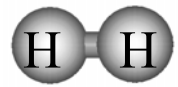
Introduction to Geometry Optimization

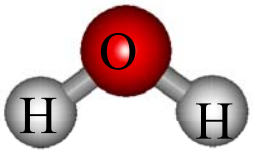
Computational Chemistry lab

2014

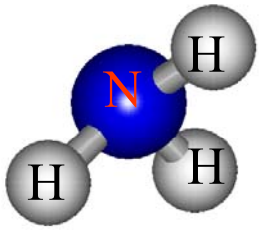
Determination of the molecule configuration



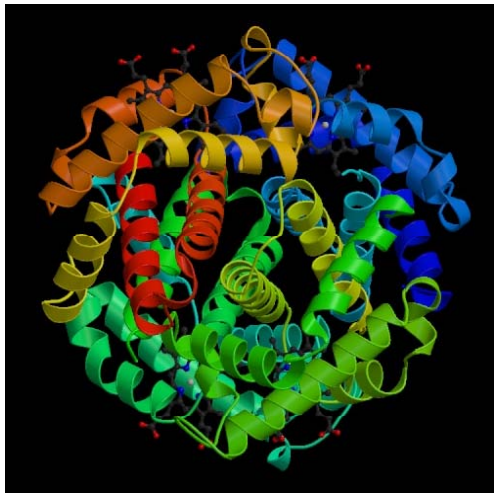
- Diatomic molecule – determine the interatomic distance



- Triatomic molecule – determine distances and the angle



- Four-atomic molecule – determine angles and distances



3N- 6 parameters for an N-atomic molecule (N>2)
(3N atomic coordinates-3 c.o.m coordinates -3 angles)

Optimal configurations correspond to minima of the energy as a function of these parameters

Solution of the Schrödinger equation in the Born-Oppenheimer approximation:

$H_{tot} = (T_n + V_n) + T_e + V_{ne} + V_e = (H_n) + H_e$

Electronic SE: $H_e \Psi(r,R) = E_e(R) \Psi(r,R)$

Ab-initio or *semi-empirical* solution

$E_e(R)$ **– electronic energy**

R **– nuclear coordinates**

$V_n(R)$ **– nuclei-nuclei interaction**

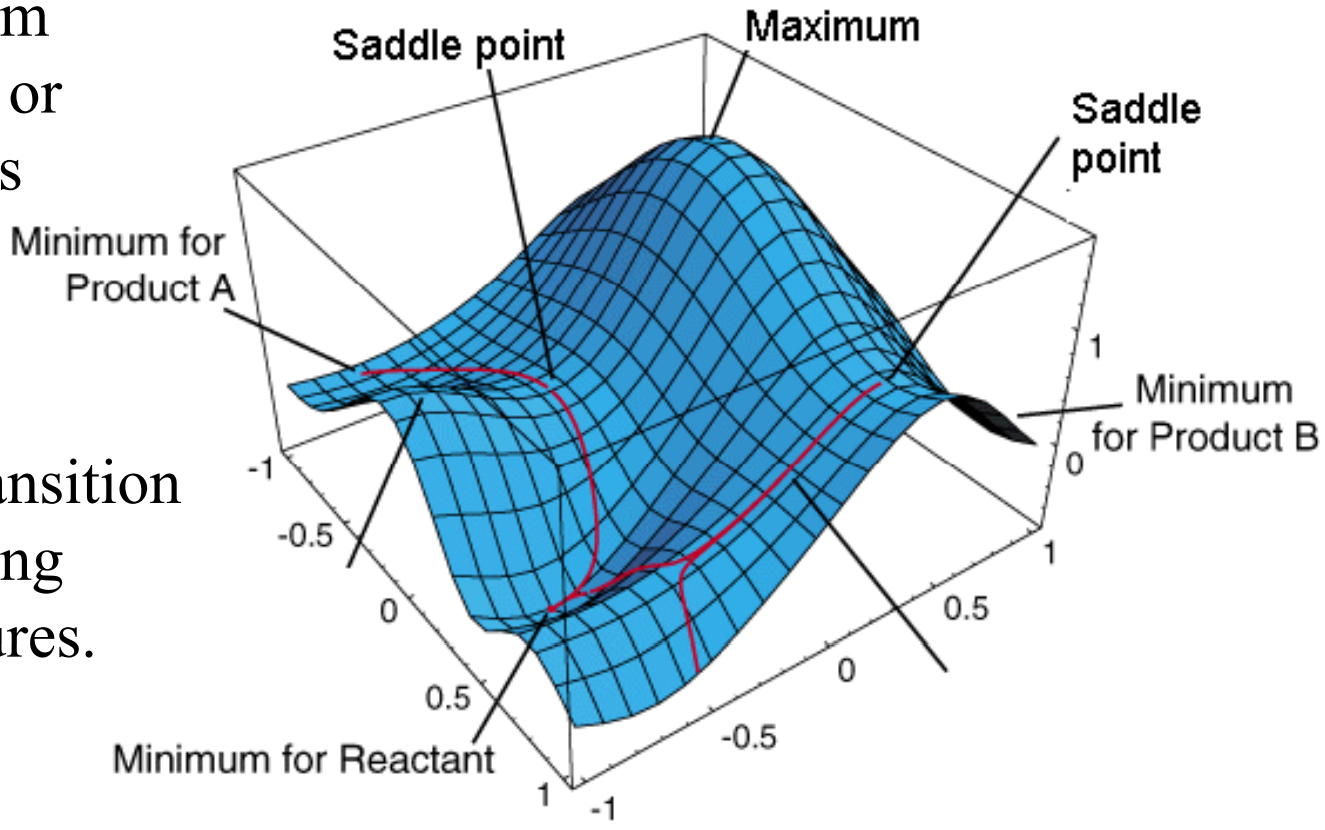
$E(R) = V_n(R) + E_e(R)$ **=** potential energy surface **(PES)**

Molecular mechanics: PES ←molecular force field

Potential Energy Surface (PES)

A hypersurface in 3*N*-6 -dimensional hyperspace, where *N* is the number of atoms.

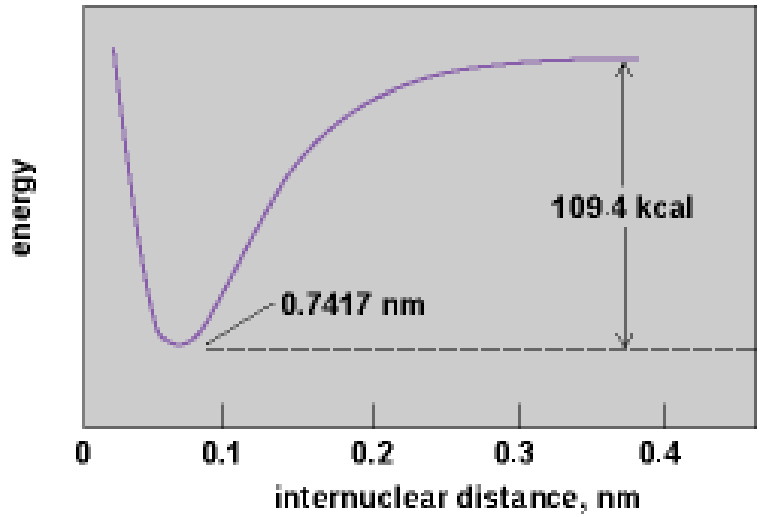
Minima– equilibrium structures of one or several molecules

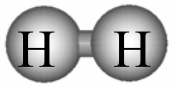


Saddle points - transition structures connecting equilibrium structures.

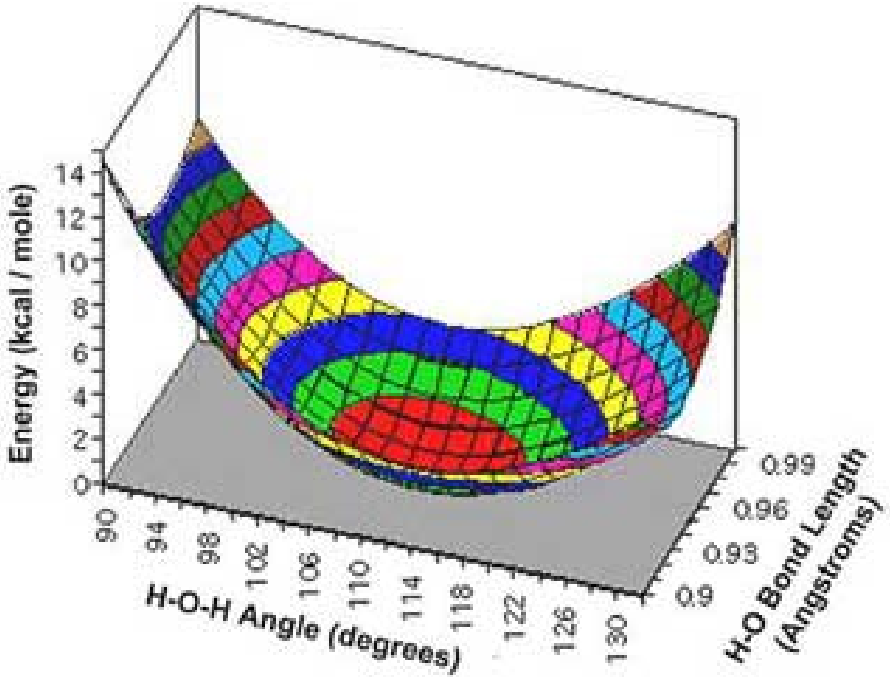
Global Minimum - that point that is the lowest value in the PES

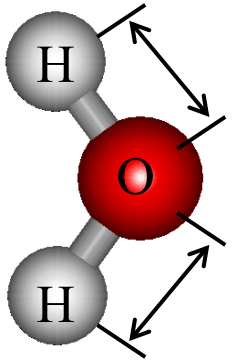
H_2

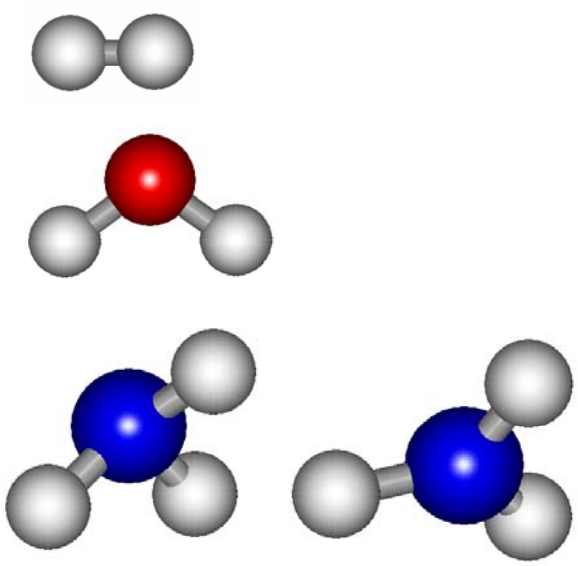

energy
109.4 kcal
0.7417 nm
0
0.1
0.2
0.3
0.4
internuclear distance, nm


H
H

H_2O – 3N-6=3


Energy (kcal / mole)
14
12
10
8
6
4
2
0
90
94
98
102
106
110
114
118
122
126
130
H-O-H Angle (degrees)
0.99
0.96
0.93
0.9
H-O Bond Length (Angstroms)

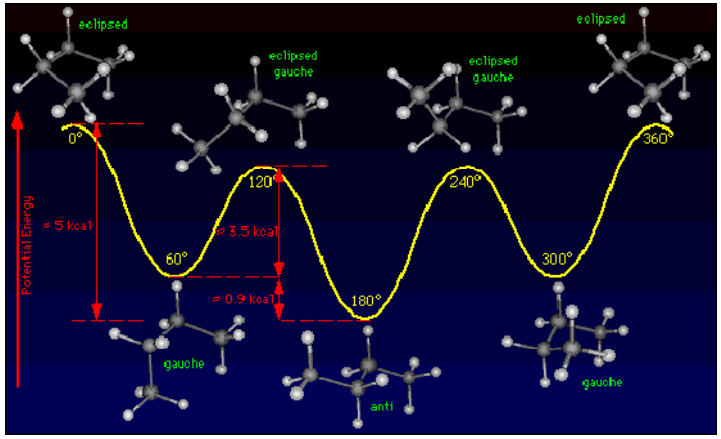

H
O
H



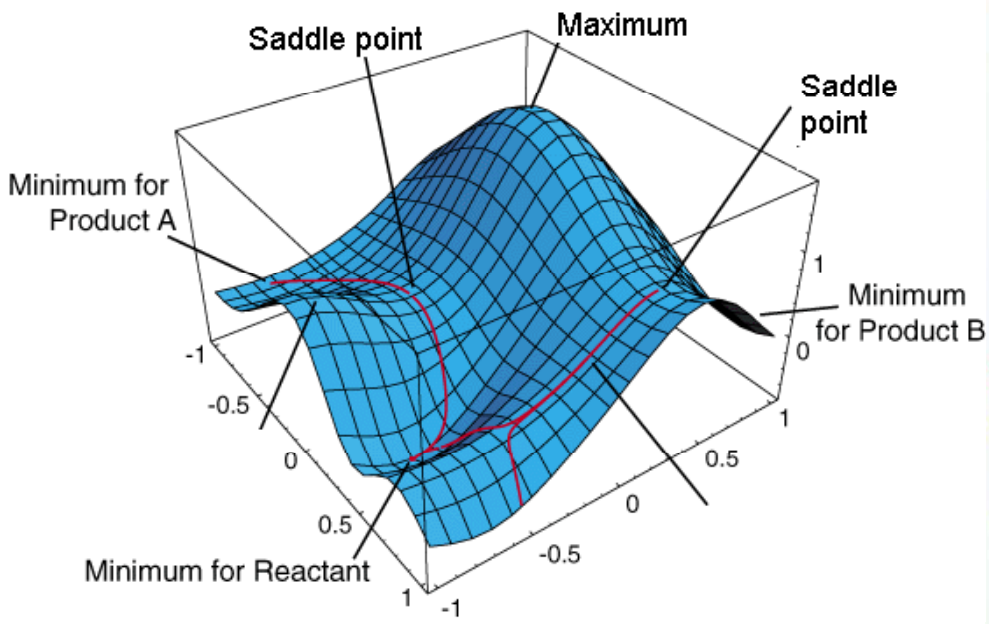
- One configuration is known for H_2
- One configuration is known for H_2O
- The planar and pyramidal configurations are known for NH_3

The number of local minima typically goes exponentially with the number of variables (degrees of freedom). Combinatorial Explosion Problem

Possible Conformations (3^n) for linear alkanes $CH_3(CH_2)_{n+1}CH_3$



$n = 1$	3
$n = 2$	9
$n = 5$	243
$n = 10$	59,049
$n = 15$	14,348,907

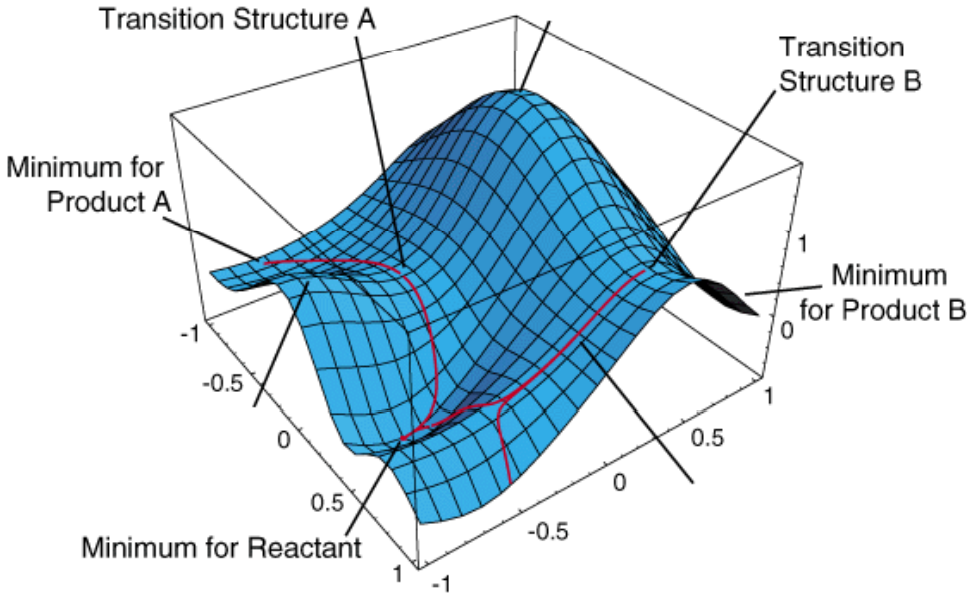


Global minimum
- Mariana Trench
in the Pacific Ocean

Optimization/Goals

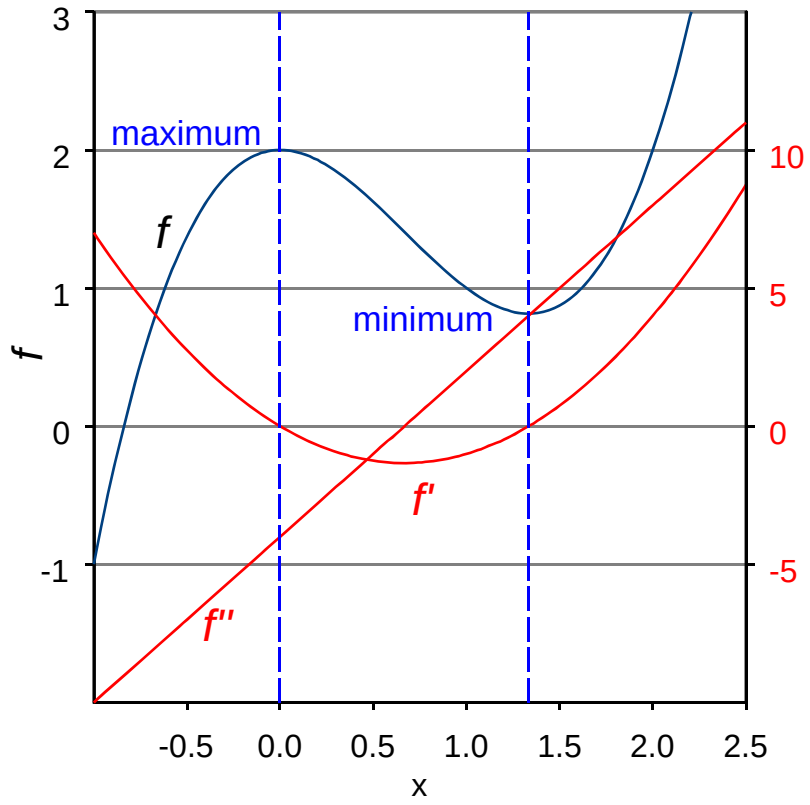
- Find the Local Minimum Structure
- Find the Global Minimum Structure
- Find the Transition State Structure

We would like to Find the Reaction Pathway Connecting Two Minima and Passing through the Transition State Structure



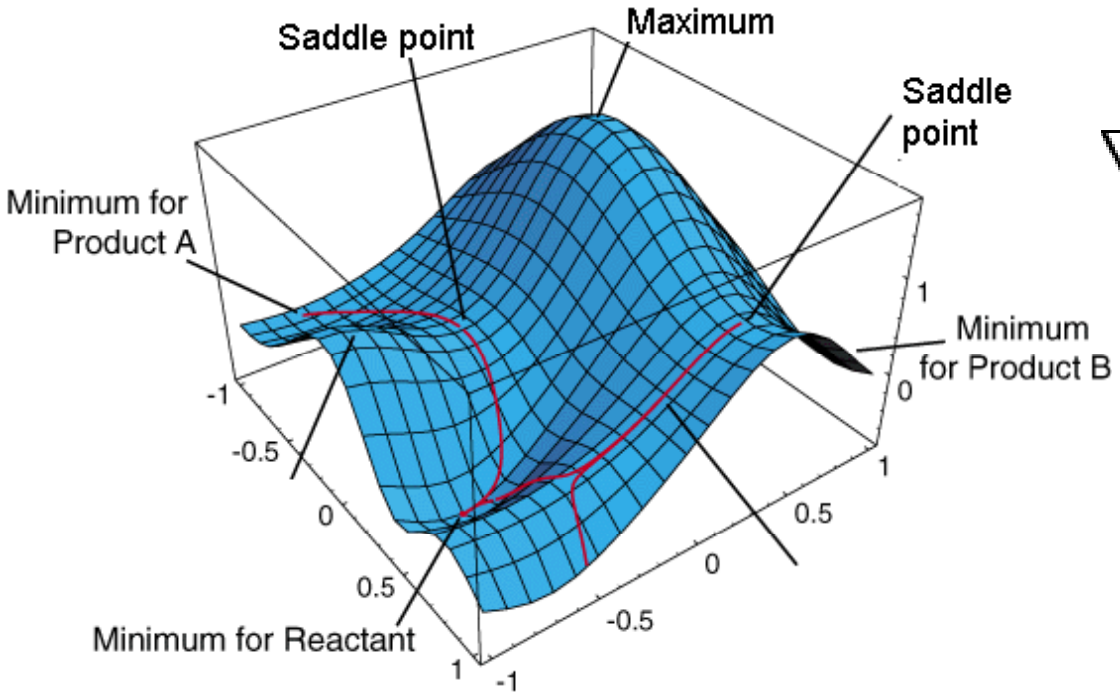
Geometry optimization is the name for the procedure that attempts to find the configuration of minimum energy of the molecule.

One-dimensional optimization



- $f'(x)=0$ – stationary point
- $f''(x)<0$ – maximum
- $f''(x)>0$ – minimum

Multidimensional Optimization



$$\nabla f = \left(\frac{\partial f}{\partial x_1}, \cdots, \frac{\partial f}{\partial x_n} \right)$$

- gradient

The coordinates can be Cartesian (x,y,z..), or internal, such as bondlength and angle displacements)

Force: $F = -\nabla E$ (Potential energy)

$\nabla f = 0$ - Stationary Point (minimum, maximum, or saddle point)

Hessian matrix

A matrix of second-order derivatives of the energy with respect to atomic coordinates (e.g., Cartesian or internal coordinates)
Sometimes called force matrix – matrix size of (3N-6)x(3N-6)

$$H_{ij}(f) = \frac{\partial^2 f}{\partial x_i \partial x_j}$$

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

Quadratic approximation

Approximate the complex energy landscape by harmonic potentials around a stationary point $(x_1^{(st)},\ldots x_n^{(st)})$ $[\nabla E(x_1^{(st)},\ldots x_n^{(st)}) = 0]$

$$E(x_1,\ldots x_n) = E(x_1^{(st)},\ldots x_n^{(st)}) + \tfrac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} H_{ij}(E)(x_i - x_i^{(st)})(x_j - x_j^{(st)})$$

$$E(x_1,\ldots x_n) = E(x_1^{(st)},\ldots x_n^{(st)}) + \tfrac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} H_{ij}(E)(x_i - x_i^{(st)})(x_j - x_j^{(st)})$$

Hessian matrix diagonalization (eigenproblem) $\varepsilon_k l_j^{(k)} = \sum_{i=1}^{n} H_{ij} l_i^{(k)}$

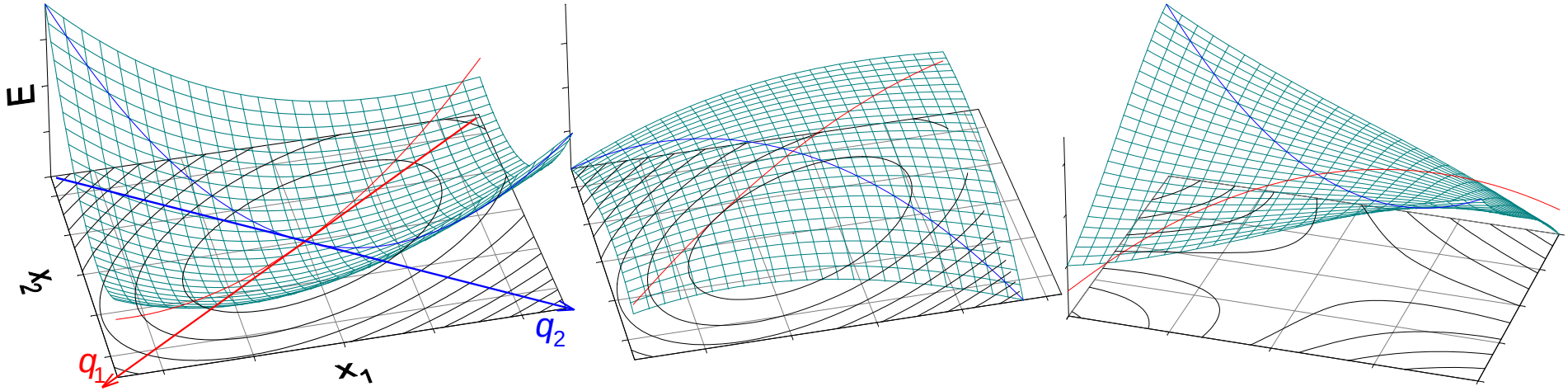
Eigenvalues $\varepsilon_k = m\omega_k^2$ ω_k - vibrational frequencies

Eigenvectors $l_j^{(k)}$ give normal coordinates $q_k = \sum_{i=1}^{n} l_i^{(k)}(x_i - x_i^{(st)})$

$$E(x_1,\ldots x_n) = E(x_1^{(st)},\ldots x_n^{(st)}) + \tfrac{1}{2}\sum_{k=1}^{n} \varepsilon_k q_k^2$$

All $\varepsilon_k > 0(\omega_k - \text{real})$ All $\varepsilon_k < 0(\omega_k - \text{imaginary})$ $\varepsilon_k <> 0(\omega_k - \text{imaginary/real})$

minimum maximum saddle point

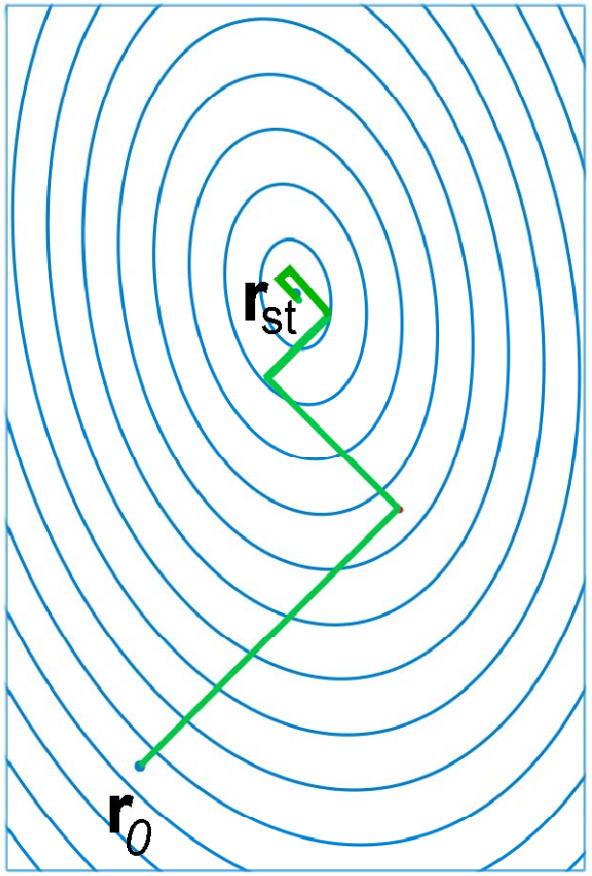


Steepest Descent

Steepest descent direction $\mathbf{g}=-\nabla E$

$\mathbf{r}=(x_1,\ldots x_n)$, $\mathbf{g}$ - (3N-6) -dimensional vectors

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \lambda_i \mathbf{g}_i / |\mathbf{g}_i|$$



Advantage:

- local minimization is guaranteed
- fast minimization far from the minimum

Disadvantage:

- slow descent along narrow valleys
- slow convergence near minima

In HYPERCHEM

$$\text{if } E(\mathbf{r}_{i+1}) < E(\mathbf{r}_i) \text{ then } \lambda_{i+1} = 1.2\lambda_i \text{ else } \lambda_{i+1} = 0.5\lambda_i$$

History gradient information is not kept

Conjugate Gradient Methods

Search direction is chosen using history gradient information

Initial direction – the steepest descent direction, $\mathbf{h}_0 = \mathbf{g}_0 = -\nabla E$

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \xi \mathbf{h}_i$$

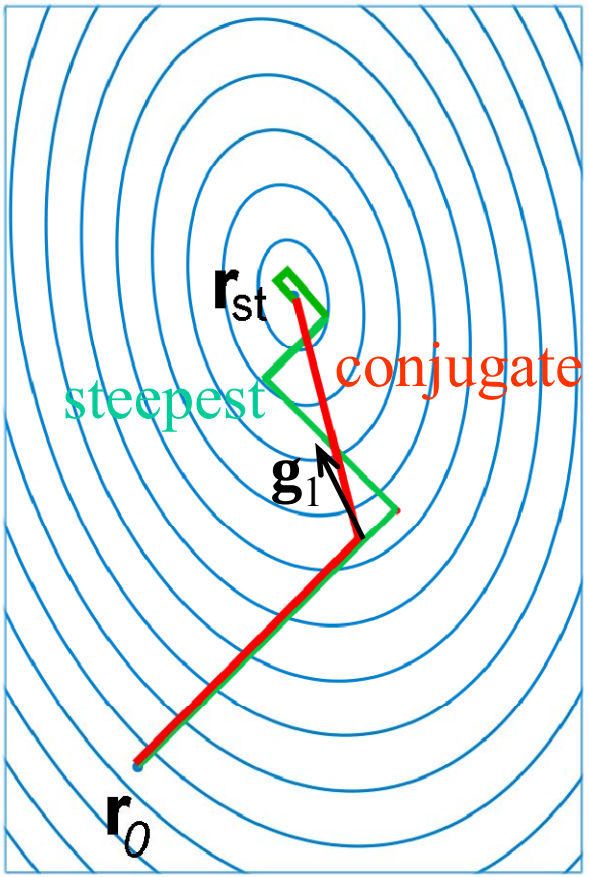
ξ is defined by a one-dimensional minimization along the search direction.

$$\mathbf{h}_{i+1} = \mathbf{g}_{i+1} + \gamma_{i+1}\mathbf{h}_i$$

Fletcher-Reeves method: $\gamma_{i+1} = \dfrac{|\mathbf{g}_{i+1}|^2}{|\mathbf{g}_i|^2}$

Polak-Ribiere method: $\gamma_{i+1} = \dfrac{(\mathbf{g}_{i+1} - \mathbf{g}_i)\mathbf{g}_{i+1}}{|\mathbf{g}_i|^2}$

Polak-Ribiere may be superior for non-quadratic functions.



Gradient history is equivalent to implicit use of the Hessian matrix.

Newton-Raphson Methods

Explicit use of Hessian matrix.

Quadratic approximation : $E(\mathbf{r}) = E(\mathbf{r}_0) - \sum_{k=1}^{n} (F_k q_k - \frac{1}{2}\varepsilon_k q_k^2)$

q_k- normal coordinates, $\mathbf{r} - \mathbf{r}_0 = \sum_{k=1}^{n} q_k \mathbf{l}_k$ $\quad \nabla E(\mathbf{r}_0) = -\sum_{k=1}^{n} F_k \mathbf{l}_k$

ε_k and $\mathbf{l}_k$ - eigenvalues and eigenvectors of the Hessian matrix at $\mathbf{r}_0$

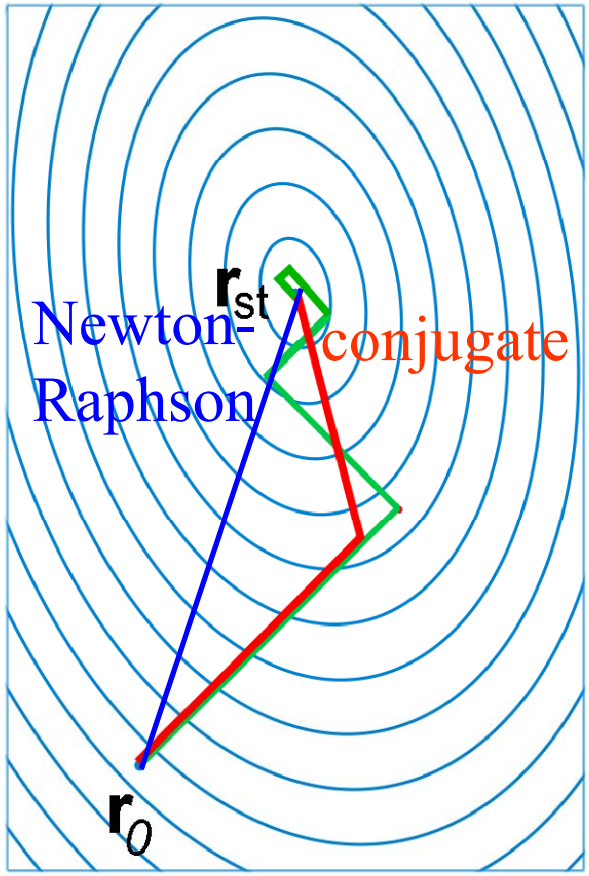
One-step optimization of quadratic functions $q_k = \frac{F_k}{\varepsilon_k} \Rightarrow \nabla E(\mathbf{r}) = 0$

For arbitrary functions

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \sum_{k=1}^{n} \mathbf{l}_k(\mathbf{r}_i) F_k(\mathbf{r}_i) / \varepsilon_k(\mathbf{r}_i)$$

Descent direction for $\varepsilon_k(\mathbf{r}_i) > 0$

Finds the closest stationary point (either minimum, maximum, or saddle point).



Obtaining, storing, and diagonalaizing the Hessian

Numerical calculation – $(3N)^2$ calculations of energy
Diagonalization - $(3N)^3$ operations
Memory - $(3N)^2$
Extremely expensive for large molecules.

Block Diagonal Newton-Raphson

$$\begin{pmatrix}
\frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial y_1} & \frac{\partial^2 E}{\partial x_1 \partial z_1} & 0 & 0 & 0 \\
\frac{\partial^2 E}{\partial x_1 \partial y_1} & \frac{\partial^2 E}{\partial y_1^2} & \frac{\partial^2 E}{\partial y_1 \partial z_1} & 0 & 0 & 0 \\
\frac{\partial^2 E}{\partial x_1 \partial z_1} & \frac{\partial^2 E}{\partial y_1 \partial z_1} & \frac{\partial^2 E}{\partial z_1^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{\partial^2 E}{\partial x_2^2} & \frac{\partial^2 E}{\partial x_2 \partial y_2} & \frac{\partial^2 E}{\partial x_2 \partial z_2} \\
0 & 0 & 0 & \frac{\partial^2 E}{\partial x_2 \partial y_2} & \frac{\partial^2 E}{\partial y_2^2} & \frac{\partial^2 E}{\partial y_2 \partial z_2} \\
0 & 0 & 0 & \frac{\partial^2 E}{\partial x_2 \partial z_2} & \frac{\partial^2 E}{\partial y_2 \partial z_2} & \frac{\partial^2 E}{\partial z_2^2}
\end{pmatrix}$$

Calculation - 9N

Diagonalization - 27N

Memory – 9N

Gaussian

The Hessian matrix is calculated and processed on the first step only
It is updated using the computed energies and gradients

Berny algorithm

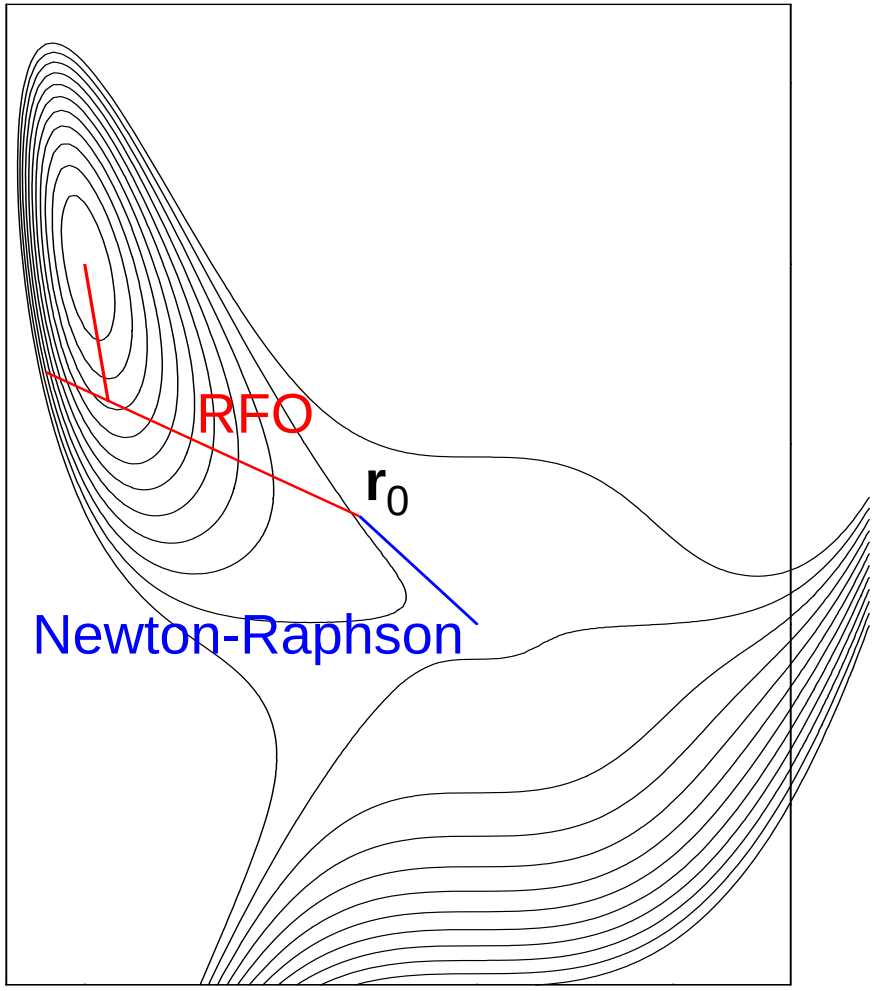
Rational function optimization (RFO) step

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \sum_{k=1}^{n} \mathbf{l}_k(\mathbf{r}_i) \frac{F_k(\mathbf{r}_i)}{\varepsilon_k(\mathbf{r}_i) - \lambda}$$

ε_k and $\mathbf{l}_k$ - eigenvalues and eigenvectors of the Hessian matrix at $\mathbf{r}_i$

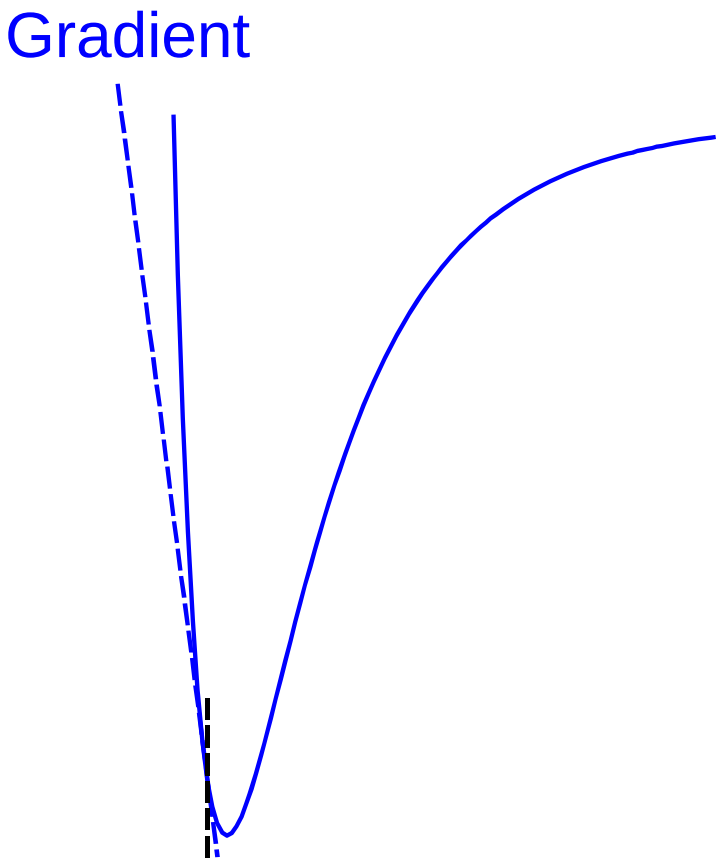
$\lambda < \min(\varepsilon_k)$ ($\lambda<0$ for $\varepsilon_k<0$)
- step always toward to a minimum.

A **linear search** between the latest point and the best previous point.



Convergence criteria

Gradient or force $\mathbf{F}=-\mathbf{g}=-\nabla E$



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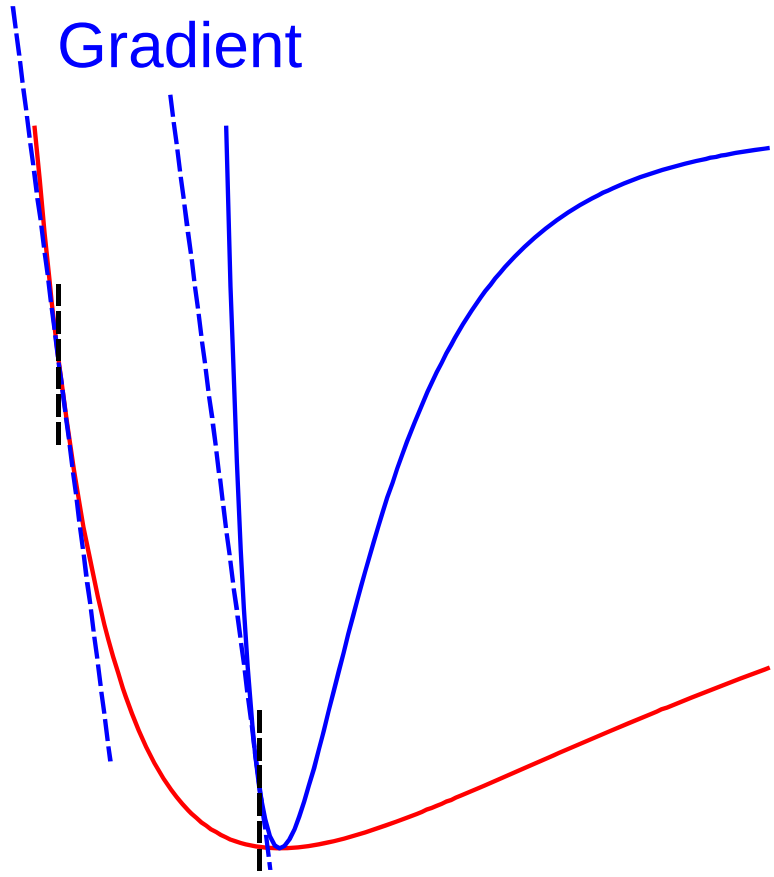


Convergence criteria

Gradient or force $\mathbf{F}=-\mathbf{g}=-\nabla E$

Predicted displacement $\mathbf{r}_{i+1}-\mathbf{r}_i$

Maximum force:

$\max(\mathbf{F})=\max(F_1,\ldots F_n)<\text{threshold}$

Root-mean-square (RMS) force:

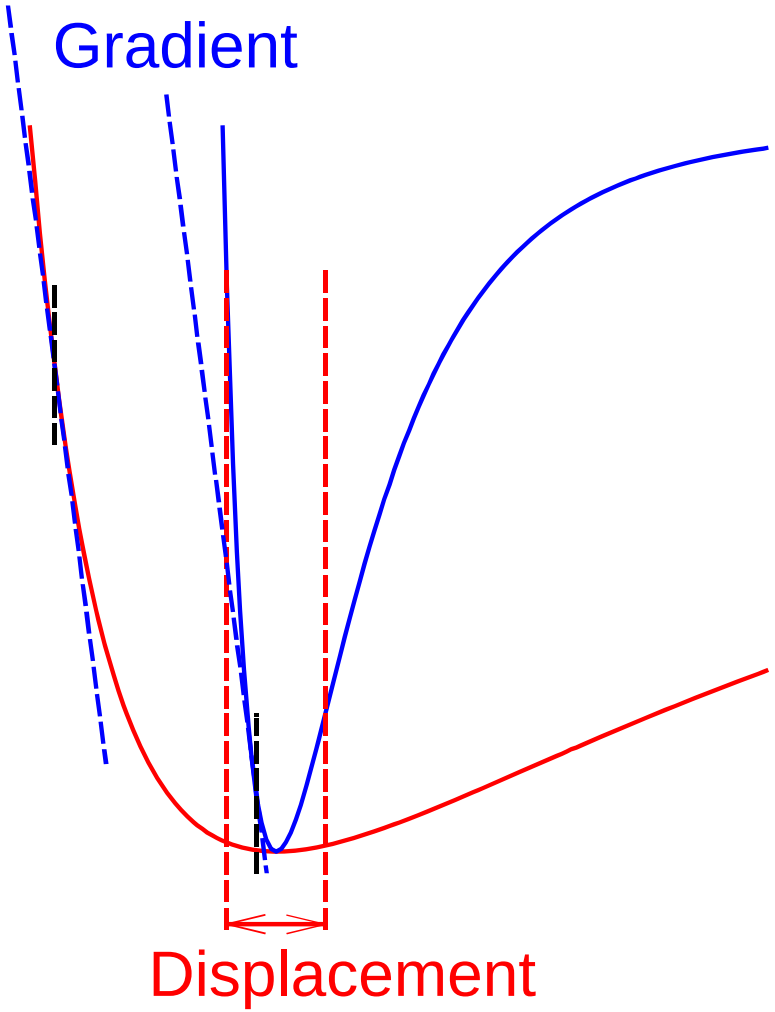
$$|\mathbf{F}|=\sqrt{(F_1^2+\cdots+F_n^2)/n}<\text{threshold}$$

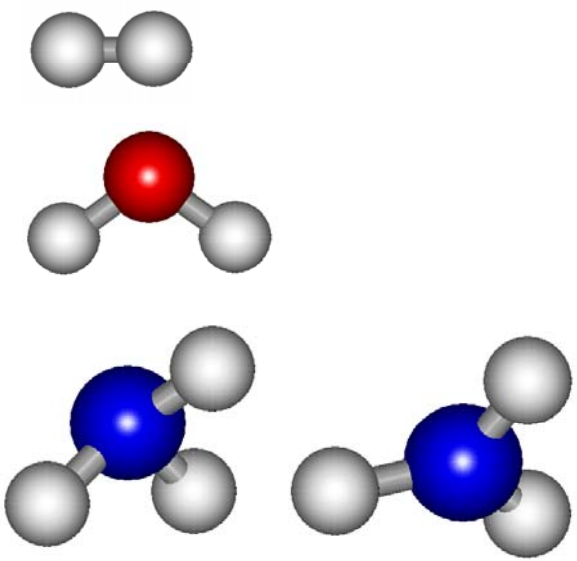
Maximum displacement:

$\max(\mathbf{r}_{i+1}-\mathbf{r}_i)<\text{threshold}$

RMS displacement:

$|\mathbf{r}_{i+1}-\mathbf{r}_i|/\sqrt{n}<\text{threshold}$





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- One configuration is known for H_2O
- The planar and pyramidal configurations are known for NH_3

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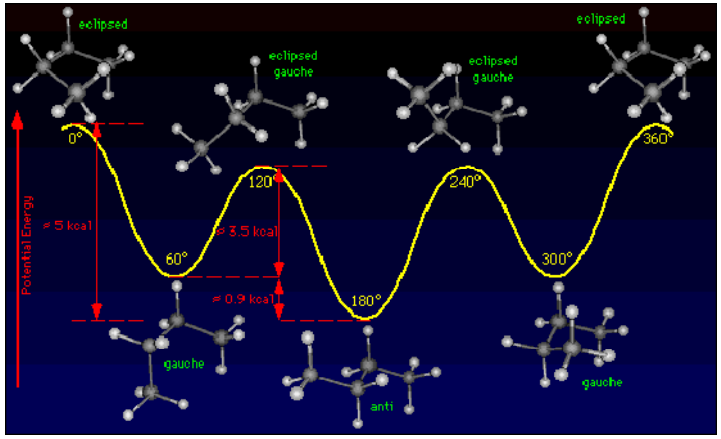

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Global minimization

- **"building up" the structure**: combining a large molecule from preoptimized fragments (protein from preoptimized aminoacids)
- **conformational sampling**: take various starting points for local minimization (simulation of nature)
- None of these are guaranteed to find the global minimum!

Global Minimum- conformational sampling

- Molecular Dynamics
- Monte Carlo
- Simulated Annealing
- Tabu search
- Genetic Algorithms
- Ant Colony Optimizations
- Diffusion Methods
- Distance Geometry Methods