

CHM 673

Lecture 3: Potential energy surfaces

Suggested reading:

geometry optimization: chapters 13.1-13.4 from Jensen;

vibrational normal coordinates: chapter 17.2.2 from Jensen;

chemical reactions: chapter 13.8 from Jensen

webinar on freezing string method in Q-Chem:

<https://www.youtube.com/watch?v=JBBblxGEXxo>

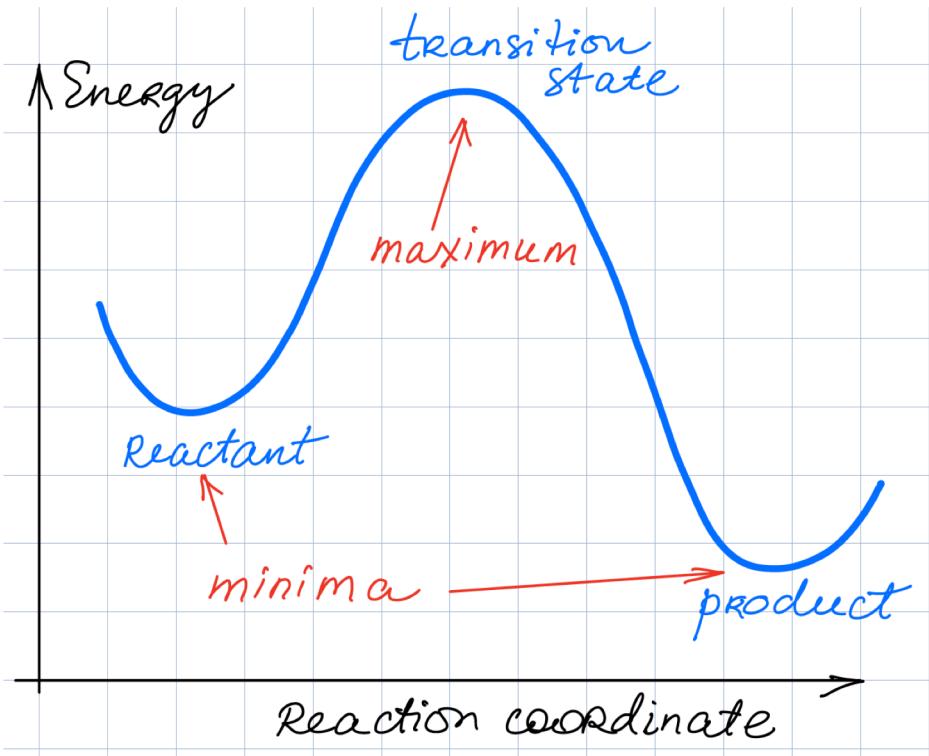
Potential energy surface (PES)

$$U_k(\mathbf{R}) = E_{e,k}(\mathbf{R}) + \sum_{A>B}^{nuc} \frac{Z_A Z_B}{R_{AB}}$$

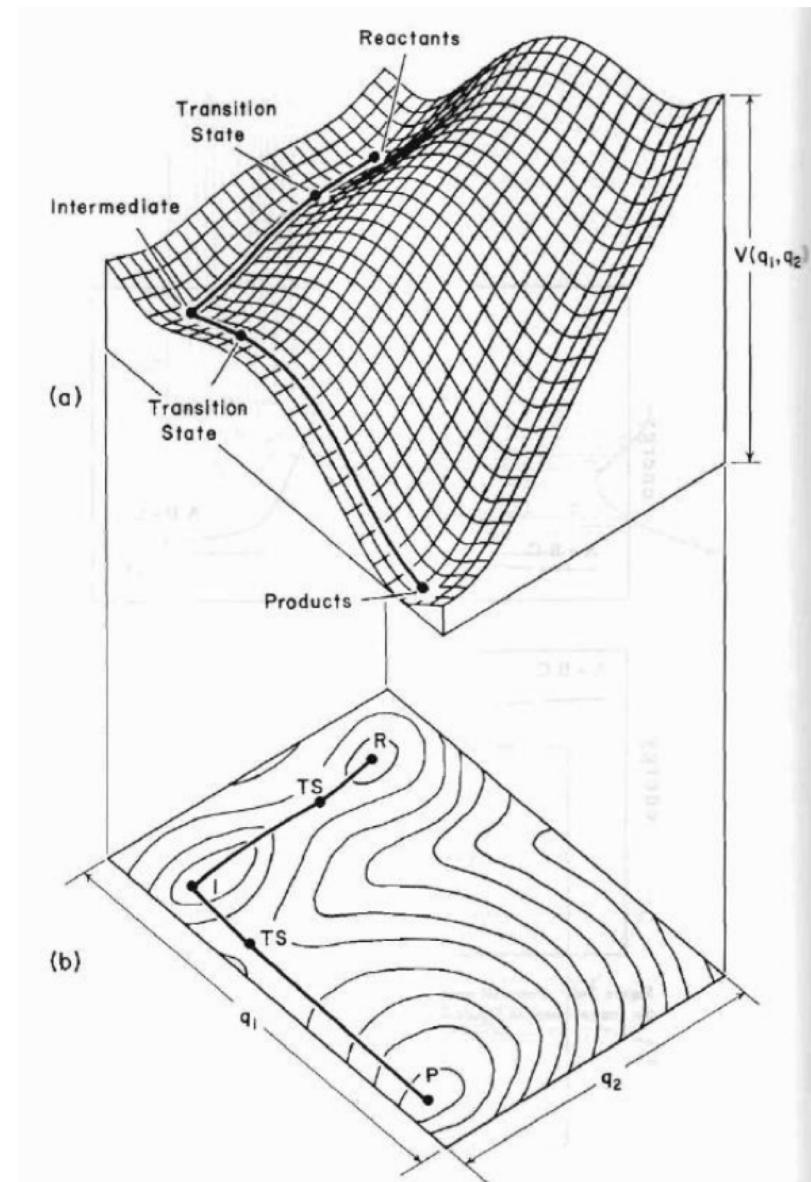
$U_k(\mathbf{R})$ are potential energy surfaces (PES) for nuclei, imposed by electrons

- The electronic energy for an individual molecule shouldn't change if we translate or rotate the molecule - it only depends on the internal degrees of freedom
- Each molecule has three translational degrees of freedom, and usually three rotational degrees of freedom (2 for linear molecules)
- For N atoms, there are 3N-6 of internal (vibrational) coordinates (3N-5 for a linear molecule)
- The potential energy surface is a function of 3N-6 coordinates

Potential energy surface (PES)



- Transition state (TS) is a maximum in only one dimension; minimum in all other dimensions
- A multidimensional PES can support multiple minima and TS's
- Ideal reaction path is a “minimum energy path” following the valleys; it can be traced using Intrinsic Reaction Coordinate (IRC) analysis



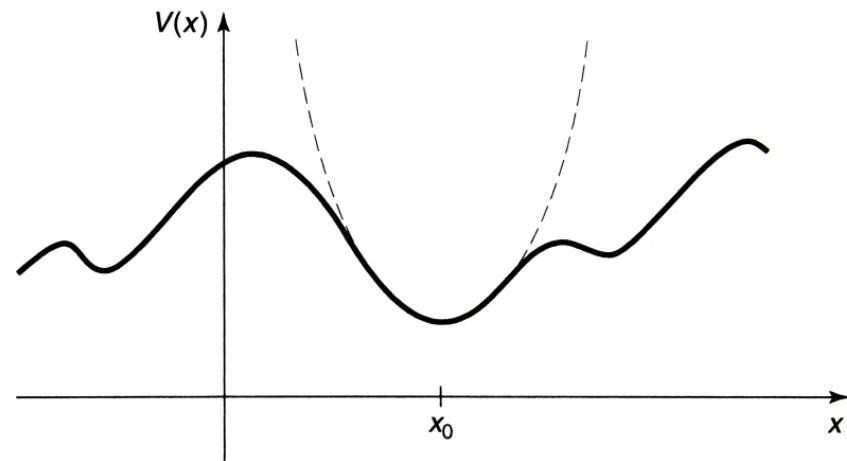
Vibrational analysis

Consider diatomic molecule first
(x is one-dimensional)

potential can be represented as
a Taylor series:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + V''(x_0)(x - x_0)^2 + \dots$$

Close to x_0 : $V(x) \approx V''(x_0)(x - x_0)^2$



Note: dropping constant $V(x_0)$ does not change the solution Ψ :

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi = E\psi$$

If you rise V , then E will also rise:

$$V \rightarrow V + C$$

$$E \rightarrow E + C$$

$$\downarrow +C\psi$$
$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) + C \right] \psi = [E + C]\psi$$

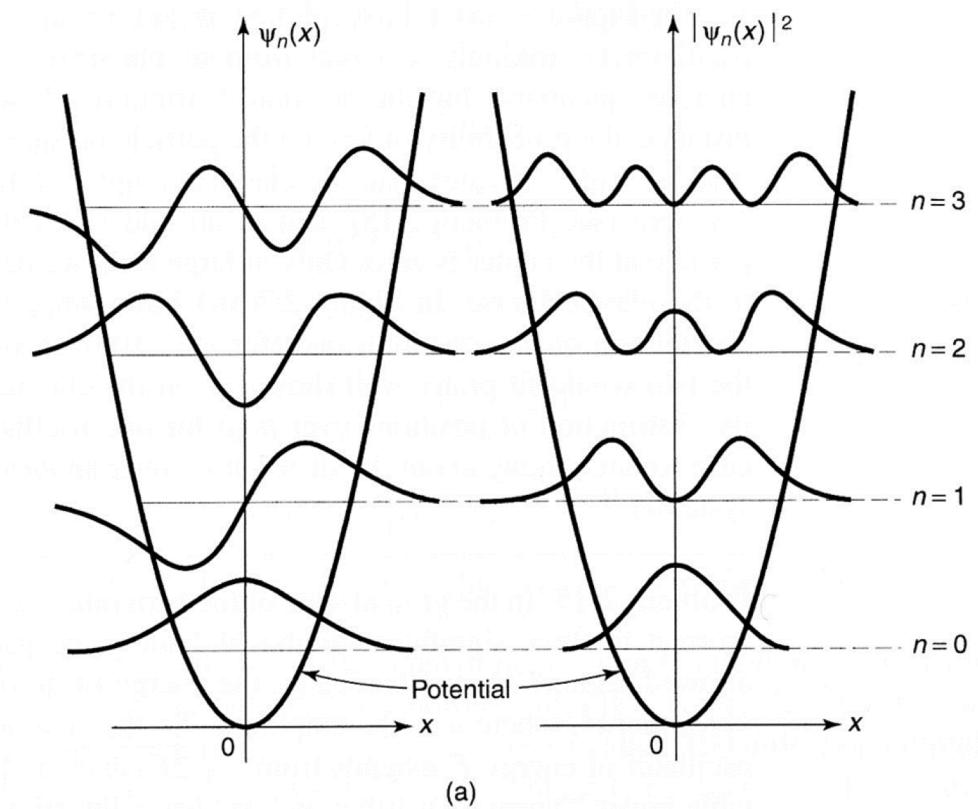
Vibrational analysis: 1 dimension

Close to x_0 : $V(x) \approx V''(x_0)(x - x_0)^2$

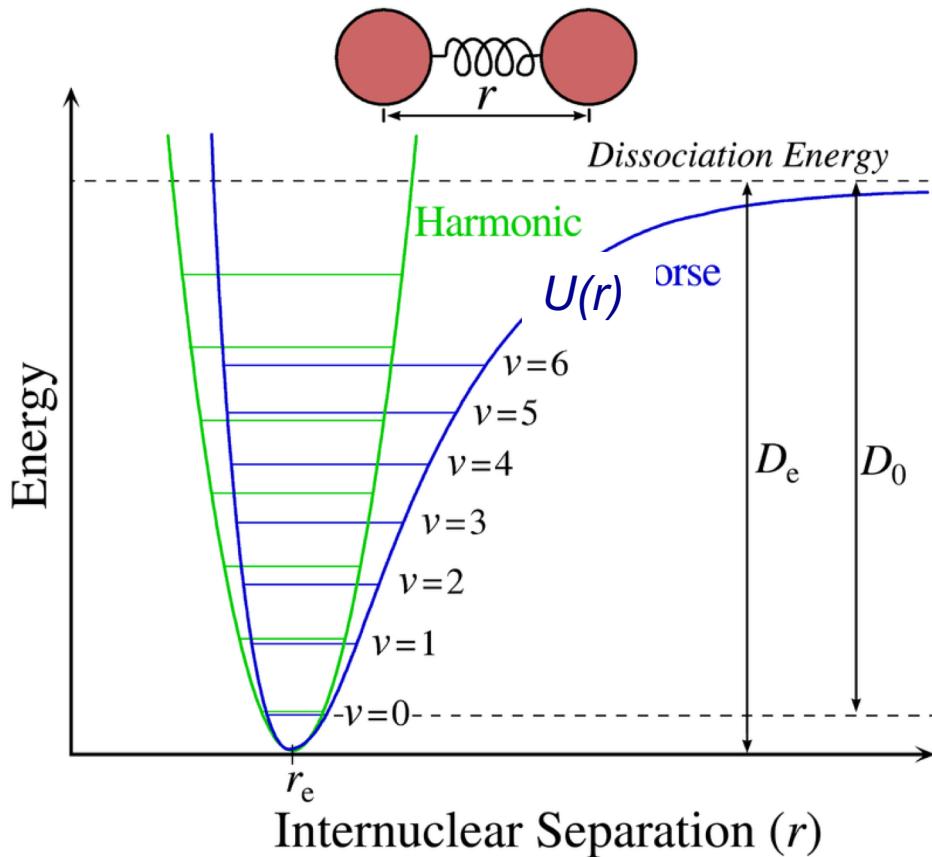
This potential corresponds to a one-dimensional quantum harmonic oscillator, with solutions:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}$$



Vibrational analysis: 1 dimension



Force constant f is proportional to the bond order (strength of bond)

Assuming that $U(r)$ is harmonic near equilibrium position r_e :

$$\text{force constant} \quad f = \left. \frac{d^2 U}{dr^2} \right|_{r=r_e}$$

$$\text{reduced mass} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}} \quad \text{vibrational frequency}$$

$$E_{vib} \approx \left(v + \frac{1}{2} \right) h\nu, \text{ for } v = 0, 1, 2, \dots$$

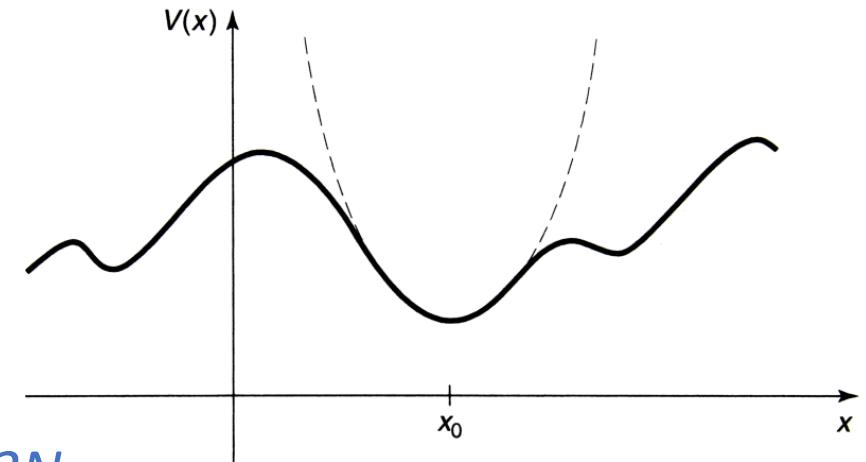
$$\frac{1}{2} h\nu \quad - \text{zero-point vibrational energy (ZPE)}$$

Note: quantum numbers (n) in vibrational spectroscopy are historically called “ v ”

Vibrational analysis: multi-dimensional case

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + V''(x_0)(x - x_0)^2 + \dots$$

Close to x_0 : $V(x) \approx V''(x_0)(x - x_0)^2$



In multi-dimensional case, \mathbf{x} becomes a vector of length $3N_{atom}$

$$V(\mathbf{x}) = V(\mathbf{x}_0) + \left(\frac{dV}{d\mathbf{x}}\right)^T (\mathbf{x} - \mathbf{x}_0) + \frac{1}{2} (\mathbf{x} - \mathbf{x}_0)^T \left(\frac{d^2V}{d\mathbf{x}^2}\right) (\mathbf{x} - \mathbf{x}_0) + \dots$$

$\vec{g} = \nabla_{\mathbf{x}} V = \frac{dV}{d\mathbf{x}}$ is $3N_{atom}$ -dimensional vector of the first derivatives of the energy, called **gradient**

$F = \nabla_{\mathbf{x}_i} \nabla_{\mathbf{x}_j} V = \frac{d^2V}{d\mathbf{x}^2}$ is $3N_{atom} \times 3N_{atom}$ matrix of the second derivatives of the energy with respect to the coordinates. It is called **Hessian**

Around the **stationary** point x_0 , the potential can be written as: $V(\Delta\mathbf{x}) = \frac{1}{2} \Delta\mathbf{x}^T F \Delta\mathbf{x}$

Vibrational analysis: multi-dimensional case

$$V(\Delta \mathbf{x}) = \frac{1}{2} \Delta \mathbf{x}^T \mathbf{F} \Delta \mathbf{x}$$

The nuclear SE for an N_{atom} system:

$$\left[\sum_{i=1}^{3N_{atom}} \left(-\frac{1}{2m_i} \frac{\partial^2}{\partial x_i^2} \right) + \frac{1}{2} \Delta \mathbf{x}^T \mathbf{F} \Delta \mathbf{x} \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

This is a system of coupled equations:

matrix F mixes coordinates of different atoms x_i

To solve, first switch to mass-dependent coordinates $y_i = \sqrt{m_i} \Delta x_i$

$$\frac{\partial^2}{\partial y_i^2} = \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2} \quad G_{ij} = \frac{1}{\sqrt{m_i m_j}}$$

$$\left[\sum_{i=1}^{3N_{atom}} \left(-\frac{1}{2} \frac{\partial^2}{\partial y_i^2} \right) + \frac{1}{2} \mathbf{y}^T (\mathbf{F} \cdot \mathbf{G}) \mathbf{y} \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

Vibrational analysis: multi-dimensional case

$$\left[\sum_{i=1}^{3N\text{atom}} \left(-\frac{1}{2} \frac{\partial^2}{\partial y_i^2} \right) + \frac{1}{2} \mathbf{y}^T (\mathbf{F} \cdot \mathbf{G}) \mathbf{y} \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

Then, find a *unitary transformation \mathbf{U}* (aka rotation) that diagonalizes matrix $(\mathbf{F} \cdot \mathbf{G})$, yielding eigenvalues ε_i and eigenvectors \mathbf{q}_i

The kinetic energy operator still remains diagonal in these coordinates:

$$\mathbf{q} = \mathbf{U}\mathbf{y} \quad \left[\sum_{i=1}^{3N\text{atom}} \left(-\frac{1}{2} \frac{\partial^2}{\partial q_i^2} \right) + \frac{1}{2} \mathbf{q}^T (\mathbf{U}(\mathbf{F} \cdot \mathbf{G})\mathbf{U}^T)\mathbf{q} \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

$$\left[\sum_{i=1}^{3N\text{atom}} \left(-\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \varepsilon_i q_i^2 \right) \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

$$\begin{pmatrix} \frac{\partial^2 V}{\partial y_i \partial y_j} & \dots & \frac{\partial^2 V}{\partial y_i \partial y_j} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 V}{\partial y_i \partial y_j} & \dots & \frac{\partial^2 V}{\partial y_i \partial y_j} \end{pmatrix} \longrightarrow \begin{pmatrix} \frac{\partial^2 V}{\partial q_i^2} & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \frac{\partial^2 V}{\partial q_i^2} \end{pmatrix} \longrightarrow \begin{pmatrix} \varepsilon_i & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \varepsilon_i \end{pmatrix}$$

Vibrational analysis: multi-dimensional case

$$\left[\sum_{i=1}^{3N_{atom}} \left(-\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \varepsilon_i q_i^2 \right) \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

$$\left[\sum_{i=1}^{3N_{atom}} \mathbf{h}_i(q_i) \right] \Psi_{nuc} = E_{nuc} \Psi_{nuc}$$

\mathbf{h}_i – Hamiltonian of 1D harmonic oscillator

q – vibrational normal coordinates

In q coordinates, the $3N_{atom}$ -dimensional SE is separated into $3N_{atom}$ one-dimensional SE for harmonic oscillators

Vibrational frequencies $v_i = \frac{1}{2\pi} \sqrt{\varepsilon_i}$

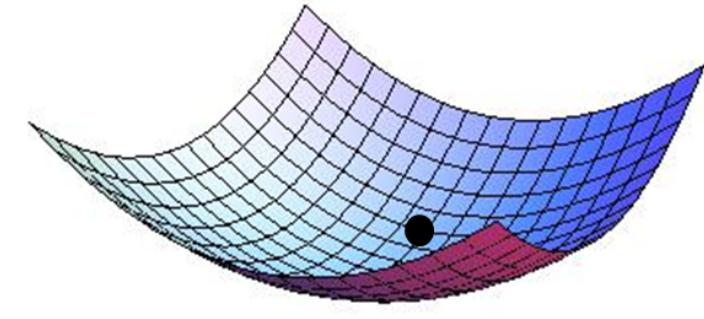
In Cartesian coordinates, 6 (5 in linear molecules) eigenvalues of $(\mathbf{F} \cdot \mathbf{G})$ correspond to translational and rotational modes and are 0.

$(3N_{atom} - 6)$ vibrational modes

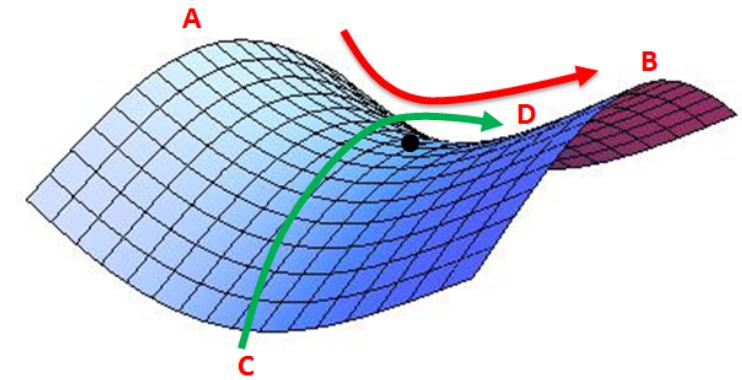
Vibrational analysis: multi-dimensional case

$$\nu_i = \frac{1}{2\pi} \sqrt{\varepsilon_i}$$

If stationary point is a **minimum**, all $\varepsilon_i > 0$



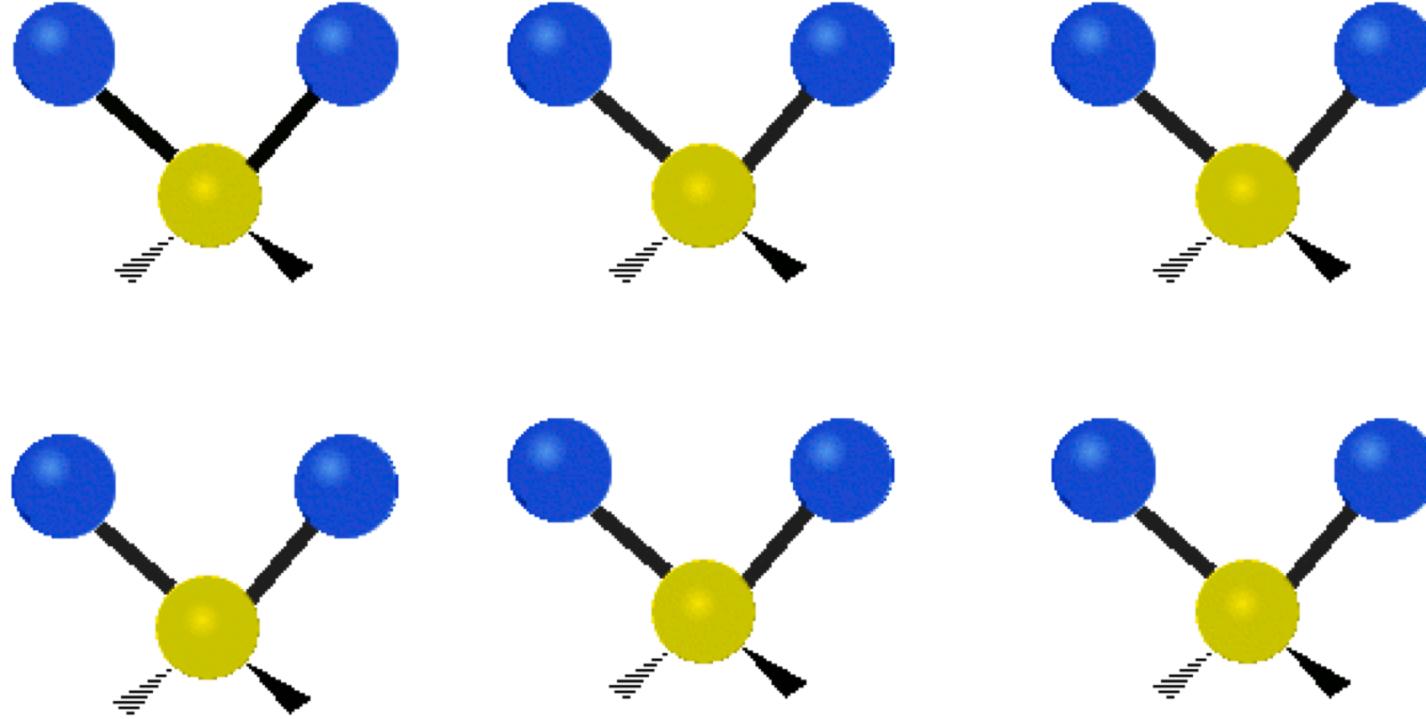
If stationary point is a **transition state**,
one ε_k will be <0 ,
and the corresponding ν_k is imaginary



Types of stationary points

- **Stationary point:** gradient $\vec{G} = \nabla_x V = 0$.
Examples of stationary points: minima, maxima, transition states
- **Minima:** minimum in all dimensions; all vibrational frequencies are real.
Correspond to stable or quasi-stable species; i.e., reactants, products, and intermediates
- **Transition states:** minimum in all dimensions but one, maximum in the remaining dimension; exactly one imaginary vibrational frequency. Corresponds to a maximum (barrier) on the minimum energy path between reactants and products
- **Higher-order saddle point:** minimum in all dimensions but n, where n>1, maximum in all other dimensions; n imaginary vibrational frequencies. No real chemical significance (higher energy parts of PES)
- **Hessian Index:** the number of imaginary vibrational frequencies for a stationary point. Should be 0 for a minimum, 1 for a TS, >1 for a higher-order saddle point.

Normal modes: example



$$N = 4 \rightarrow (3N-6) = 6 \text{ normal modes}$$

Normal modes are symmetric (belong to irreducible representations allowed by molecule's symmetry group)

Vibrational analysis

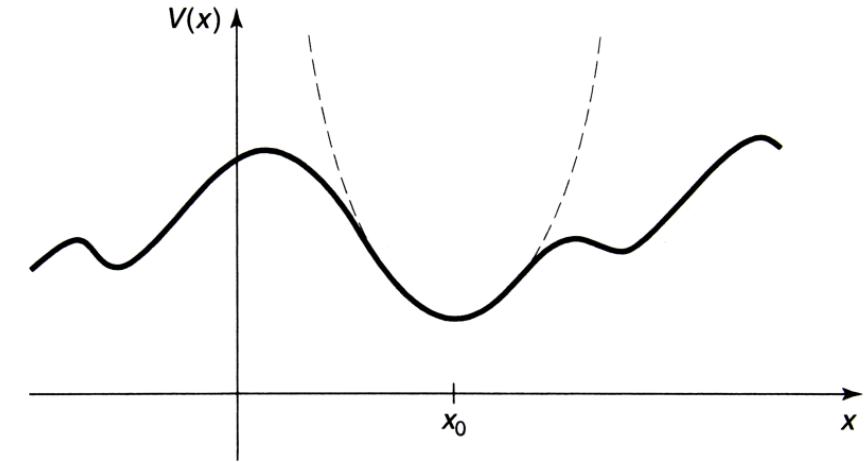
Q: Can you perform vibrational analysis at any point of PES?

Formally yes (computer will not complain and produce some numbers), but:

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + V''(x_0)(x - x_0)^2 + \dots$$



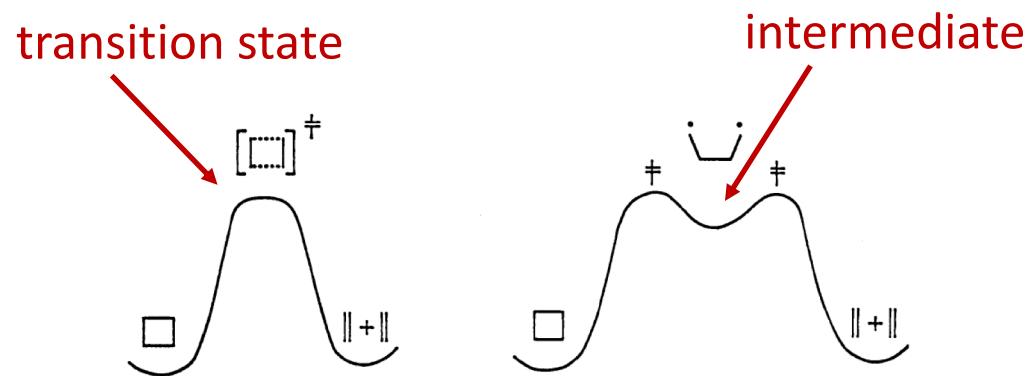
=0 only at stationary points (minima and TS)



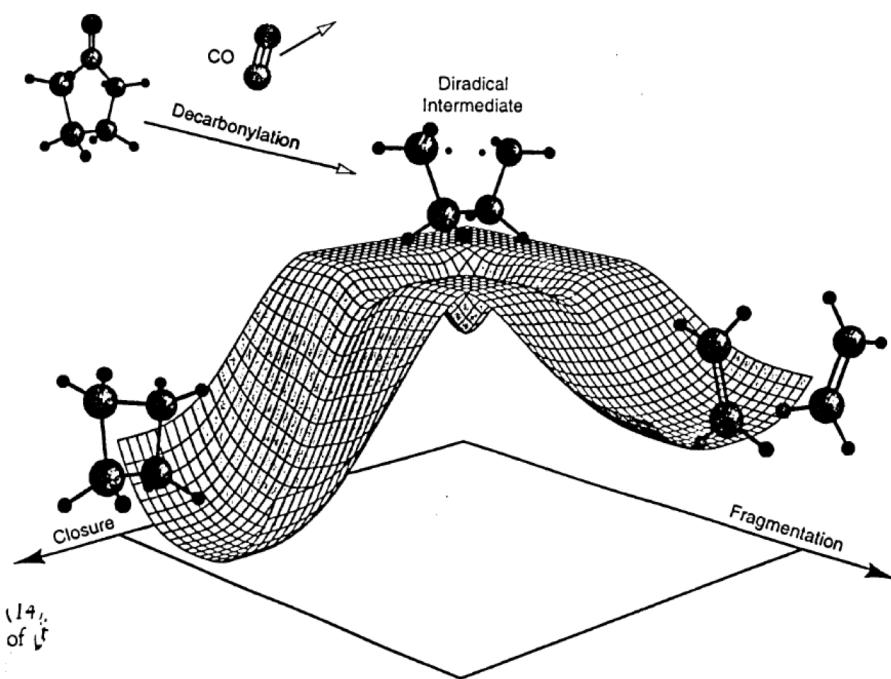
Vibrational analysis at *non-stationary points* might produce incorrect vibrational frequencies

(because anharmonic potential is assumed to be harmonic)

Reaction intermediates and transition states

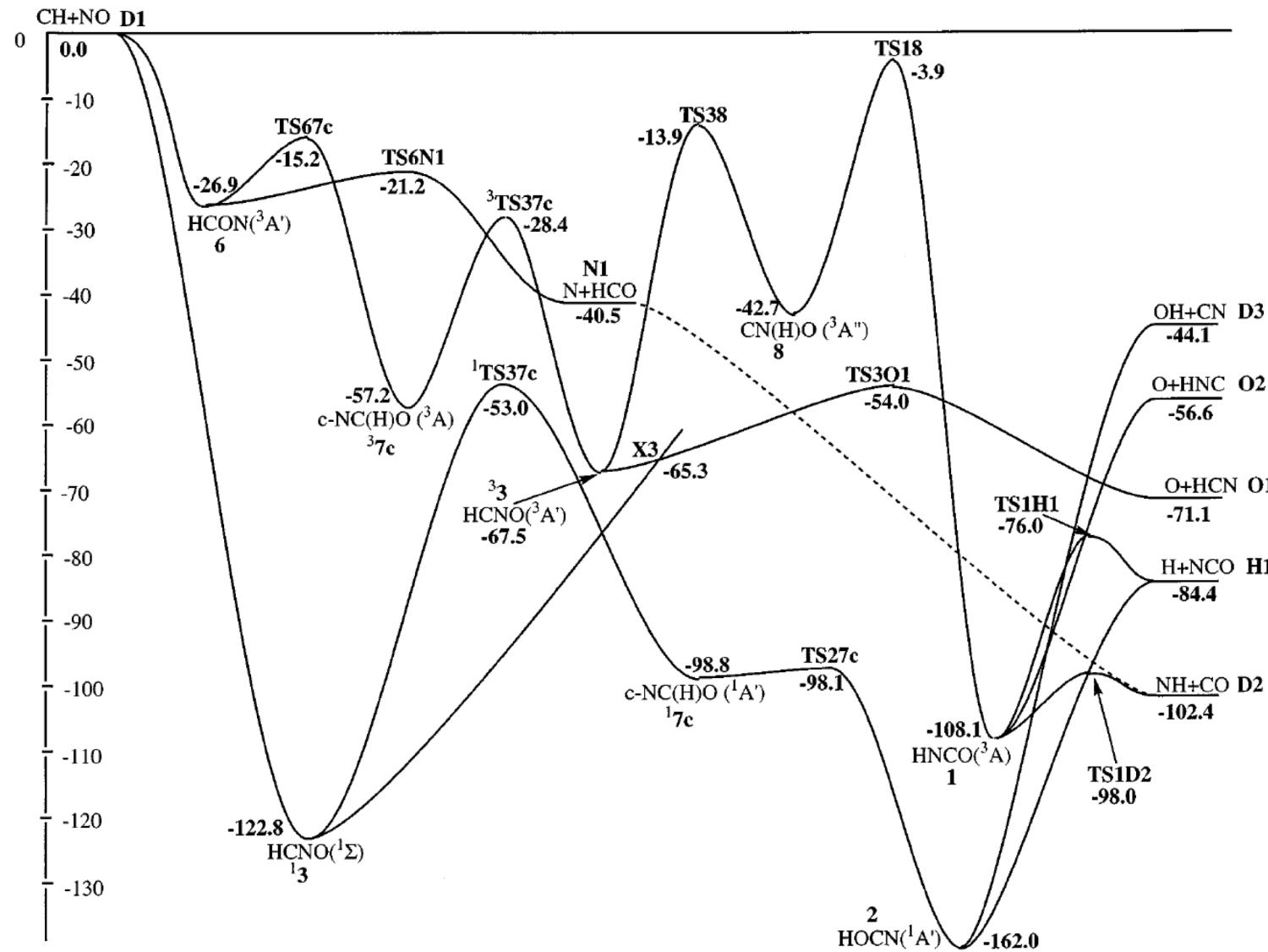


Schematic depiction of two possible pathways for ring opening in cyclobutane. The two diagrams depict the transition state and diradical mechanisms, respectively.



Reproduced from S. Pedersen, J.L. Herek, and A.H. Zewail, The validity of the diradical" hypothesis: Direct femtosecond studies of the transition-state structures, Science 266, 1359 (1994).

Reaction PES: example



Profile of PES for the $\text{CH} + \text{NO}$ reaction. Note different isomers and transition states.

Reproduced from: A.M. Mebel, A. Luna, M.C. Lin, and K. Morokuma, A density functional study of the global potential energy surfaces of the $[\text{H,C,N,O}]$ system in singlet and triplet states, J. Chem. Phys. 105, 6439 (1996).

Exploring molecular PES: geometry optimization methods

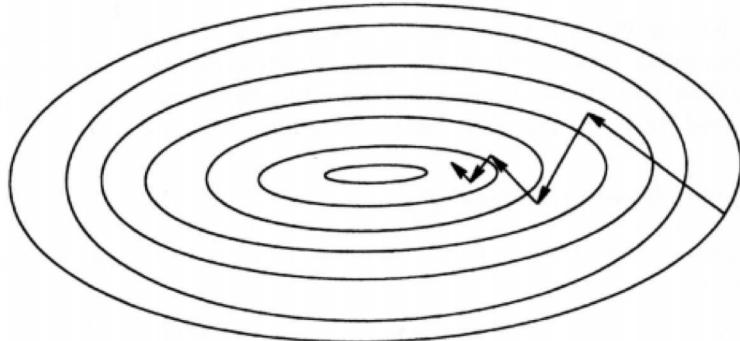
Finding a minimum on a multidimensional PES:

- Dumb method: step one variable until the function is a minimum in this dimension, then go on to other variables, repeat until no change. This won't normally work for complicated functions/many variables.
- Most methods assume an analytic (i.e., directly calculated, not numerical) **gradient** is available.
- Some methods assume the **Hessian** (second derivative) or an approximation of it is also available.

Typically, each package has several variants of geometry optimizers, which differ by rigor and computational cost:

- Steepest decent
- Conjugate gradient method
- Newton-Raphson method
- Newton-Raphson with diagonal Hessian
- DIIS extrapolations

Steepest Descent



- Step in the opposite gradient direction $\mathbf{d} = -\mathbf{g}$ (\mathbf{d} : direction of step; \mathbf{g} : gradient)
- Do a “line minimization” until the minimum in that direction is reached;
repeat.
- Simple approach guaranteed to find minimum but may be slow; suffers from
zig-zags.

Conjugate gradient methods

- Improvement on Steepest Descent; attempts not to spoil previous progress
- Do line minimizations in a direction which is a combination of the current gradient and the previous one:

$$\mathbf{d}_i = -\mathbf{g}_i + \beta_i \mathbf{d}_{i-1}$$

- The different conjugate-gradient methods provide different ways to choose β ; they involve dot products of current and previous gradients, e.g., Polak-Ribiere:

$$\beta_i^{PR} = \frac{\mathbf{g}_i^\dagger (\mathbf{g}_i - \mathbf{g}_{i-1})}{\mathbf{g}_{i-1}^\dagger \mathbf{g}_{i-1}}$$

Newton-Raphson (NR) Methods

Expand the energy function to second order around the current geometry \mathbf{x}_0 :

$$V(\mathbf{x}) \approx V(\mathbf{x}_0) + \mathbf{g}^T(\mathbf{x} - \mathbf{x}_0) + \frac{1}{2}(\mathbf{x} - \mathbf{x}_0)^T \mathbf{F}(\mathbf{x} - \mathbf{x}_0)$$

If we find the stationary point ($dV/d\mathbf{x}$) of this energy expression, we obtain:

$$(\mathbf{x} - \mathbf{x}_0) = -\mathbf{F}^{-1}\mathbf{g}$$

This makes intuitive sense: think of 1D harmonic oscillator. We would need larger geometry displacement if **gradient is larger** or **force constant is smaller**.
The step is exact in case of quadratic PES and exact gradient and Hessian

Newton-Raphson with Diagonal Hessian

Suppose the Hessian matrix \mathbf{F} is diagonalized to give normal modes and eigenvalues:

$$\mathbf{F}\mathbf{q}_i = \varepsilon_i \mathbf{q}_i$$

The Newton-Raphson step in terms of the normal modes becomes

$$(\mathbf{x} - \mathbf{x}_0) = \sum_i \frac{-(\mathbf{g}^T \mathbf{q}_i)}{\varepsilon_i} \mathbf{q}_i$$

i.e. component of the gradient in each normal mode direction

NR step **minimizes** along directions with a positive Hessian eigenvalue ε_i and **maximizes** along directions with a negative eigenvalue. It finds minimum if all ε_i are positive (\mathbf{F} positive definite), otherwise a saddle point if some ε_i are negative.

Big problems if the Hessian has the wrong “local structure.” This can sometimes solve by level shifting to make Hessian \mathbf{F} positive definite:

$$(\mathbf{x} - \mathbf{x}_0) = \sum_i \frac{-(\mathbf{g}^T \mathbf{q}_i)}{\varepsilon_i - \lambda} \mathbf{q}_i$$

Obtaining the Hessian

Can compute analytically if the program allows it, but can be slow (can take 10 times as long as energy alone) and memory demanding; cost scales at least as $O(N^3)$

Can approximate using tables or lower level computations

lower-level computations are often used to provide initial Hessian, e.g.

Target geometry optimization at B3LYP/cc-pVTZ → initial Hessian calculation with HF/cc-pVDZ

Can improve approximate Hessian using gradient information gained during optimization: Davidon-Fletcher-Powell (DFP), Broyden-Fletcher-Goldfarb-Shanno (BFGS), Powell, etc.

Choice of coordinates

- Z-matrix coordinates: old-style, inefficient
- Cartesian coordinates: even worse, un-natural, not like normal modes, more of them ($3N$ vs $3N - 6$)
- Internal coordinates: simple and symmetry-adapted
- Natural internal coordinates/redundant internal coordinates (Peter Pulay): similar to symmetry-adapted internals, commonly used now

Multiple minima

- For large molecules, multiple minima become possible
- Thermodynamic properties arise from Boltzmann distribution of all energetically accessible minima
- Can be hard to locate all relevant minima; search depends on initial guess geometries (and Hessians)
- Methods to help find additional minima:
 - genetic algorithms
 - molecular dynamics
 - Monte Carlo methods
 - simulated annealing

Constrained geometry optimization

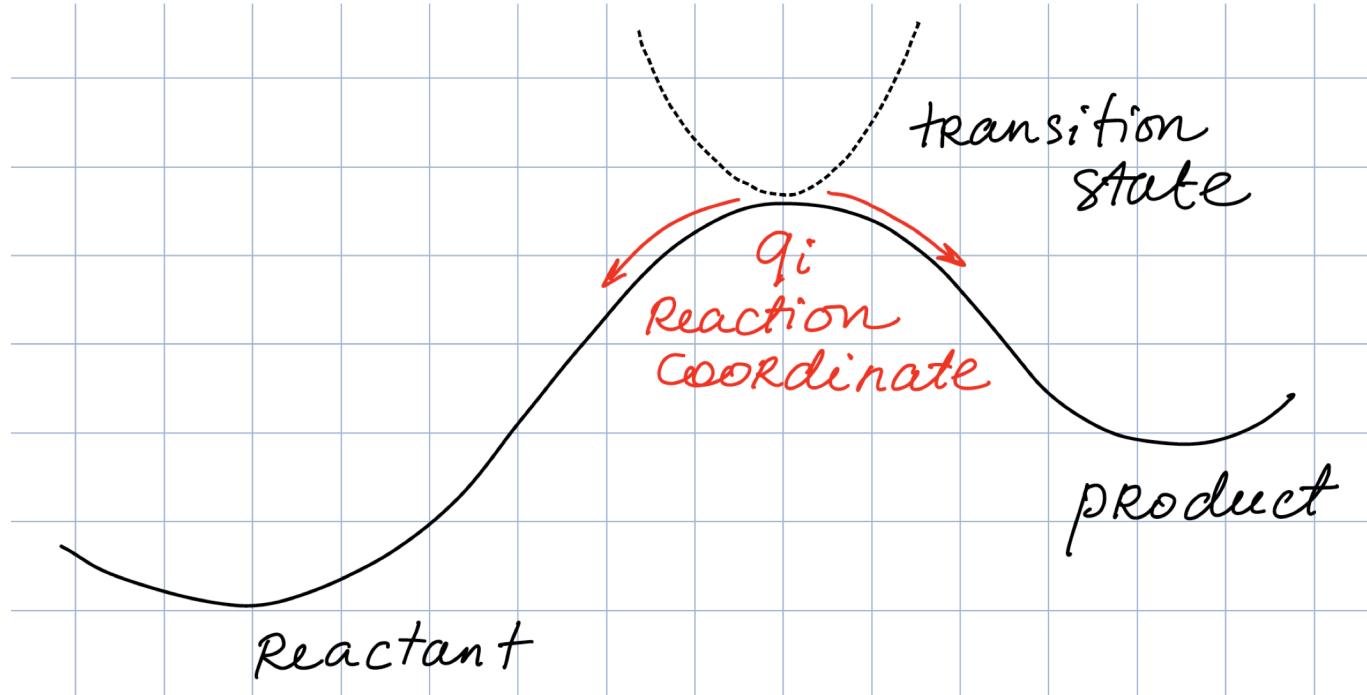
Sometimes it's useful to fix a geometrical parameter and perform the optimization subject to this constraint

Can rewrite function to be minimized as a Lagrange function L which is the original function minus a Lagrange multiplier λ times a constraint function g :

$$L(x_1, x_2, \dots, x_N, \lambda) = f(x_1, x_2, \dots, x_N) - \lambda g(x_1, x_2, \dots, x_N)$$

Constrained optimizations might be more cumbersome to converge

Locating transition state



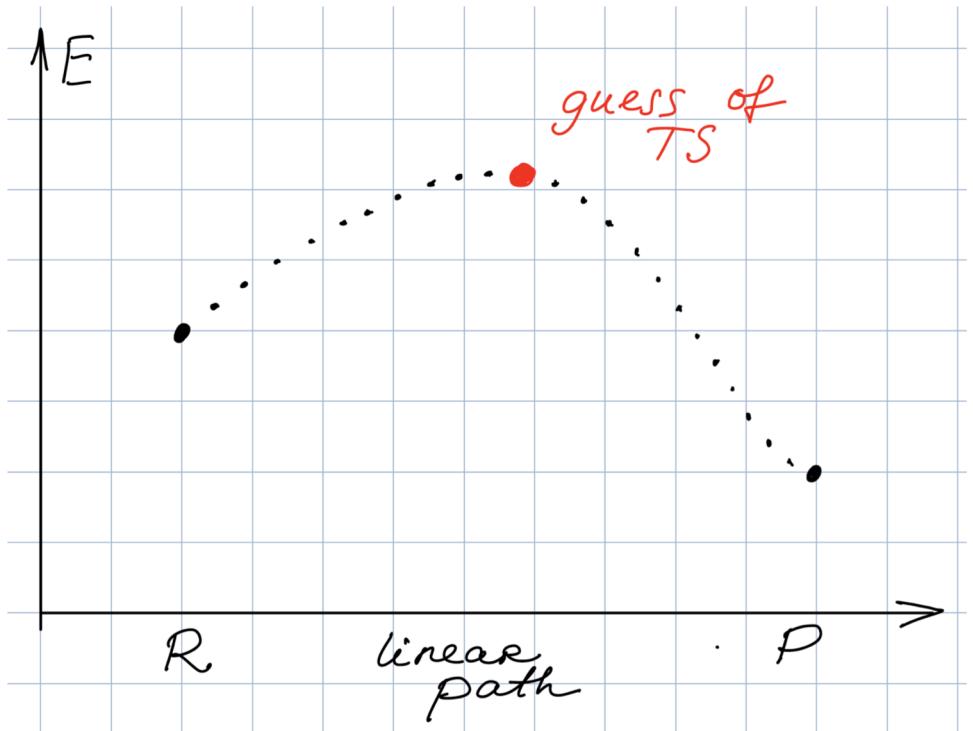
The normal mode corresponding to the imaginary frequency at TS leads downhill to reactants and products. This is a **reaction coordinate**.

The whole reaction path may be computed by sliding downhill to each side of the TS. The reaction path in mass-weighted coordinates is called the **Intrinsic Reaction Coordinate (IRC)**.

To prove that reaction goes between particular reactants and products, reactants and products should be connected by IRC.

Locating Transition State

- Finding a local minimum on a molecular PES is typically straightforward
- Finding a saddle point (TS) is much more challenging: we need to find a minimum for all but one normal coordinates; going uphill along a particular normal coordinate might be a problem



Linear Least Motion (LLM) path: connects reactants and products with a guess reaction path by displacing all coordinates linearly

Better, perform constrained optimizations at LLM geometries (optimize all but reaction coordinate)

The point with the highest energy along LLM path is a **guess of the TS**

1. At the guess TS, compute Hessian.
2. If only one imaginary frequency, perform a transition state calculation (follow this imaginary frequency normal mode uphill).
3. If successful, perform IRC calculations in two directions - toward reactants and products – this is following imaginary frequency coordinate downhill.
4. Check obtained reactant and product structures. Success?

Locating transition state

First-hand experience:

- Locating the TS is tricky
- LLM – useful, but thinking is required
 - $\text{H}_2 + \text{CH}_3$
 - $\text{HCN} \rightarrow \text{CNH}$ (choice of reaction coordinate!)
- Common problems in locating TS:
 - HF (or DFT) might not converge (TS is often near electronic state crossings, mixed wf character)
 - More than one imaginary frequency in Hessian at the guessed TS
- TS calculation (going uphill along imaginary normal mode) often does not work if started far from a real TS. Why? Vibrational analysis is not valid at non-stationary point, i.e. imaginary normal mode is not accurate.

Locating TS state in Q-Chem

Geometry optimization: `jobtype=opt`

Computing Hessian & vibrational frequencies: `jobtype=freq`

Finding a guess of TS with a freezing string method (need reactant and product structures):
`jobtype=fsm`

(see webinar by Martin Head-Gordon <https://www.youtube.com/watch?v=JBBblxGEXxo>)

TS search (following the imaginary normal mode uphill): `jobtype=ts`

Calculating IRC path starting from the TS: `jobtype=rpath` (need to start from a real TS,
need hessian as an input)

Potential energy scan with constrained geometry optimizations `jobtype=pes_scan`