The n-butane molecule can be configured in an infinite number of ways.

There are three things that raise the energy potential of conformers and lowering their stability.

➢ Steric interactions take place when alkyl groups or even other substituents are crowded together closely.

➢ Torsional strain represents the tendency for s-bonds to twist in order to accomplish a more steady conformation.

➢ Angle strain is a rise in electric potential caused by bond degrees in cycloalkanes as well as other rings becoming pushed to deviate from desired values.

The lowest-energy arrangement, called the **antiperiplanar** (or *anti*) conformation, is the one in which the two large methyl groups are as far apart as possible. As rotation around the C(2)–C(3) bond occurs, another eclipsed conformation (*anticlinal*) is reached in which there are two Me–H interactions and one H–H interaction.

If we assign the energy value (4 kJ/mol) for H–H eclipsing interactions that was previously derived from ethane, we can predict that each Me–H interaction in the anticlinal conformation costs about 5 kJ/mol.

As bond rotation continues, an energy minimum is reached at the staggered conformation where the methyl groups are 60° apart (a **gauche** relationship). This lies 3.2 kJ/mol higher in energy than the *anti* conformation even though it has no eclipsing interactions.

The energy difference is due to the fact that the hydrogen atoms of the methyl groups are near each other in the *gauche* conformation, resulting in **steric strain**, which is the repulsive interaction that occurs when atoms would otherwise tend to occupy the same space.

As the dihedral angle between the methyl groups approaches 0°, an energy maximum is reached. The methyl groups are forced even closer together than in the *gauche* conformation, and both ***torsional*** strain and ***steric*** strain are present. A total strain energy of 25 kJ/mol has been estimated for this conformation, allowing to calculate a value of 17 kJ/mol for the Me–Me eclipsing interaction.

Completing the 360° rotation after the *synperiplanar* point produces the mirror images of what we've already seen; another **gauche** conformation, another eclipsed conformation and finally a return to the ***anti*** conformation.
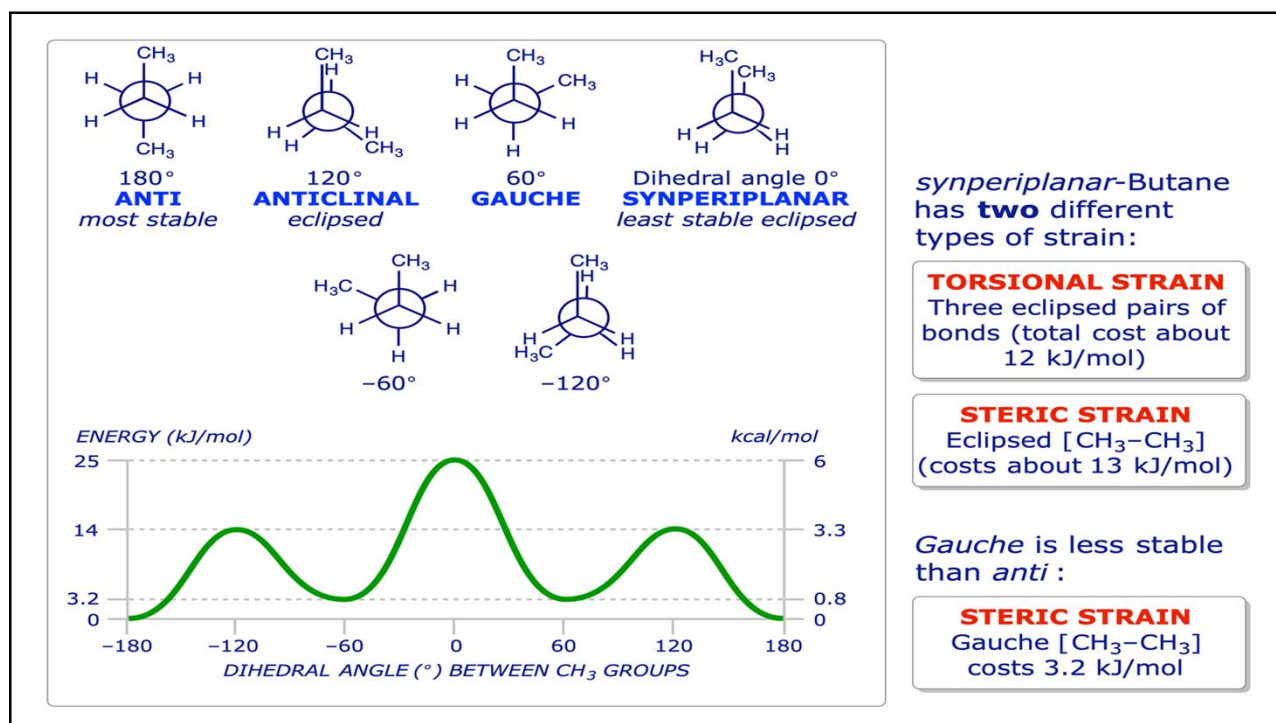
Application of Potential Energy Curves

A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics. Once the necessary points are evaluated on a PES, the points can be classified according to the first and second derivatives of the energy with respect to position, which respectively are the gradient and the curvature.

Stationary points (or points with a zero gradient) have physical meaning: energy minima correspond to physically stable chemical species and **saddle points** correspond to transition states, the highest energy point on the reaction coordinate (which is the lowest energy pathway connecting a chemical reactant to a chemical product).

➢ PES do not show kinetic energy, only potential energy.
➢ At T = 0 K (no KE), species will want to be at the lowest possible potential energy (i.e. at a minimum on the PES).
➢ Between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a **saddle point**, this saddle point is the transition-state structure.

Pair additivity

The meaning of this term is easy to grip in a qualitative and natural way: an ideal single bond has a bond order of one and ideal double and triple bonds have bond orders of two and three, respectively.

Invoking Lewis electron-dot structures, one might say that the order of a bond is the number of electron pairs being shared between the two bonded atoms.

Calculated quantum mechanical bond orders should be more widely applicable than those from the Lewis picture because electron pairs are not localized between atoms in a clean pairwise manner; thus a weak bond, like a hydrogen bond or a long single bond, might be expected to have a bond order of less than one.

There is no unique definition of bond order in computational chemistry because there seems to be no single, correct method to assign electrons to particular atoms or pairs of atoms.

Various quantum mechanical definitions of bond order can be devised based on basis-set coefficients. Naturally these coefficients for a pair of atoms should be relevant to calculating a bond order since the bigger the contribution two atoms make to the wave function (whose square is a measure of the electron density) the bigger should be the electron density between them.

Molecular Mechanics

Molecular mechanics is a non-quantum mechanical technique for calculating energies and some properties of molecules. Molecular Mechanics treats the nuclei and electrons in the molecule.

Molecular mechanics is based on a mathematical model of a molecule as a collection of balls (corresponding to the atoms) held together by springs (corresponding to the bonds).

In this model the energy of the molecule changes with geometry because the springs resist being stretched or bent away from some "natural" length or angle and the balls resist being pushed too closely together.

The principle behind MM is to express the energy of a molecule as a function of its resistance toward bond stretching, bond bending, and atom crowding and to use this energy equation to find the bond lengths, angles and dihedrals corresponding to the minimum-energy geometry – or more precisely to the various possible potential energy surface minima.

In other words MM uses a conceptually mechanical model of a molecule to find its minimum-energy geometry (for flexible molecules, the geometries of the various conformers).

The form of the mathematical expression for the energy and the parameters in MM constitute a force field and molecular mechanics methods are sometimes called force field methods.

The potential energy of a molecule can be written

$$E = \sum_{bonds} E_{Stretch} + \sum_{angles} E_{Bend} + \sum_{dihedral} E_{Torsion} + \sum_{Pairs} E_{Non\,bond}$$

Where $E_{stretch}$ etc. are contributions from bond stretching, angle bending, torsional motion (rotation) around single bonds and interactions between atoms or groups which are non-bonded (not directly bonded together).

The sums are over all the bonds, all the angles defined by three atoms A–B–C, all the dihedral angles defined by four atoms A–B–C–D, and all pairs of significant non-bonded interactions. The mathematical form of these terms and the parameters in them constitute a particular **force field.**
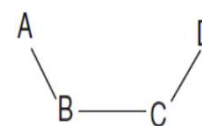
Bond Stretching

The increase in the energy of a spring (considering molecule as a collection of balls held together by springs) when it is stretched (Fig. 3.2) is approximately proportional to the square of the extension:

$$\Delta E_{stretch} = k_{stretch}(l - l_{eq})^2$$
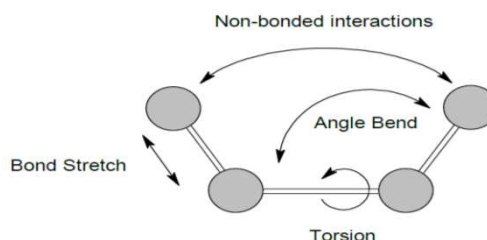
$k_{stretch}$ = the proportionality constant (actually one-half the force constant of the spring or bond; but identifying MM force constants with the traditional force constant from say, spectroscopy – the bigger $k_{stretch}$, the stiffer the bond/spring – the more it resists being stretched.
l = length of the bond when stretched.
l_{eq} = equilibrium length of the bond its "natural" length.

If we take the energy corresponding to the equilibrium length leq as the zero of energy, we can replace $\Delta E_{stretch}$ by $E_{stretch}$:

$$E_{stretch} = k_{stretch}(l - l_{eq})^2$$

Angle Bending

Angle bending between atoms that are geminal to each other (bonded to the same central atom).

$$V_{bending} = 1/2k_b(\theta - \theta_0)^2$$

K_b is the bending force constant that is determined empirically. Θ is the actual bond angle in the molecule and Θ_0 is the "natural" bond angle. If the optimal bond angle for H-Csp^2-Csp^3 is 122°, then any change in angle $(\theta - \theta_0)$, either wider or narrower, will increase the energy of the molecule. The angle-bending term is summed over all bond angles in the molecule.

Torsion Energy

Torsional angle rotation between atoms that are *vicinal* (bonded to adjacent atoms) to each other.

$$V_{torsion} = 1/2 V_0 (1 + \cos n\omega)$$

Here, V_0 is the barrier to free rotation for the "natural" bond, n is the periodicity of the rotation (number of cycles in 360°), and ω is the torsion angle. The torsion term is summed over all rotating bonds in the molecule.

Non-bonded Interaction

Atoms (greater than two bonds apart) interact through van der Waals attraction, steric repulsion and electrostatic attraction/repulsion depending on their distance from each other. For two approaching non-bonded atoms, the interaction is attractive (London dispersion force) until the atoms get too close and start to repel each other (van der Waals repulsion/steric strain)