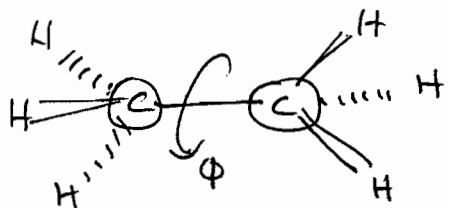# Potential Energy Surface

Once we have chosen a force field, we can analyse the conformations and dynamics of molecules of interest.
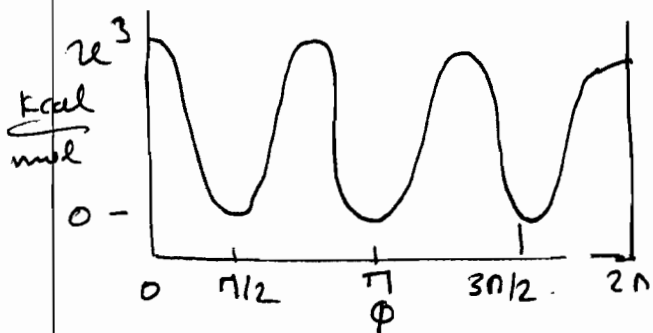
In one dimension, things are simple

e.g. rotation of CH_3-CH_3 Single bond in ethane

minima at $60°, 180°, 200°$

maxima " $0, 120°, 240°$

In general

$f(x)$ has extremum if

$$\frac{df}{dx} = 0 \quad \left\{ \begin{array}{l} \text{to check} \\ \text{max of min,} \end{array} \right. \Rightarrow \frac{d^2f}{dx^2} > 0 \text{ min}; \quad \frac{d^2f}{dx^2} < 0 \text{ max}$$

For functions of many variables, things are not so simple; for N atoms, we have in principle $3N$ degrees of freedom (variables), but 6 are trivial (position + rotation of molecule as a whole). There are $3N-6$ <u>internal coordinates</u>

$$\mathcal{U} = \mathcal{U}(\vec{q}) \quad \text{where} \quad \vec{q} = \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_P \end{pmatrix} \quad \begin{array}{l} P = 3N-6 \\ (3N-5 \text{ for} \\ \text{linear}) \end{array}$$

A _stationary point_ of the function u is one for which

$$\vec{g} = \nabla u = \left\{ \begin{array}{c} (\partial u/\partial q_1)_{q_2,\ldots q_p} \\ (\partial u/\partial q_2)_{q_1, q_3 \ldots q_p} \\ \vdots \\ (\partial u/\partial q_p)_{q_1, q_2 \ldots q_{p-1}} \end{array} \right\} = 0$$

Of course, we do not know if a stationary point is a maximum or a minimum until we check the eigenvalues of the Hessian matrix:

$$\underline{\underline{H}} = \begin{bmatrix} \dfrac{\partial^2 u}{\partial q_1^2} & \cdots & \dfrac{\partial^2 u}{\partial q_1 \partial q_p} \\ \vdots & & \\ \dfrac{\partial^2 u}{\partial q_p \partial q_1} & \cdots & \dfrac{\partial^2 u}{\partial q_p^2} \end{bmatrix}$$

If all eigenvalues > 0 ⇒ min

If all eigenvalues < 0 ⇒ min

If some are < 0 and some > 0 ⇒ "saddle point"

Finding Minima

For functions of many variables, it is impractical to try to evaluate them on a grid. Instead, one uses sophisticated numerical methods developed over many years by applied mathematics researchers. A few common methods:

    (a) _First-order methods_ : only use $\vec{g} = \nabla u$ the gradient of u

Steepest descent : calculate $\nabla u = \vec{g}$, move along $-\vec{g}$ to a local (linear) minimum ; repeat.
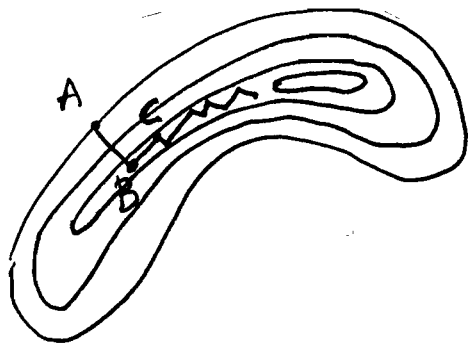
$$A \rightarrow B \rightarrow C \rightarrow \cdots .$$

Can take a long time to locate minimum ; fairly robust

Conjugate Gradient (Fletcher-Reeves, 1964)

iteration (k) is at $\vec{q}^{(k)}$; move along

$$\vec{V}^{(k)} = -\vec{g}^{(k)} + \gamma^{(k)} \vec{V}^{(k-1)} \quad \text{where} \quad \gamma^{(k)} = \frac{\left(\vec{g}^{(k)}\right)^T \vec{g}^{(k)}}{\left(\vec{g}^{(k-1)}\right)^T \vec{g}^{(k-1)}}$$

Method is faster than steepest descent - does not move just at right angles

ⓑ Second-order Methods

These require calculation of the Hessian, analytically or numerically; they are faster, but may fail to converge if the initial guess is poor.
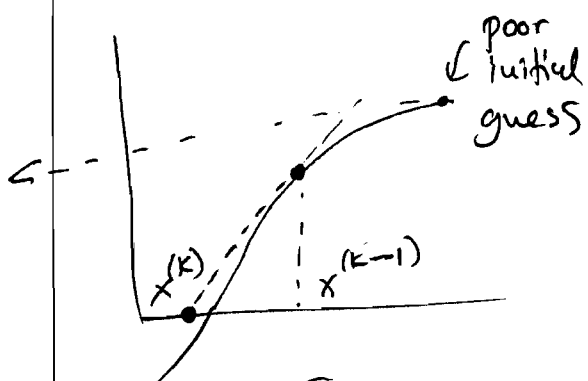
Newton-Raphson

Solves $f(x) = 0$ by setting

$$x^{(k)} = x^{(k-1)} - \frac{f^{(k)}}{g^{(k)}} \leftarrow \text{derivative in 1D}$$

poor
← initial
guess

For minimization, need $f'(x) = 0$

$$\vec{X}^{(k)} = \vec{X}^{(k-1)} - \left(\underline{\underline{H}}^{(k-1)}\right)^{-1} \cdot \nabla f$$

$f^{(k)}$, $x^{(k)}$, $x^{(k-1)}$

(Gives quadratic (fast) convergence near solution)

All energy minimitation methods require a numerical criterion for ending the calculation —

e.g. * maximum tolerance for final gradient

* maximum number of iterations

Intro to Hyperchem

(from online notes)

- creating a molecule

- adding H

- selecting a force field, looking at parameters

- energy minimizing the structure

- measuring molecular parameters (bond lengths, angles)

- 1D potential

- Simple "grid" properties: molecular volume + surface area