Potential Energy Surfaces

- For a (nonlinear) molecule with $N$ atoms there are
  - 3 degrees of translational freedom for the whole molecule
  - 3 degrees of rotational freedom
  - $(3N-6)$ internal degrees of freedom remaining

- The most stable geometry is a minimum with respect to all of the $(3N-6)$ internal degrees of freedom.

- A reaction proceeds along one coordinate for which the energy is a maximum.

In a multidimensional space the potential energy surface is a "hypersurface" and the "transition state" is a maximum with respect to the reaction coordinate, but a minimum with respect to all the other coordinates.
Thus we picture the transition state as a "saddle point" on a multidimensional potential energy surface, sort of a high spot on a pass between the mountains.

We imagine that reactants must have enough energy (an "activation energy") to get up and over the high spot.

Tunneling can also occur and for certain types of reactions (e.g., electron transfers, hydrogen abstractions) this passage through the barrier may be more important than the classical process of going over the barrier.

One reaction that has been very much studied, both experimentally and theoretically, is the reaction between a hydrogen atom and a hydrogen molecule. (A hydrogen abstraction, this is the simplest reaction possible in which one bond is broken and another is formed.)

For the linear encounter the activation energy is 42 kJ/mol, and the linear transition state has both H–H distances at 93 pm (the bond distance in molecular hydrogen is 74.1 pm).
Figure 19.3 Potential energy surface for the reaction $H_A + H_BH_C \rightarrow H_AH_B + H_C$ for a linear approach and departure.

$$H_A + H_BH_C \rightarrow H_AH_B + H_C$$

The potential energy surface for this reaction for $\theta = 180^\circ$ is described by means of a contour diagram in Fig. 19.3. This surface has been calculated using ab initio methods with configuration interaction (as discussed in Section 11.4), and the error at any point on the surface is believed to be less than 0.03 eV (2.9 kJ mol$^{-1}$). As $H_A$ approaches $H_BH_C$, along the minimum energy path, the potential energy of the system increases until the saddle point is reached at $\pi$. At this point $R_{AB} = R_{BC} = 93$ pm, and the potential energy of the system is 0.43 eV (42 kJ mol$^{-1}$), the highest along the dashed line. Since the saddle point is 0.43 eV higher than the potential of $H_A$ and $H_{BC}$ at an infinite distance, this energy must be supplied from relative kinetic energy or vibrational energy in order for the reaction to occur. In the upper right-hand corner of Fig. 19.3, there is a high plateau with energy of 432 kJ mol$^{-1}$. 
Figure 19.4  (a) Trajectory for a nonreactive, inelastic collision of a hydrogen atom and a hydrogen molecule. (b) Trajectory for a reactive collision. [From P. Siegbahn and B. Liu, J. Chem. Phys. 68:2457 (1978), and C. J. Horowitz, J. Chem. Phys. 68:2466 (1978).]