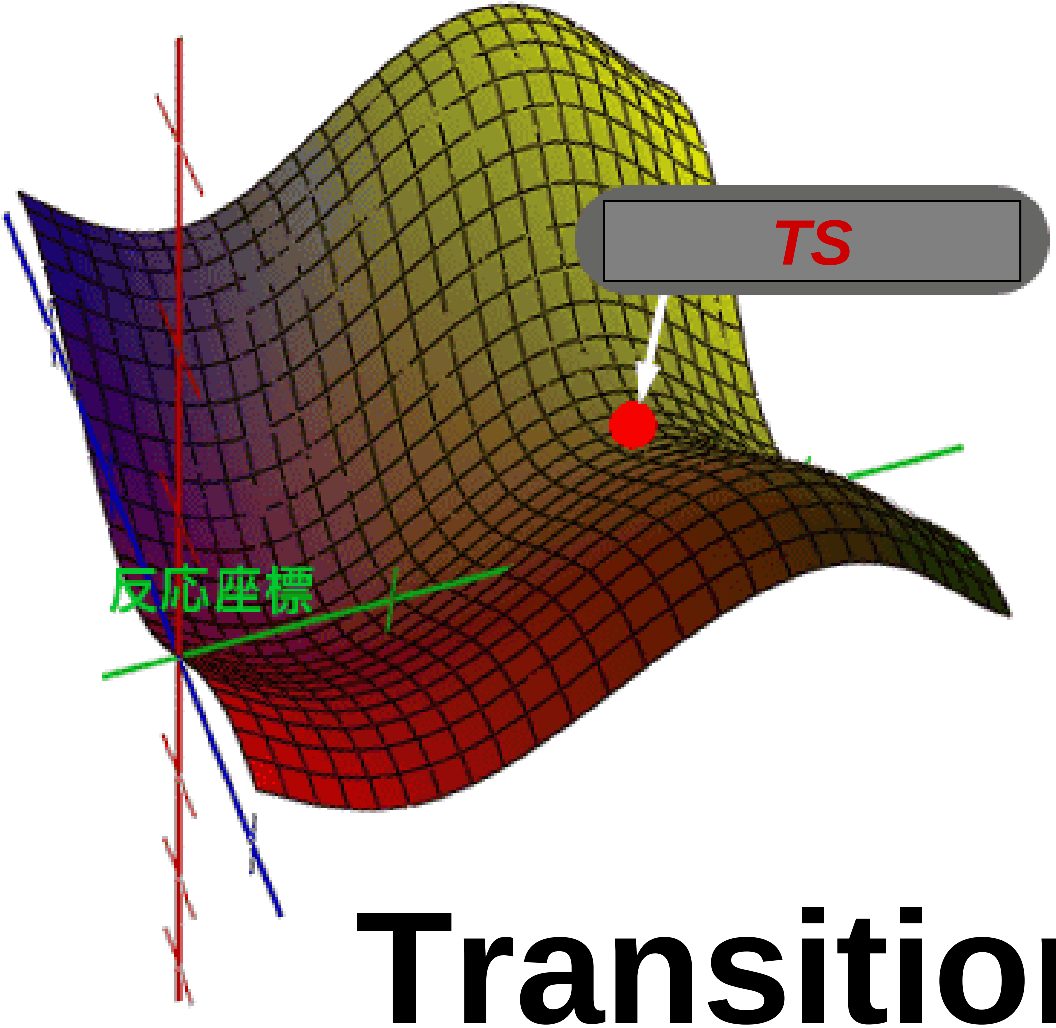
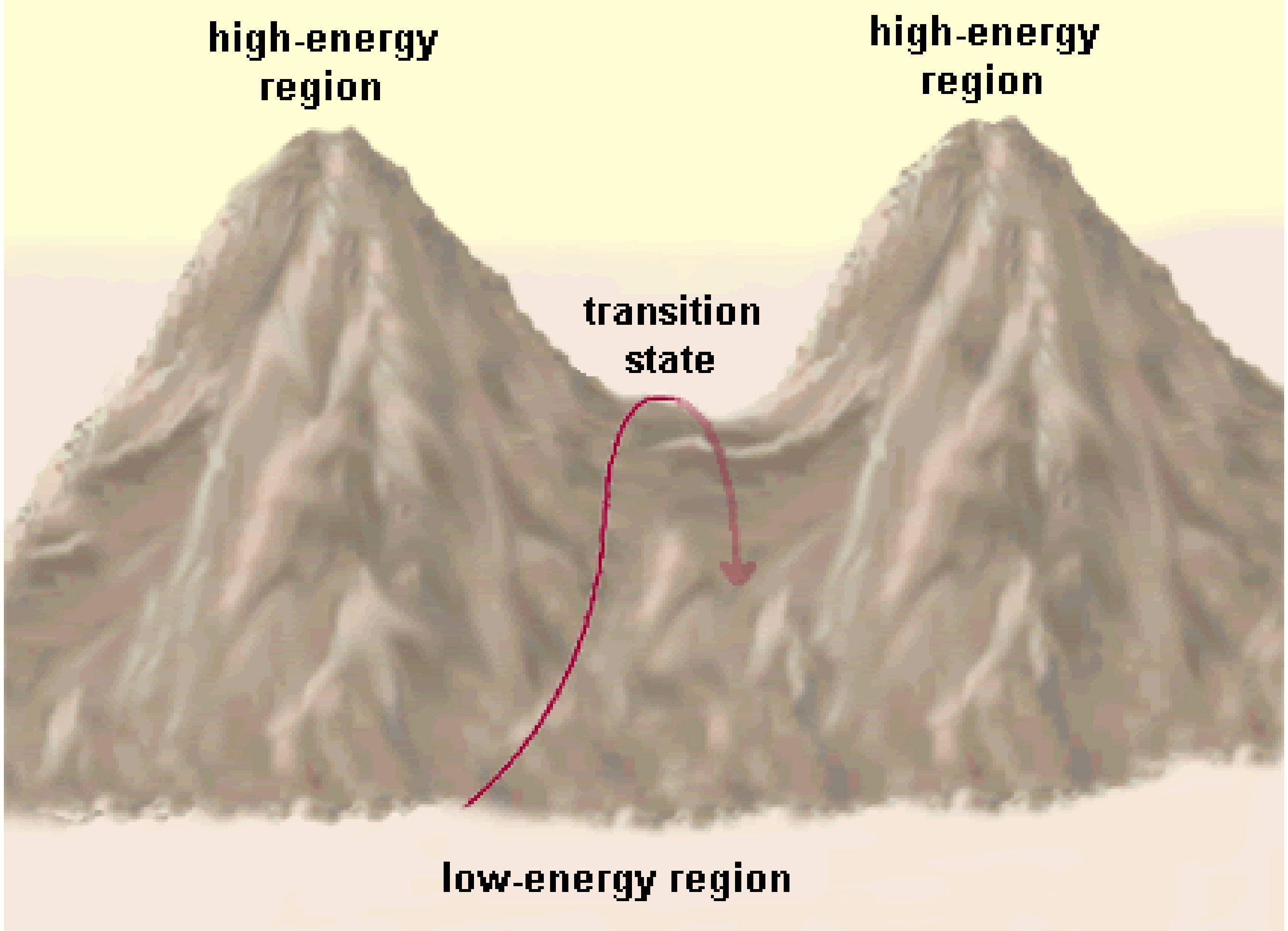
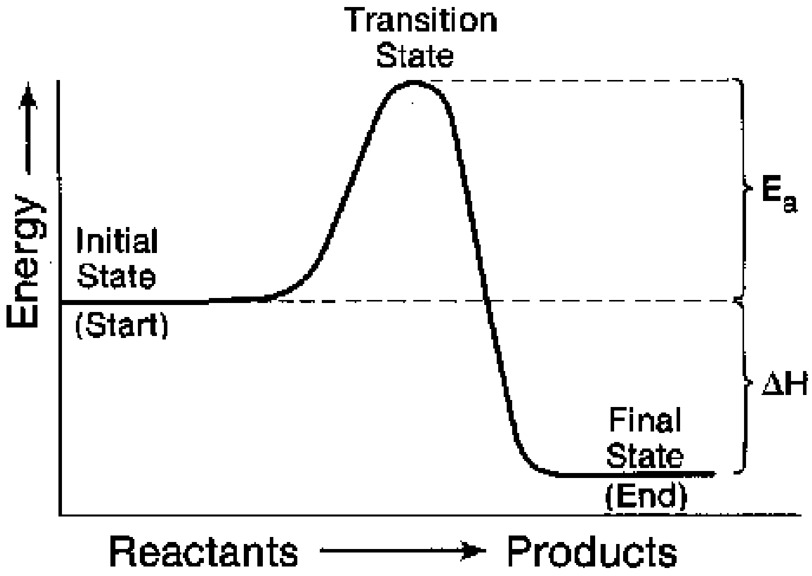


Transition States and Reaction Paths

Transition State (TS)



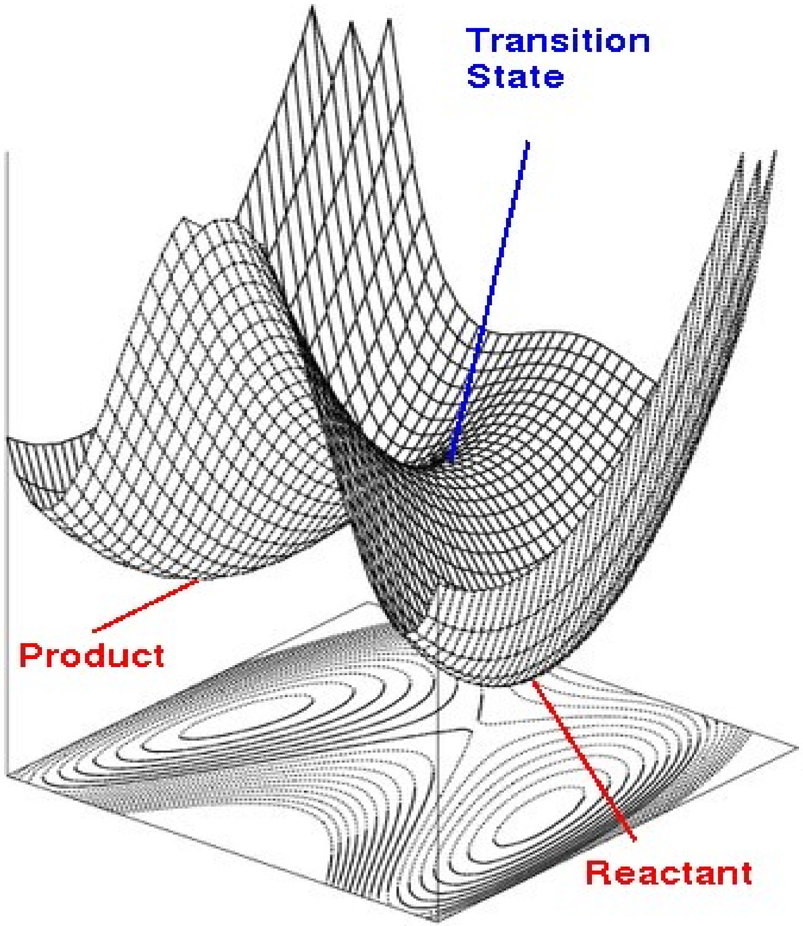
Transition State – 1D System



$$k = Ae^{-E_A / k_b T}$$

k - rate constant
E_A – activation energy
T – temperature
k_b – Boltzmann constant

Transition State-General Case



A saddle point on the multidimensional molecular potential surface:

$$\frac{\partial E}{\partial q_i} = 0 \qquad \text{for all } i$$

$$\frac{\partial^2 E}{\partial q_i^{\,2}} > 0 \qquad \text{for all } i \text{ but one}$$

$$\frac{\partial^2 E}{\partial q_i^{\,2}} < 0 \qquad \text{for one } i$$

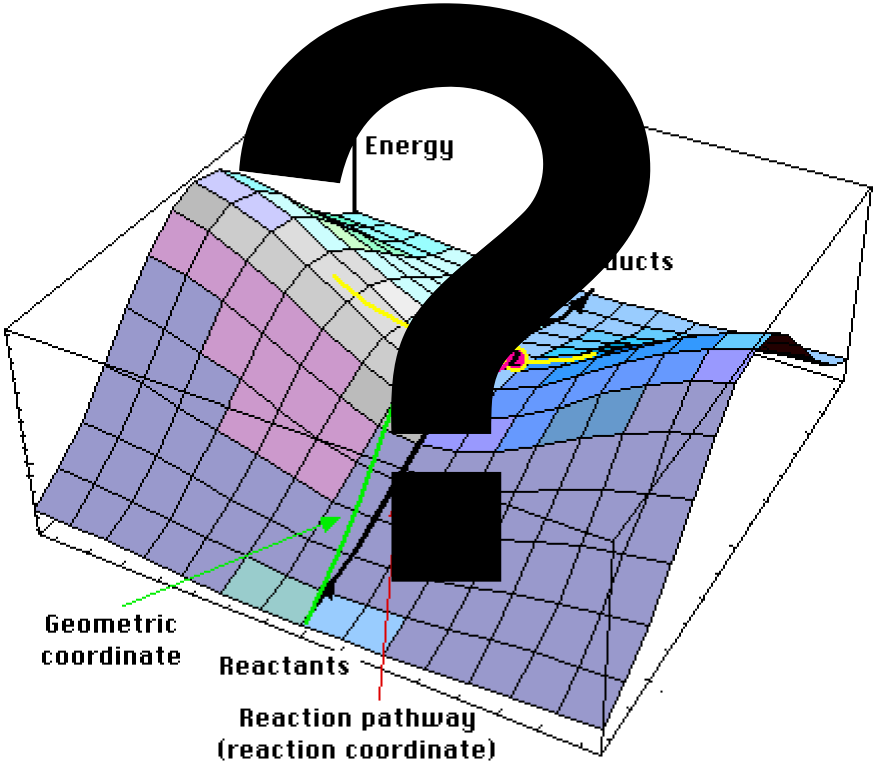
Hessian matrix of the transition state

$$H(f) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1\,\partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1\,\partial x_n} \\ \\ \frac{\partial^2 f}{\partial x_2\,\partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2\,\partial x_n} \\ \\ \vdots & \vdots & \ddots & \vdots \\ \\ \frac{\partial^2 f}{\partial x_n\,\partial x_1} & \frac{\partial^2 f}{\partial x_n\,\partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

For TS, after the diagonalization of the Hessian matrix, all the eigenvalues are positive, except one, which is negative.

Finding Transition Structures

?



Optimization Algorithms – Quasi-Newton Techniques

- Guess the approximate structure of the transition state.

- Calculate the Hessian matrix eigenvalues.

- For $H_{ij} > 0$ $\Delta E < 0$ ↓
  For $H_{ij} < 0$ $\Delta E > 0$ ↑

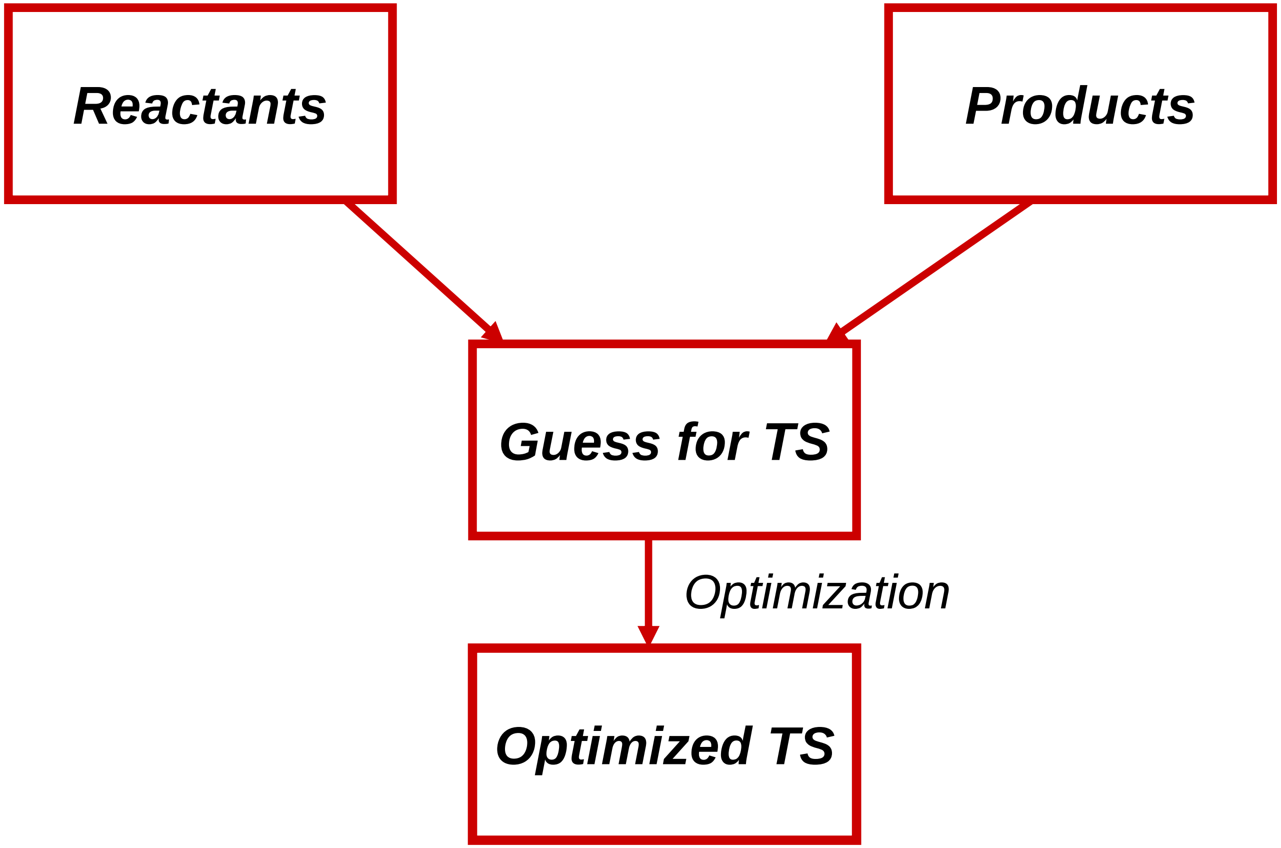
- The explicit calculation of the Hessian matrix is quite costly

- The **Berny Algorithm** - construct an approximate Hessian at the beginning of the optimization procedure and then use the energies and first derivatives calculated along the optimization pathway to update this approximate Hessian matrix.

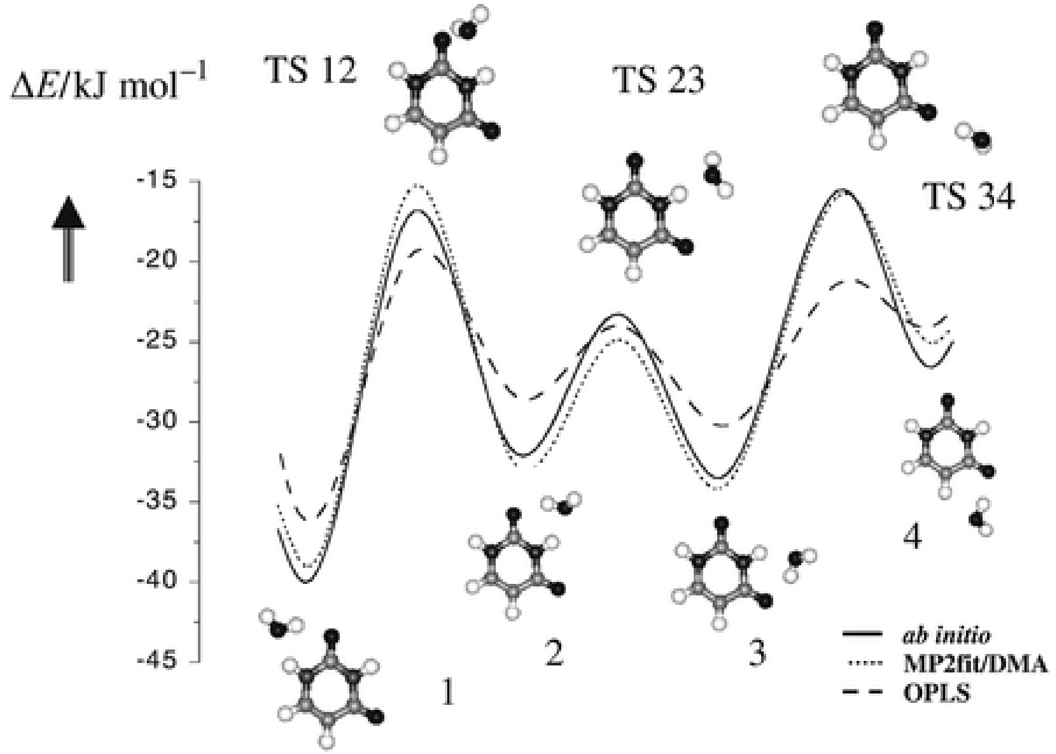
- The main disadvantage is the sensitivity of the calculation to the starting geometry.

- Possible to start with the optimized transition structure for a similar reaction.

From Initial and Final Structures

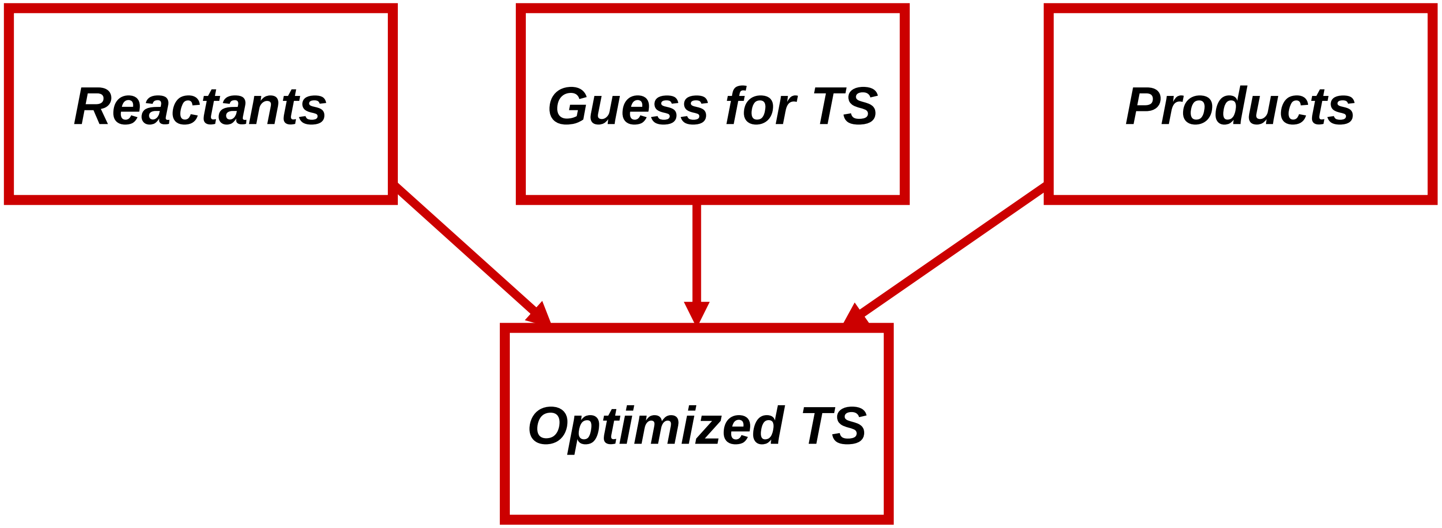


- Linear Synchronous Transit (LST)
- Quadratic Synchronous Transit (QST2)



Sometimes the reaction proceeds through more than one transition state. In this case each transition state can be calculated separately.

QST3



Reactants

Guess for TS

Products

Optimized TS

Reaction Coordinate Techniques

- A transition state is a maximum on the reaction pathway.
- A well defined reaction path is the least energy or intrinsic reaction path (IRC)

- Scan the reaction path to identify the saddle points (and thus transition state)

- Use a pseudo coordinate approach

Verifying that the correct geometry was obtained

- Compute the vibrational frequencies. A saddle point should have one imaginary frequency.

- Look at the transition state geometry to make sure it's the right one.