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Expt. No. 9-3 Energy Minimisⁿ & TS search Page No. .....

- Method of energy minimisⁿ :
  - Multivariate grid search
  - Steepest descent method
  - Newton Raphson
  - Hessian matrix

→ In order to reach the energy minᵐ the 1st derivative of the system wrt each parameter must be zero and derivative must be +ve.

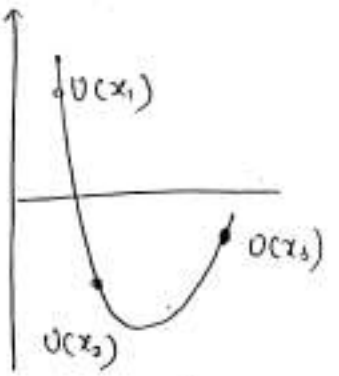
Zero order methods: No requirement of derivative
First " " : 1st order derivative
and " " : Hessian ; 1st order + 2nd order derivative

→ Ideal minimisⁿ algorithm is one that provides the minᵐ as quickly as possible using the least amt of minᵐ & no single minimisⁿ method has yet proved to be best for all the MM problems.

① Multivariate Grid Search

1. Choose a suitable grid for the variable
2. Choose a starting point on this grid.
3. For each variable $q_1, q_2 \cdots q_p$ evaluate the molecular PE (U) at the two point surrounding A.
4. Select the new point for which U is min^m & repeat the step 3 & 4 until the local min^m is identified.

This method is intuitive & it is apparent that a local min^m will eventually be found.



(a) Univariate Search

→ also called cyclic search, for we perform successive 1-D searches for each of the variable in turn. for each coordinate a new str are generated by changing the current coordinate The energy for these 2 are calculated & a parabola is fitted through these points & the minimum of the parabola is completed

→ In this case we choose a starting point minimise the U(q) potential for each variable $q_1, q_2, q_3 \cdots q_n$ in turn. To minimise U(q) we carry out quadratic interpolation or we fit a parabola through these 3 points such that they bracket the min^m in the particular variable.

$$\alpha \cdot \frac{1}{2} \left(\frac{U(x_1)(x_3^2 - x_2^2) + U(x_2)(x_1^2 - x_3^2) + U(x_3)(x_2^2 - x_1^2)}{U(x_1)(x_3 - x_2) + Ux_2(x_1 - x_3) + Ux_3(x_2 - x_1)} \right)$$

First Order Derivative Method:

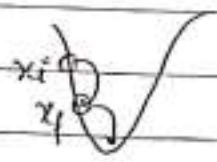
(1) Steepest Ducent Method
(2) Conjugate - gradient

The 1st order derivative is gradient or the dirⁿ of the 1st derivative indicate that where the minᵐ lie. The magnitude indicate the steepness of the local slope. The energy of the system can be lowered by moving each atom in response to the force acting on it. The force is equal to minus of gradient.
The 2nd derivative indicate the curvature of the fn which can be used to predict that where the fn will change the dirⁿ i.e, whether it will pass through a minᵐ or some other stationary point.

1) Steepest ducent Method-

a) Calculate U for the initial structure
b) Calculate U for structure where each atom is moved along x, y and z-axis by a small increment. Movement of some atoms will lead to a small change in U, whilst movements of other atoms will lead to large change in U.
c) Move the atoms to new posⁿ such that the energy U ↓ by the maxᵐ possible amt.
d) Repeat the relevant steps until a local minᵐ is found

for 1D PES



$\gamma \rightarrow$ Const (empirically determined)

$V(x_i) : \Delta V(x_i)$

$x_f : x_i - \gamma \Delta V(x_i)$

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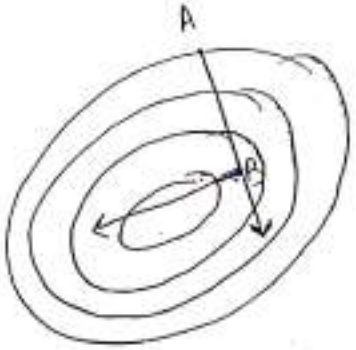
$|| V(x_i) - V(x_{i+1})|| \simeq 0$ ⟶ Converges

$|| \Delta V(x_i) - \Delta V(x_{i+1})|| \simeq 0.$

$|x_i - x_{i+1}| \simeq 0$



2D - Surface

for a 2D PES we calculate the U for the initial str where each atom is moved along x,y,z axis by small increment. Move the atom to the new posn such that the energy loss by the maxm possible and taking the gradient into consider. So point B would be the new geometry. Starting B again we identify the fastest way down by utilising the gradient value & move to the new posn & to this n no of times till the convergence criteria is reached.

→ The -ve of the gradient of U at pt A gives the maxm rate of loss of the potential. So the dirn in which the geometry proceeds would be ⊥r to the contour A

Disadvantage of this method:

(i) Need to choose step size.

(ii) It takes many tiny steps when proceeding down along narrow valley bc it is tried to make a right angled turn at every pt even though it might not be the best route towards the minm.

for dirn: $S_k = \frac{-g_k}{|g_k|}$

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(2) Conjugate - Gradient Method

$x_f \cdot x_i - \beta \Delta v(x_i) + \gamma(h_i)$ — h → history factor

$h_i \cdot \Delta v(x_i) + \gamma(h_{i-1})$ — T → transpose

K → iterⁿ

γ = empirical factor

g → gradient

$$\gamma^{(K)} = \frac{(g^{(K)})^T g^{(K)}}{(g^{(K-1)})^T (g^{(K-1)})}$$ → fletcher & reeves

In the steepest descent method both the gradient & the dirⁿ of successive steps are orthogonal but in conjugate - gradient the gradients at each pt are orthogonal but dirⁿ are conjugate.

$$\gamma^{(K)} = \frac{(g^{(K)} - g^{(K-1)})^T g^{(K)}}{(g^{(K-1)})^T g^{(K-1)}}$$ (E. Polak & G. Ribiere)

~~for posⁿ $x_{K+1} = x_K - \gamma(\Delta v(x_K)) + \beta h_i$~~

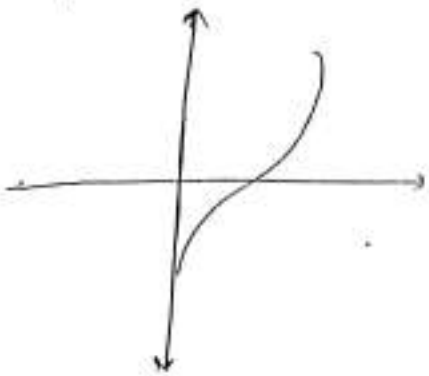
~~for dirⁿ $v_K = -g_K + \gamma v_{K-1}$~~

for dirⁿ ; $v^{(K)} = -g^{(K)} + \gamma^{(K)} v^{(K-1)}$

for posⁿ ; $x^{(K+1)} = x^{(K)} - \gamma(\Delta v(x_i)) + \beta(h_i)$

Second Order Methods:

① Newton - Raphson Method -



$$V_x = V_{x_k} + (x - x_k) V'(x_k) + (x - x_k)^2 V''(x_k)/2! + \cdots$$

$$V'_x = x V'(x_k) + (x - x_k) V''(x_k) + \cdots$$

at min^m;

$x = x^*$

$V'(x) = 0$

$$x^* = x_k - \frac{V'(k)}{V''(k)}$$

$$x^* = x_k - V''^{-1}_{(k)} V'(k)$$

↳ Inverse hessian matrix

→ valid for quadratic method.

→ Inverse Hessian matrix must be +ve.

Since $V''^{-1}(k)$ is the inverse hessian matrix of 2nd derivative, calculating this be computationally demanding for the system for many atoms & thus require significant amt of storage.

∴ NRM is suited for small molecules i.e; around 100 atom

For a purely quadratic fn NR can find the min^m in just one step. Ex:

$$f(x,y) = x^2 + 2y^2$$

guess value = $\begin{pmatrix} 9 \\ 9 \end{pmatrix}$

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$x^2 + 2y^2$.

$\frac{\partial f}{\partial x} = 2x \quad ; \quad \frac{\partial f}{\partial y} = 4y$

$= 18 \qquad 36$

$g_k = \begin{pmatrix} 18 \\ 36 \end{pmatrix} \qquad H_k = \begin{pmatrix} 2 & 0 \\ 0 & 4 \end{pmatrix} \qquad H^{-1}_k = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/4 \end{pmatrix}$

$x^* = \begin{pmatrix} 9 \\ 9 \end{pmatrix} - \begin{pmatrix} 1/2 & 0 \\ 0 & 1/4 \end{pmatrix} \begin{pmatrix} 18 \\ 36 \end{pmatrix}$

$x^* = 0$

If the surface is not quadratic, a greater no. of steps would be reqd & for each step the hessian matrix must be calculated and inverted ∴ makes this method computationally demanding.

→ $\nabla^2 f(x_k)$ must be a +ve definite matrix i.e; one for ∀ all the eigen values are +ve. This is b/c if it is not +ve than NR moves to a point where energy rises & in addⁿ to this the harmonic approximation is not appropriate & the minimiser becomes unstable.

Advantages of NR method:

→ fast converging

→ well adopted for molecular geometry ~~optimiser~~ optimiser with the quadratic fn.

→ It is very useful if the hessian is cheaper.

Disadvantages of NR method:

→ computationally very expensive; require a lot of storage & space.

→ They are not applicable to noisy function

→ Always converge to nearest local minima.

Teacher's Signature : _____

Block Diagonal NR method:

In this method just one atom is moved at each iteration; consequently all other terms of the form $\frac{\partial^2 v}{\partial x \partial y}$ would be zero & this leads to only the diagonal term ω involve the coordinates of the atom being moved so reduces the problem of inverting the $3n \times 3n$ matrix. Problem is less efficient when motion of some atom are closely coupled i.e; concerted movement of connected atoms in ring systems.

Quasi-Newton Method: (variable matrix method)

Since the calculation of inverse hessian matrix is potentially time consuming and in some cases one may not be able to calculate the analytical 2nd derivative which are reqd. In such cases we make use of quasi-newton method also known as variable matrix method. In these methods the inverse hessian matrix is gradually build up in successive iteration i.e; the sequence of matrices H_k is constructed that has the property limit:

$$\lim_{k \to \infty} H_k = \nabla^{-1} \qquad x_{k+1} = x_k - H_k g_k.$$

At each iteration k the new pos x_{k+1} is created or obt from the current pos x_k, the gradient g_k & inverse hessian matrix H_k having moved to the new pos x_{k+1} the 'H' is updated from its value at the previous step. Acc to a formula depending upon the specific method used;

- DFP - Deviden-Fletcher-powell
- BFGS - Broyden-Fletcher-goldfab-shanno
- MS - Murtaugh-Sargent

The choice of the minimisn algorithm depends on the no of factors

1. Storage & Computational requirement.
2. Relative speed with which the various parts of calcn can be performed.
3. availability of analytical derivative (both 1st & 2nd order)
4. Robustness of the method