Molecular Reaction Dynamics

Reference:

1. Molecular Reaction Dynamics and Chemical Reactivity, R. D. Levine and R. B. Bernstein, Oxford University Press, Oxford 1987.
2. Molecular Reaction Dynamics, R. D. Levine, Cambridge University Press, Cambridge, 2005.
3. Femtochemistry-Ultrafast Dynamics of the Chemical Bond, A. H. Zewail, World Scientific, New Jersy, Singapore, 1994.

Potential energy surfaces (PESs):
[2-p150]

Chemistry is a dynamical process with interactions between molecules and atoms dependent on the forces between the atoms: $F_r = -\frac{dV}{dr}$.

To understand the dynamics of a chemical system we need to understand all the forces operating within the system, hence we need to know V (r). In a multi-dimensional system V (r) is known as the potential energy surface. The potential energy surface is typically defined within the Born-Oppenheimer approximation: electrons are much lighter than nuclei, thus they move much faster and adjust adiabatically to any change in nuclear configuration. This means that a separate PES is defined for each possible electronic state. Generally, the dynamics are studied on the ground electronic state surface. Unless stated otherwise the discussion here is for the ground electronic state surface. (This is also known as the electronic adiabatic approximation).

A potential energy surface is a mathematical function that gives the energy of a molecule as a function of its geometry, i.e., nuclear coordinates. As we had discuss in CHM 304(P): Quantum Mechanics, this can be done using Born-Oppenheimer approximation.

Recap of BOA:
Born-Oppenheimer Approximation:

An electron is a light particle compared to the mass of a proton (~1836 times heavier than an electron). The nuclei are expected to move much more slowly than the electrons. As a matter of fact the electrons in a molecule may have an average distribution over a time interval during which the nuclei hardly move. This means that the vibrational and rotational motions of a molecule are separable from the electronic motions.

Levine, p-366
Assuming the nuclei and electrons to be point masses and neglecting spin-orbit and other relativistic interactions one can write molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{M_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - \sum_\alpha\sum_i \frac{Z_\alpha e^2}{R_{i\alpha}} + \sum_j\sum_{i>j}\frac{e^2}{R_{ij}}$$

Where $\alpha, \beta, ...$ refer to nuclei and $i, j, ...$ refer to electrons. For example the H_2 molecular Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2M_p}\nabla_\alpha^2 - \frac{\hbar^2}{2M_p}\nabla_\beta^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{e^2}{R_{\alpha\beta}} - \frac{e^2}{R_{1\alpha}} - \frac{e^2}{R_{1\beta}} - \frac{e^2}{R_{2\alpha}} - \frac{e^2}{R_{2\beta}} + \frac{e^2}{R_{12}}$$

The wave functions and energies of a molecule can be found from the SE:

$\hat{H}\psi(R,r) = E\psi(R,r)$, where R and r symbolize the nuclear and electronic coordinates, respectively.

The Hamiltonian forbids the solution of the SE as there are electronic repulsive terms that can not be separated. Fortunately, a highly accurate, simplifying approximation exists.

The nuclei are much heavier than electrons: $M_\alpha >> m_e$. Hence the electrons move much faster than the nuclei. Hence, to a good approximation as far as electrons are concerned, one can regard the nuclei as fixed while electrons carry out their motions. In other words, during the time of a cycle of electronic motion, the change in nuclear configuration is negligible. Thus, neglecting the nuclear kinetic energy terms we obtain the SE for electronic motion:

$\left(\hat{H}_{el} + V_{NN}\right)\psi_{el} = U\psi_{el}$ where the purely electronic Hamiltonian $\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{R_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{R_{ij}}$ and the nuclear repulsion term $V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}}$. The energy U is the electronic energy including internuclear repulsion.

The internuclear distances $R_{\alpha\beta}$ are not variable in the above SE, but are each fixed at some constant value. For each fixed nuclear configurations i.e. for each fixed $R_{\alpha\beta}$ values we can solved the electronic SE to get a set of electronic wave functions and corresponding electronic energies; each member of the set corresponds to a different molecular electronic state. The electronic wave functions and energies thus depend parametrically on the nuclear configuration: $\psi_{el} = \psi_{el,n}(r;R)$ and $U = U_n(R)$, where n symbolizes the electronic quantum numbers.

For the nuclear motion we use *U(R)* as a potential energy function to describe the nuclear motion. Therefore, the nuclear wave functions are obtained from the SE $\left(\hat{H}_{nu}(R) + U(R)\right)\chi_{nu}(R) = \varepsilon\chi_{nu}(R)$, where $\chi_{nu}(R)$ is the nuclear wave function.

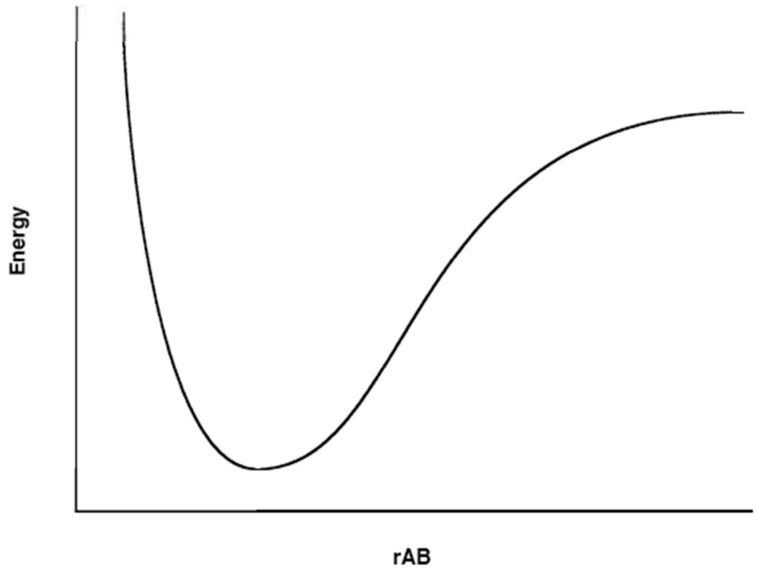
The approximation of separating electronic motions is called Born-Oppenheimer approximation that is basic to quantum mechanics. The true molecular wave function is adequately approximated as $\psi(r,R) = \psi_{el}(r;R)\chi_{nu}(R)$ if $\left(\frac{m_e}{M_{nu}}\right)^{1/4} << 1$. In general BOA introduces very little error for the ground electronic state compared to the excited electronic states, which is also small.

Diatomic potential energy curves

To understand what a potential energy surface is, it is useful to start with something we have all seen - the potential energy curve for a diatom:

Simplest Example is One-dimensional

Standard Diatomic Bond Stretch



For polyatomic system the potential energy is a function of more than one internuclear distances and we call it potential energy surface (PES) instead of potential energy curve (PEC) for diatomic molecules, shown above.

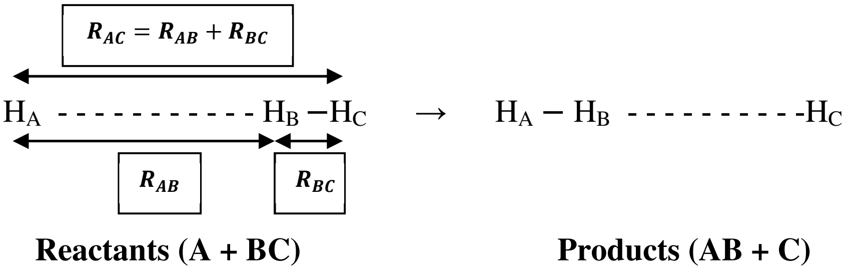
We can now expand upon what we learned from diatomics to polyatomic systems. All that really changes is the number of degrees of freedom. But it becomes increasingly more important as the size of the system grows to use chemical intuition as a guide when representing chemical interactions with mathematical formulas.

Instead of a simple one dimensional curve we now have a multi-dimensional hypersurface. For a linear 3 atom system the surface is in 3 dimensions and we can draw it.

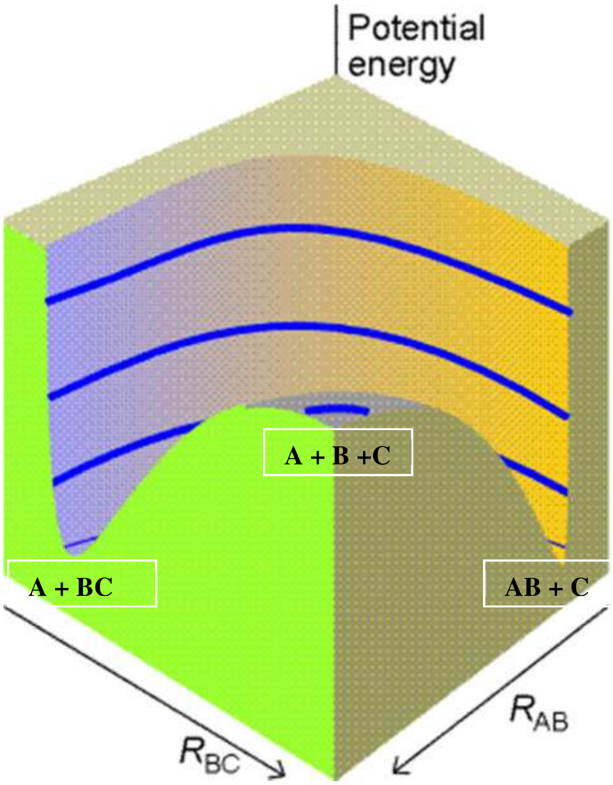
To start with let us consider a simplest tri-atomic case (H + H_2) of collinear configurations for simplicity. A collision between a hydrogen atom (H) and hydrogen molecule (H_2), the potential energy surface is the plot of the potential energy for all relative locations of the three hydrogen nuclei. Two parameters are required to define the nuclear separations:

1. The H_A-H_B separations, R_{AB}, (= infinite at the start of the encounter, equilibrium H_2 bond length at the end of the successful encounter)
2. The H_B-H_C separation, R_{BC}, (= the equilibrium H_2 bond length at the start of the encounter, infinite at the end of the successful encounter)

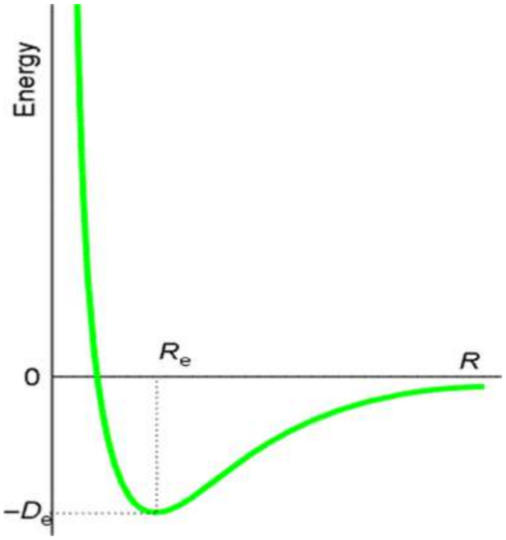
as illustrated in figure below.



The plot of the total energy of the system against R_{AB} and R_{BC} is the potential energy surface of this collinear thermo-neutral ($\Delta\varepsilon = \varepsilon_P - \varepsilon_R = 0$) reaction and is depicted in figure below.

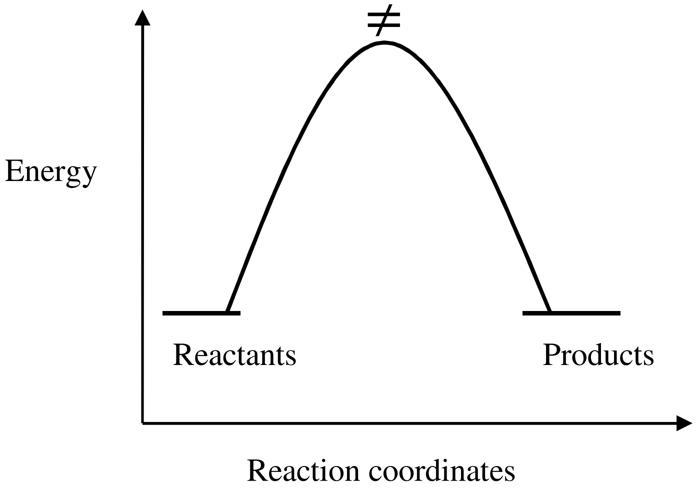


Note that reactants (A + BC) zone at the start of the encounter is nothing but when R_{AB} is very large and R_{BC} is at equilibrium distance (R_e, as shown in the surface an isolated H_2 (BC) molecule shown in figure below).

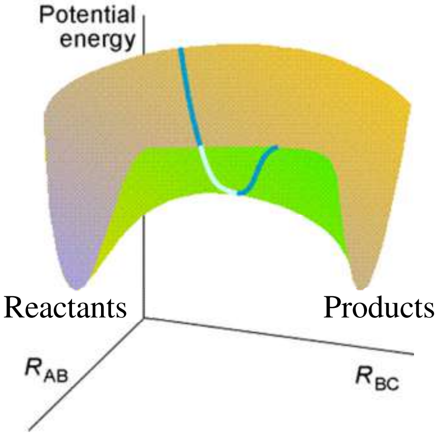


Similarly, the products (AB + C) zone at the end of a successful encounter is when R_{BC} is very large and R_{AB} is at equilibrium bond distance of H_2. Plateau location indicates when all the three atoms are infinitely separated (A + B + C).

The reaction path may be deduced from the shape of the potential energy surface, as this corresponds to path of least potential energy. During the course of the encounter AB bond is being formed and simultaneously BC bond is being broken while encompassing from reactants valley to products valley through a maximum called saddle point of the surface. This path is the reaction coordinate we normally discuss in the activated complex reaction in terms of energy profile diagram shown in figure below.



The transition state region resembles 'saddle'. Saddle is one on which horse rider sits during horse riding. When we go from left (reactants) to right (products) leg or vice versa we find maximum (like the figure above, also see figure below) and in perpendicular direction it has a minimum (see figure below to anticipate).



The location of the barrier is a point at which we find maximum potential energy while going from reactants to products, i.e., along reaction coordinate and it is minimum potential energy when we move exactly in perpendicular direction of the reaction coordinate, is called ‘saddle point’. Region around saddle point is nothing but the transition state region in an activated complex reaction. The configurations about the saddle point are the *transition state region.*

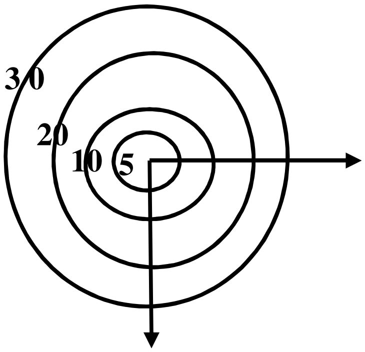
The minimum energy reaction path or MEP is defined as the path of steepest descents from the saddle point to the reactants and products. The “mountain pass’ en route from the reactant to products along the minimum energy route. The coordinate used to define the location along this path is the reaction coordinate(s). The reaction coordinate is defined to be zero at the saddle point and – at reactants and + at products.

Contour plot of potential energy surface

Potential energy surface perhaps can be understood better in the form of contour diagram. Contours are drawn by connecting the points of same potential energy for different nuclear separations.

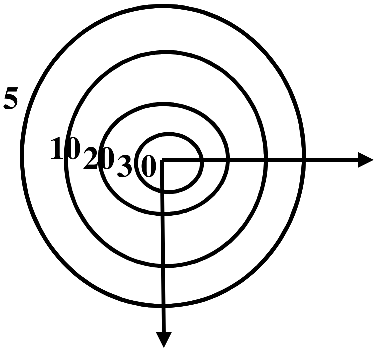
To illustrate, consider half coconut shells: upward face and downward face as shown in figure below.

When half coconut shell is facing upward and we do slicing from top to bottom with very fine cutter then we get concentric circular rings with sequentially reduced diameter. All the rings when we put on a plane of a paper to get two dimensional plot following contour diagram:



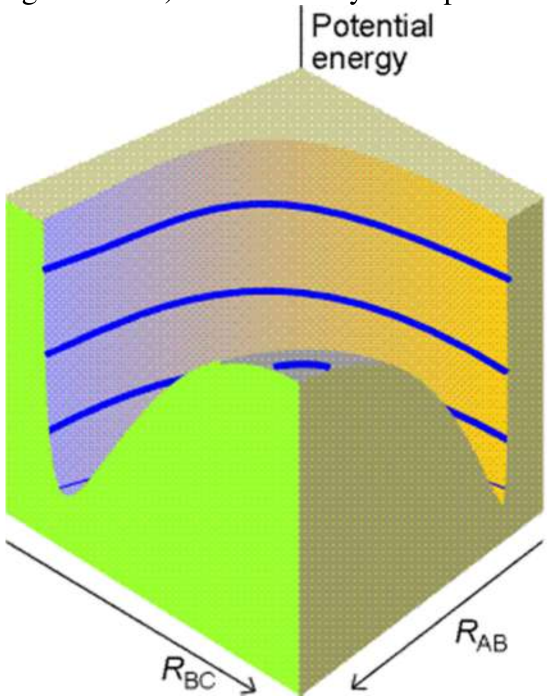
In this figure the values indicate the height (from the bottom) and values at any point on a circle is same. For example, the outer circle of value 30 indicates that each point on this circle has a value of 30 unit. When one moves toward centre of the coconut shell the diameter of the circle reduces as well as height from the bottom also decreases: representing contour diagram of a half coconut shell facing upward.

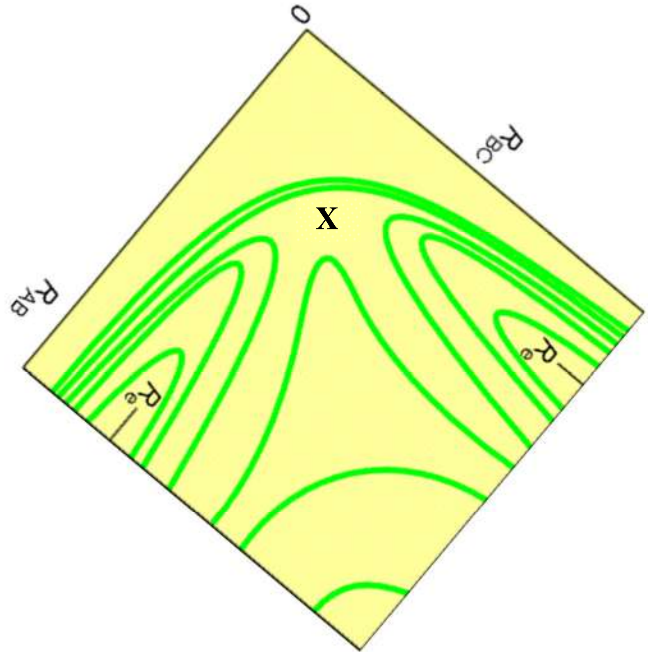
Look at the following contour diagram and can you guess what does it represent?



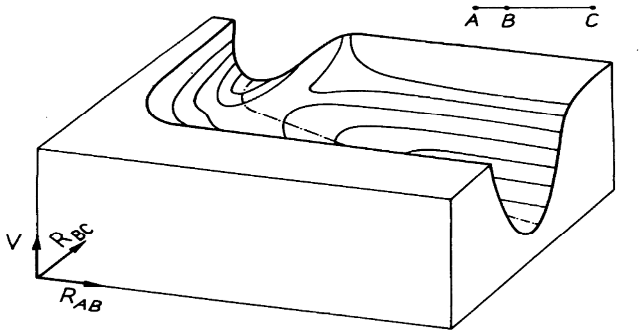
In this contour diagram when one moves toward centre of the coconut shell the diameter of the circle reduces but unlike previous diagram height from the bottom increases (the inner most of 30 unit): representing contour diagram of a half coconut shell inverted one. From the above discussion one should understand how the similar contour plots indicate two different three dimensional surfaces due to change of the magnitude of the contours values i.e., height.

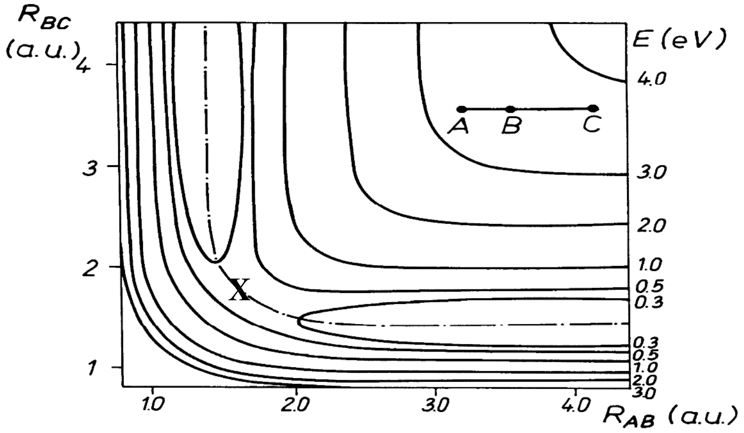
Coming back to 3D potential energy surface (PES) along with its contour diagram (see figure below) one can easily anticipate the shape of a PES from its 2D contour diagram.





Also you can look at another picture below of slight different orientation for better correlation between 3D PES and 2D contour diagram.

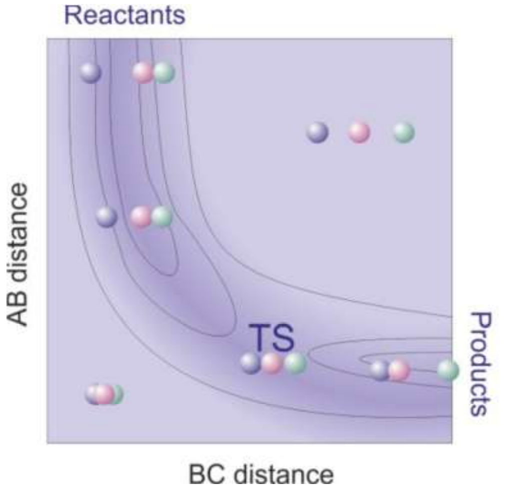


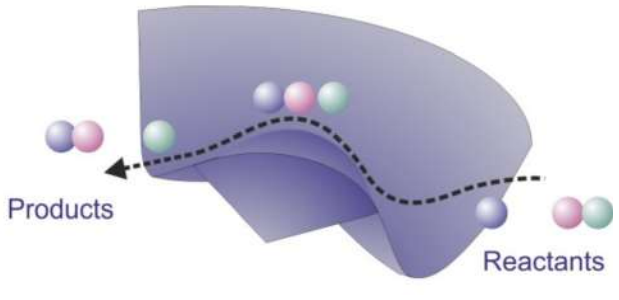


Until now we were restricting our discussion mainly for a thermoneutral reaction, where both reactant side and product side with respect saddle point, denoted by X in both the contour diagrams above, are symmetric.

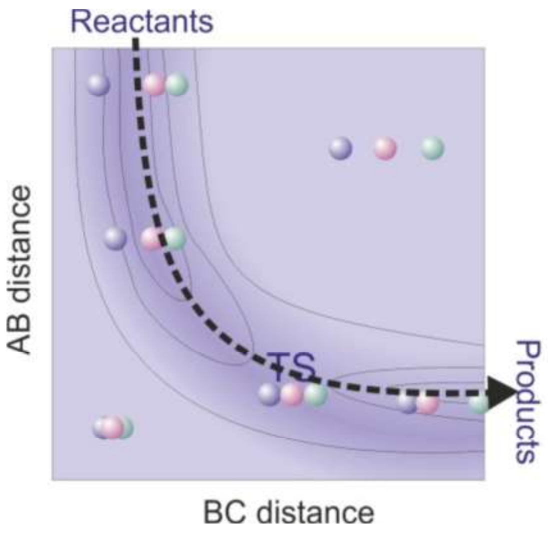
Lest us now consider endoeargic and exoergic reactions also and to understand their corresponding contour diagrams.

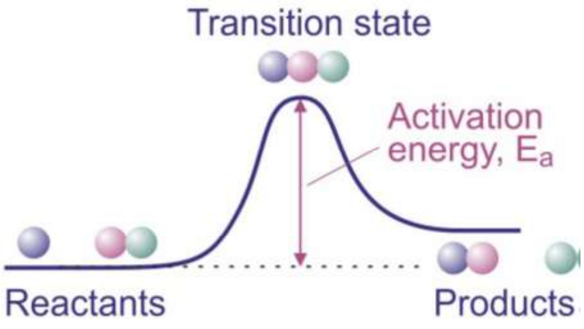
Contour diagram of an endoergic reaction:



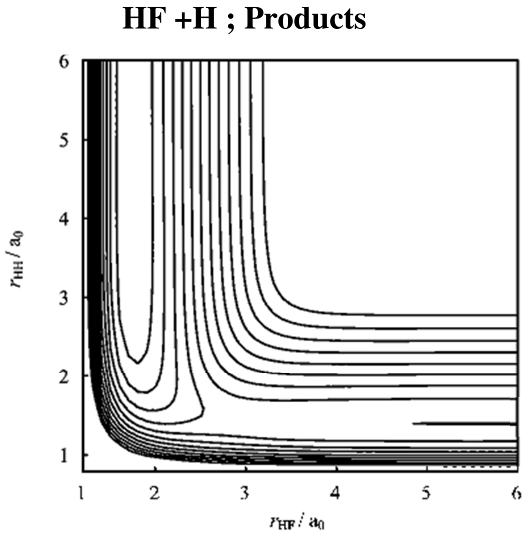


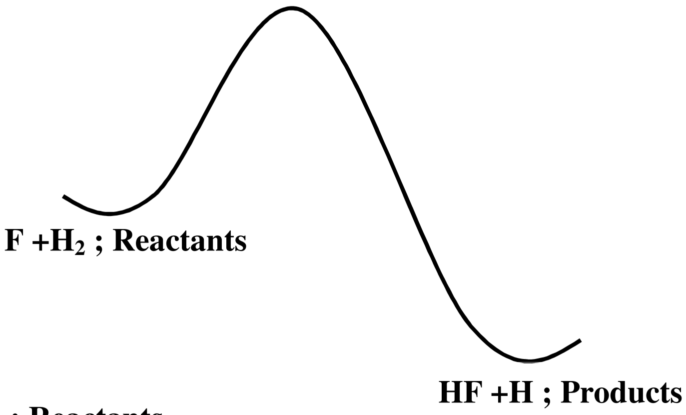
The minimum energy path across the surface follows the base of the ‘half pipe’, and is known as the *reaction coordinate*. Note that the transition state appears as a ‘hump’ along the reaction coordinate, which the reactants must surmount to form products. As shown below, if we plot the potential energy along the reaction coordinate, we recover the familiar reaction potential energy profile.



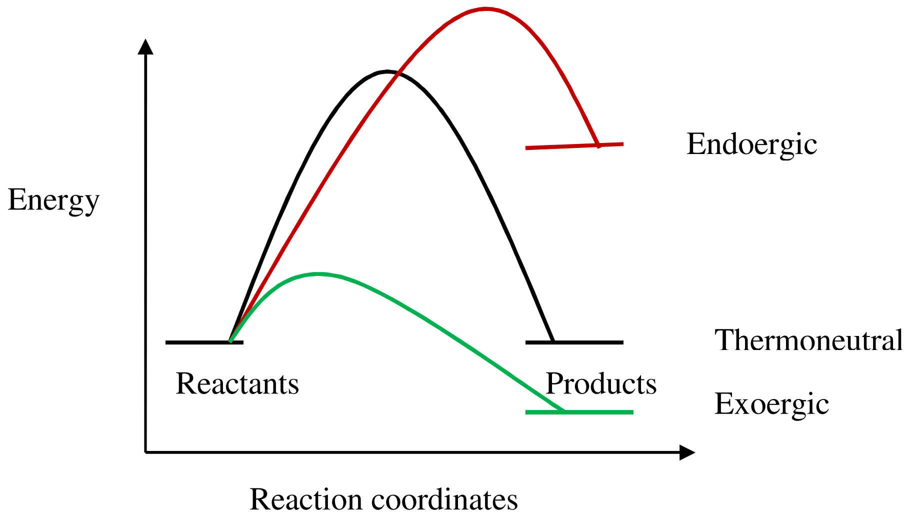


To understand the contour diagram of an exoergic reaction (e.g., F + H_2 reaction) we need to run the movie in the reverse direction, i.e., that going along reaction coordinates from products to reactants.





To get more insight into the potential energy surface of the thermoneutral, endoergic and exoergic reactions perhaps we can combine the energy profile diagram of all the reaction in a same plot as shown in figure below.



From the above figure one can anticipate that for endoergic reaction (red curve) has a late barrier which indicates that saddle point on the PES will be closer to the products zone (see potential energy contour diagram for endoergic reaction above). While on the other hand for an exoergic reaction (green curve) has an early barrier indicating the saddle point will be located closer to the reactant (see contour diagram for the F + H_2 reaction above). It is obvious that for thermoneutral reaction saddle point will be at the middle position as can be seen from the PES contour diagram of the H + H_2 reaction (see above).