Geometry optimization/Energy Minimization

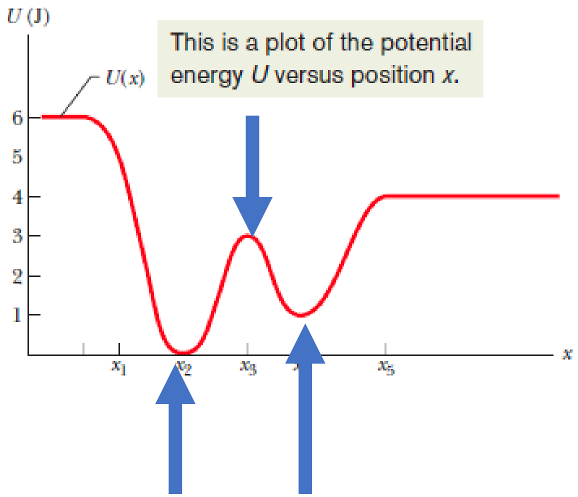
P. SATPATI, BSBE

Materials taken from

https://www.intechopen.com/chapters/74105#B5

RECAP…

What can you do with Force- Field ?



If you starting structure is bad.
You can optimize the energy (U) and find the optimum point.

Geometry Optimization/ Minimization

Why minima and maxima’s are important ?

- Thermodynamic Properties (e.g, ΔG) ⇔ Population in the minima’s
- Kinetic Parameters (rate-constants) ⇔ Transition state

Energy minimization: a brief description about the problem

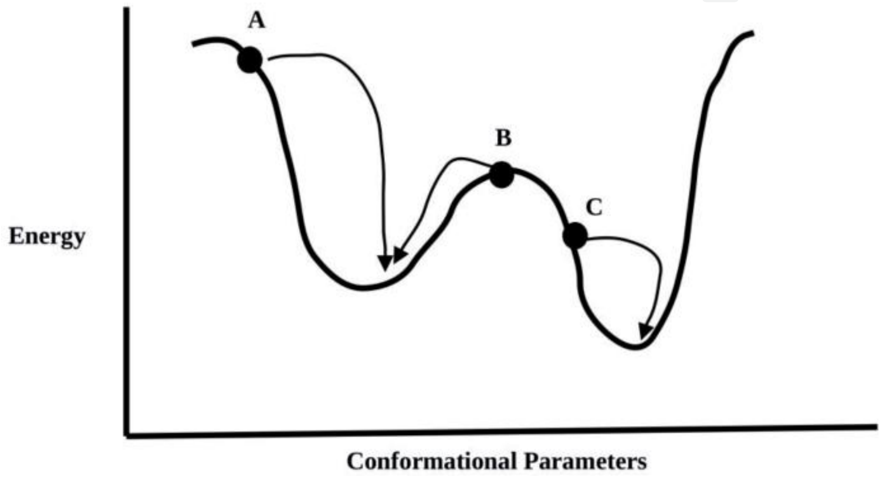
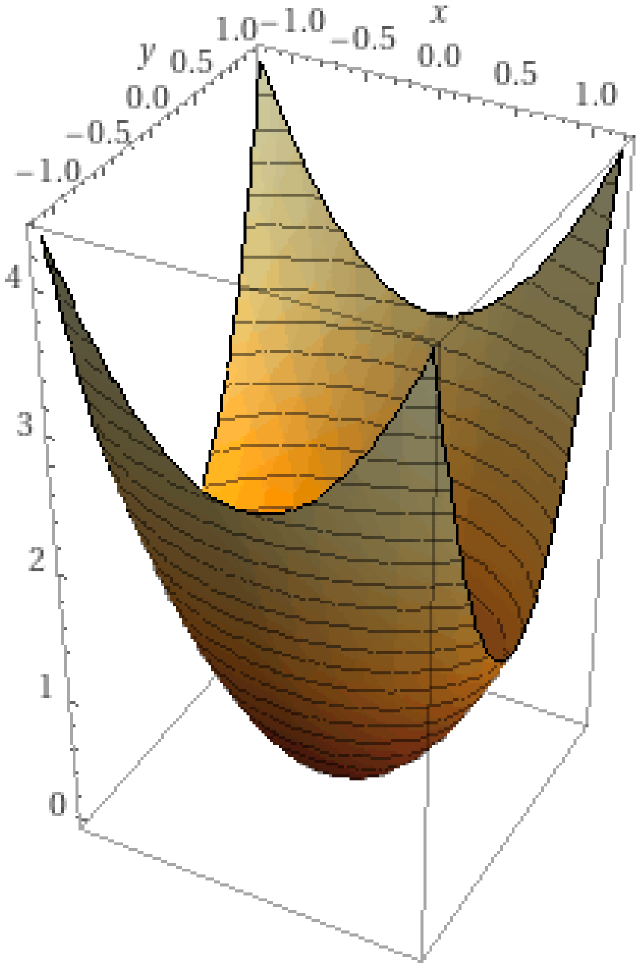


Figure 1.
A one-dimensional energy surface showing minimization methods movement downwards or downhill towards the closest energy minimum.

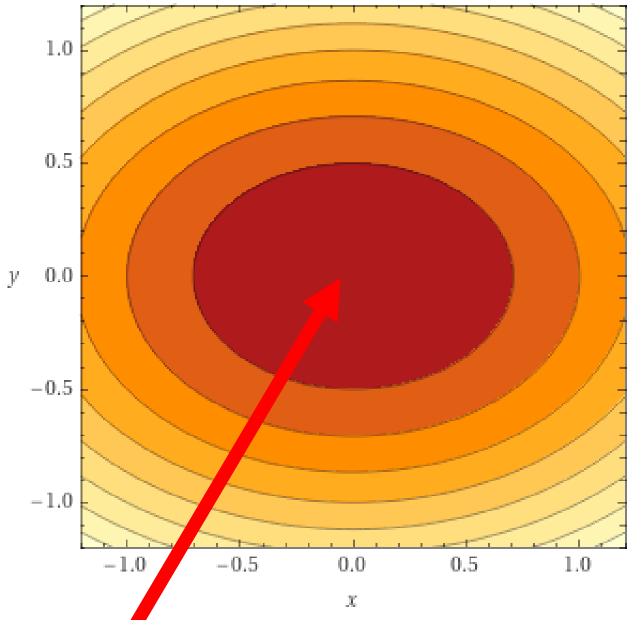
$$\partial f / \partial x_i = 0; \;\; \partial^2 f / \partial x_i^2 > 0$$

f = Energy (U)
x_i = variables (e.g, r_i, θ_i, ϕ_i ..)

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



3D plot	$x^2 + 2y^2$



Contour plot

Q: How to find the minima from an arbitrary point ?

Classification of Energy minimization algorithm

1. Does not use derivative (Non-derivative)
2. Use derivative

Why we are interested in the minima's ?

- Thermodynamic Properties (e.g, ΔG) ⇔ Population in the minima's

1. NON-derivative minimization method

1.1 The Simplex Method

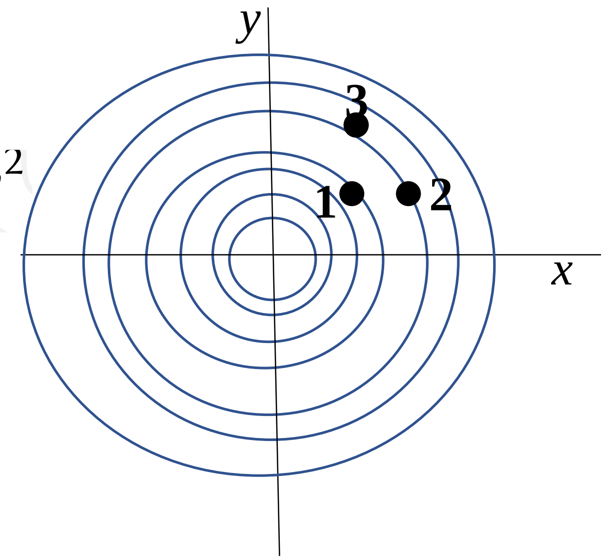
Simplex = Geometrical figure with (M+1) vertices.
'M' = dimensionality of the energy function.

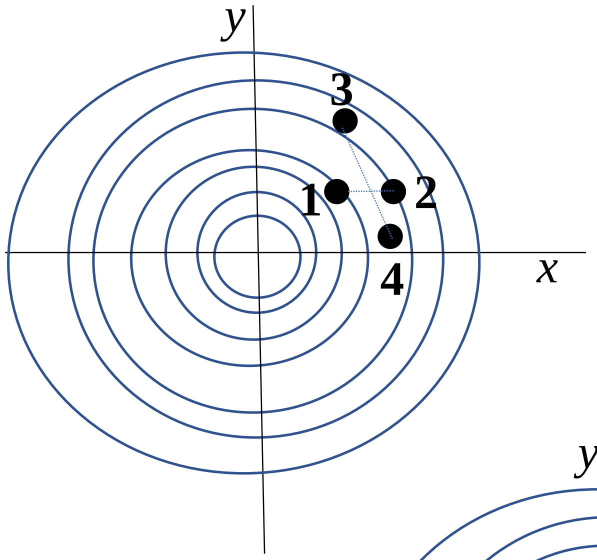
$$f(x,y) = x^2 + 2y^2$$

- M = 2
- Simplex = Triangle

Setp1: Initial Simplex vertices generated by adding 2 to each column from an arbitrary point (9,9).

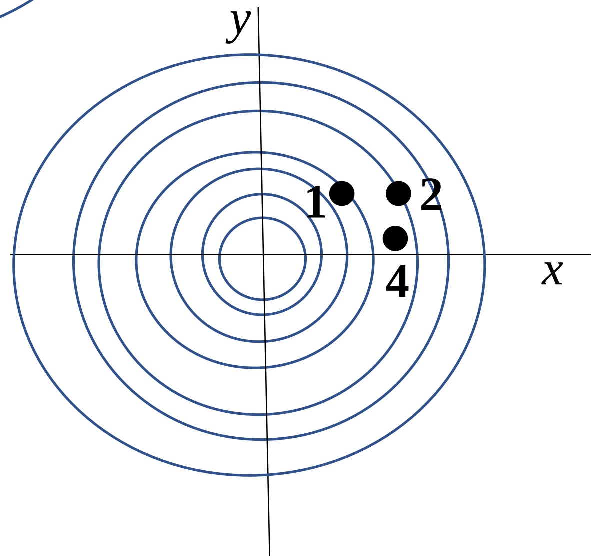
$f(x,y) = x^2 + 2y^2$





Point 1 = (9, 9) = 243
Point 2 = (11, 9) = 283
Point 3 = (9, 11) = **323**

Step 2: The vertex of highest point *f* **(9,11) = 323 (Point 3).**



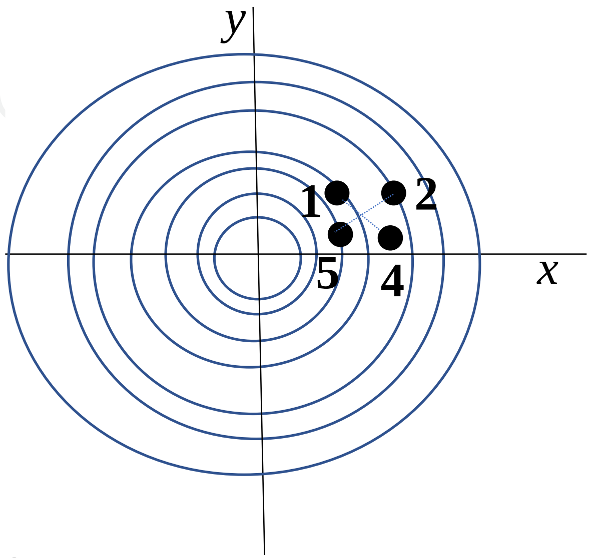
Step 3: The highest vertex (Point 3) is reflected through the "opposite side" of the triangle. ➔ Point 4 = (11, 7)

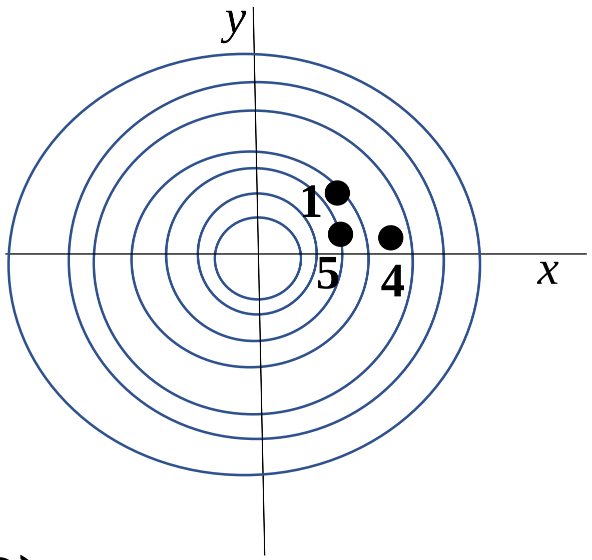
Step 4: Forget **(Point 3).**

Step 5: Repeat step 1 considering Point 1,2, 4.

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

Point 1 = (9, 9) = 243
Point 2 = (11, 9) = **283**
Point 4 = (11, 7) = 219





Now, The vertex of highest point *f* **(11, 9) = 283 (Point 2)**

The highest vertex (Point 2) is reflected through the "opposite side" of the triangle. ➔ **Point 5 = (9, 7)**

…Repeat and approach to the minima.

Four Basic Moves of simplex

Energy Minimization
DOI: http://dx.doi.org/10.5772/intechopen.94809

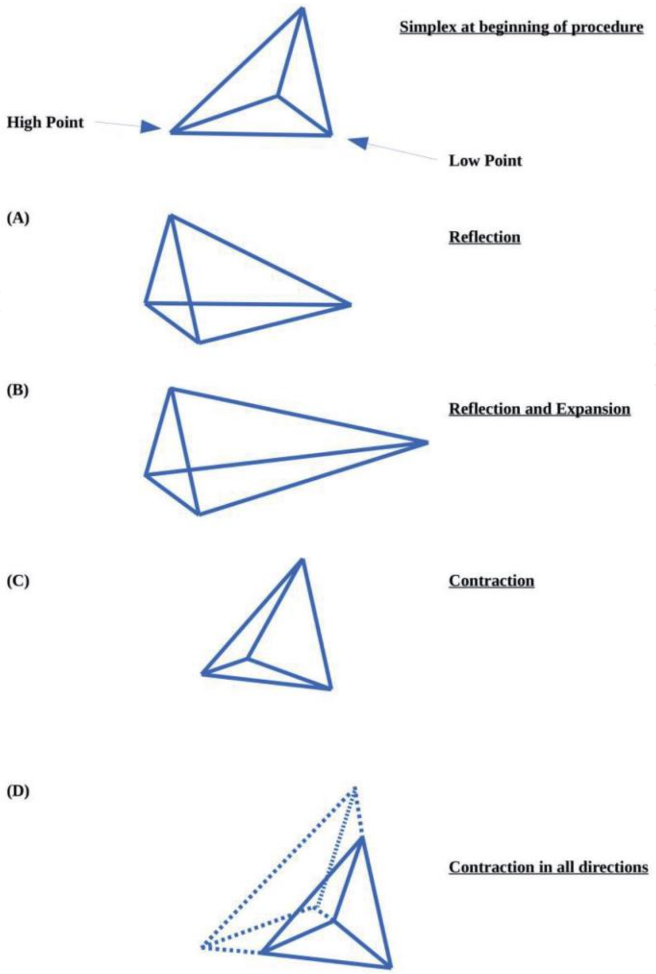


Figure 2.
The three basic moves permitted to the simplex algorithm (reflection, and its close relation reflect-and-expand; contract in one dimension and contract around the lowest point).

Problem:

Too many energy calculations…

1.2 The sequential univariate search method

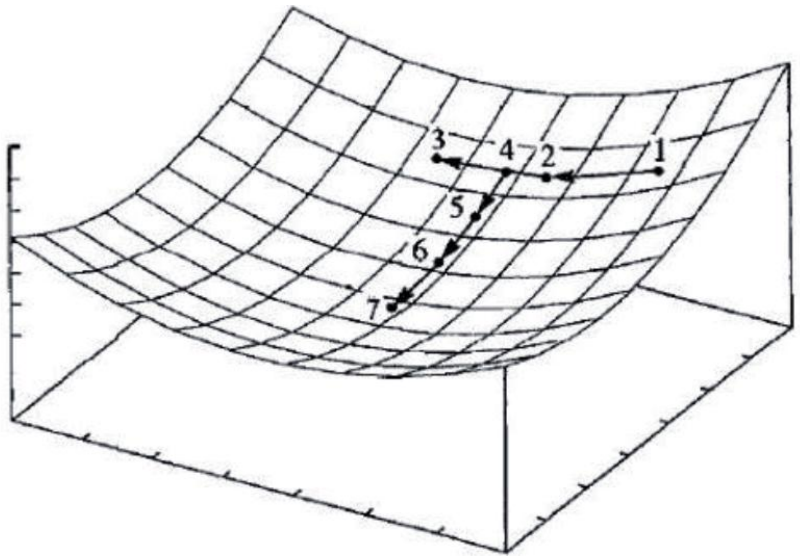


Figure 3.
The sequential univariate search procedure. From the starting point 1, two steps are created along one of the coordinates to give points 2 and 3. A parabola is fitted to these three points and the minimum located (point 4). The same steps is then repeated along the next coordinate (points 5, 6 and 7) (Figure adapted from Schlegel H B 1987. Optimization of equilibrium geometries and transition structures In Lawley K P (editor) ab initio methods in quantum chemistry - I New York, John Wiley, pp. 249–286).

Step 1: For each coordinate x_i. Two new coordinate generated $(x_i+\delta x_i)$, $(x_i-\delta x_i)$

Point 1 = x_i
Point 2 = $(x_i+\delta x_i)$
Point 3 = $(x_i-\delta x_i)$

Step 2: calculate energy or f at the three points [x_i , $(x_i+\delta x_i)$, $(x_i-\delta x_i)$]

Step 3: Fit parabola through the calculated energy values $f(x_i)$, $f(x_i+\delta x_i)$, $f(x_i-\delta x_i)$.

Step 4: Find the minimum point in the fitted parabola (Point 4)

Step 5: Repeat Step 1

1.2 The sequential univariate search method

Problems…

Not good if strong coupling between two or more variables.

Energy surface is analogous to a long narrow valley.

2. Derivative based minimization method

2.1 Steepest Descent Method

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

Q1. What should be the best direction to move from a point (say, x_i) ?

Ans1. Find the derivative, ∇f.

$$\nabla f = \left(\frac{\partial f}{\partial x}\right)_y \vec{x} + \left(\frac{\partial f}{\partial y}\right)_x \vec{y}$$

Q2. Along that direction how far one should move

Ans2. "h". Need to find "h".

$$x^{i+1} = xi + h\,(\nabla f)_x$$

$$f = x^2 + 2y^2$$

$$\nabla f = \left(\frac{\partial f}{\partial x}\right)_y \vec{x} + \left(\frac{\partial f}{\partial y}\right)_x \vec{y}$$

$$=)\ \nabla f = 2x\,\vec{x} + 4y\,\vec{y}$$

Say, x^i, yi = (2, 1)

$$\nabla f(x^i = 2) = 4$$
$$\nabla f(y^i = 1) = 4$$

Plan 1

$$\begin{pmatrix} x^{i+1} \\ y^{i+1} \end{pmatrix} = \begin{pmatrix} 2 \\ 1 \end{pmatrix} + h \begin{pmatrix} 4 \\ 4 \end{pmatrix}$$

Plan 2: Find "h"

Minimize "f" with respect to "h"

At the point (x^{i+1}, y^{i+1})

$$f = (2 + 4h)^2 + 2(1 + 4h)^2$$

$$=)\ \frac{df}{dh} = 2 *(2+4\ h)*\ 4 + 2*2*(1+4\ h)*4$$

=) 0 = 32 + 96 h

=) h = -(32/96) ~ - 0.3

After 1st iteration

$$\begin{pmatrix} x^{i+1} \\ y^{i+1} \end{pmatrix} = \begin{pmatrix} 2 \\ 1 \end{pmatrix} + \mathrm{h} \begin{pmatrix} 4 \\ 4 \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} x^{i+1} \\ y^{i+1} \end{pmatrix} = \begin{pmatrix} 2+4(-0.3) \\ 1+4(-0.3) \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} x^{i+1} \\ y^{i+1} \end{pmatrix} = \begin{pmatrix} 0.8 \\ -0.2 \end{pmatrix}$$

$$f(0.8, -0.2) = 0.72$$

Start 2nd iteration

2.2 Newton-Raphson method

Taylor Series

$$V(x_i+h) = V(x_i) + V^{/}(x_i)\,h + V^{//}(x_i)\,\frac{h^2}{2!} + V^{///}(x_i)\,\frac{h^3}{3!} + \ldots$$

Provided:

- All the derivatives at x_i are known (Infinite number).
- The function and all its derivatives are continuous and well defined.

Say, new point $x = x_i + h$

$\Rightarrow h = (x - x_i)$

Substitute, $h = (x - x_i)$ in the Taylor series

$$V(x) = V(x_i) + V^{/}(x_i)\,(x - x_i) + V^{//}(x_i)\,\frac{(x - x_i)^2}{2!} + \ldots$$

$$V(x) = V(x_i) + V'(x_i)\,(x - x_i) + V''(x_i)\,\frac{(x - x_i)^2}{2!} + \ldots$$

> Neglect higher order terms

$$V(x) = V(x_i) + V'(x_i)\,(x - x_i) + V''(x_i)\,\frac{(x - x_i)^2}{2!}$$

> First derivative with respect to "x"

$$V'(x) = 0 + V'(x_i) + V''(x_i)\,\frac{2 * (x - x_i)}{2!}$$

> If the function is quadratic, the 2nd derivative

$$V''(x) = V''(x_i)$$

> At minima x = x*, V'(x) = 0

$$0 = 0 + V'(x_i) + V''(x_i)\,(x^* - x_i) \longrightarrow \boxed{x^* = x_i - \frac{V'(x_i)}{V''(x_i)}}$$

For a quadratic function, Newton Rapson Method finds the minima in a SINGLE step from any point of the surface

$$x* = x_i - \frac{V^{/}(x_i)}{V^{//}(x_i)}$$

$$x* = x_i - [V^{//}(x_i)]^{-1}\, V^{/}(x_i)$$

Inverse

$$A = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

The inverse of a matrix is found using the following formula:

$$A^{-1} = \begin{bmatrix} a & b \\ c & d \end{bmatrix}^{-1}$$

$$A^{-1} = \frac{1}{ad-bc}\begin{bmatrix} d & -b \\ -c & a \end{bmatrix}$$

$$f = x^2 + 2y^2$$

Say, $x_i, y_i = (9, 9)$

$$\boxed{f^{/} = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \end{pmatrix} = \begin{pmatrix} 18 \\ 36 \end{pmatrix}}$$

$$\mathbf{f}^{//} = \begin{pmatrix} \frac{d^2 f}{dx^2} & \frac{d^2 f}{dx\, dy} \\ \frac{d^2 f}{dy\, dx} & \frac{d^2 f}{dy^2} \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 4 \end{pmatrix}$$

$$[\mathbf{f}^{//}]^{-1} = \frac{1}{|f|}\begin{pmatrix} 4 & 0 \\ 0 & 2 \end{pmatrix} = \frac{1}{8}\begin{pmatrix} 4 & 0 \\ 0 & 2 \end{pmatrix} = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/4 \end{pmatrix}$$

$$\boxed{[\mathbf{f}^{//}]^{-1} = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/4 \end{pmatrix}}$$

$$f' = \begin{pmatrix} \frac{df}{dx} \\ \frac{df}{dy} \end{pmatrix} = \begin{pmatrix} 18 \\ 36 \end{pmatrix}$$

$$x* = x_i \text{ - } [\mathbf{V}''(\boldsymbol{x}_i)]^{-1}\, V'(x_i)$$

$$[\mathbf{f}'']^{-1} = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/4 \end{pmatrix}$$

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

$$=) \begin{pmatrix} x* \\ y* \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Limitation:

(1) Quadratic Surface. Hessian matrix should be calculated and inverted

(2) Harmonic approx. is very bad if away from minimum

Solution:

(1) First use steepest descent method. Come close to the minima

(2) Then apply Newton Rapson method

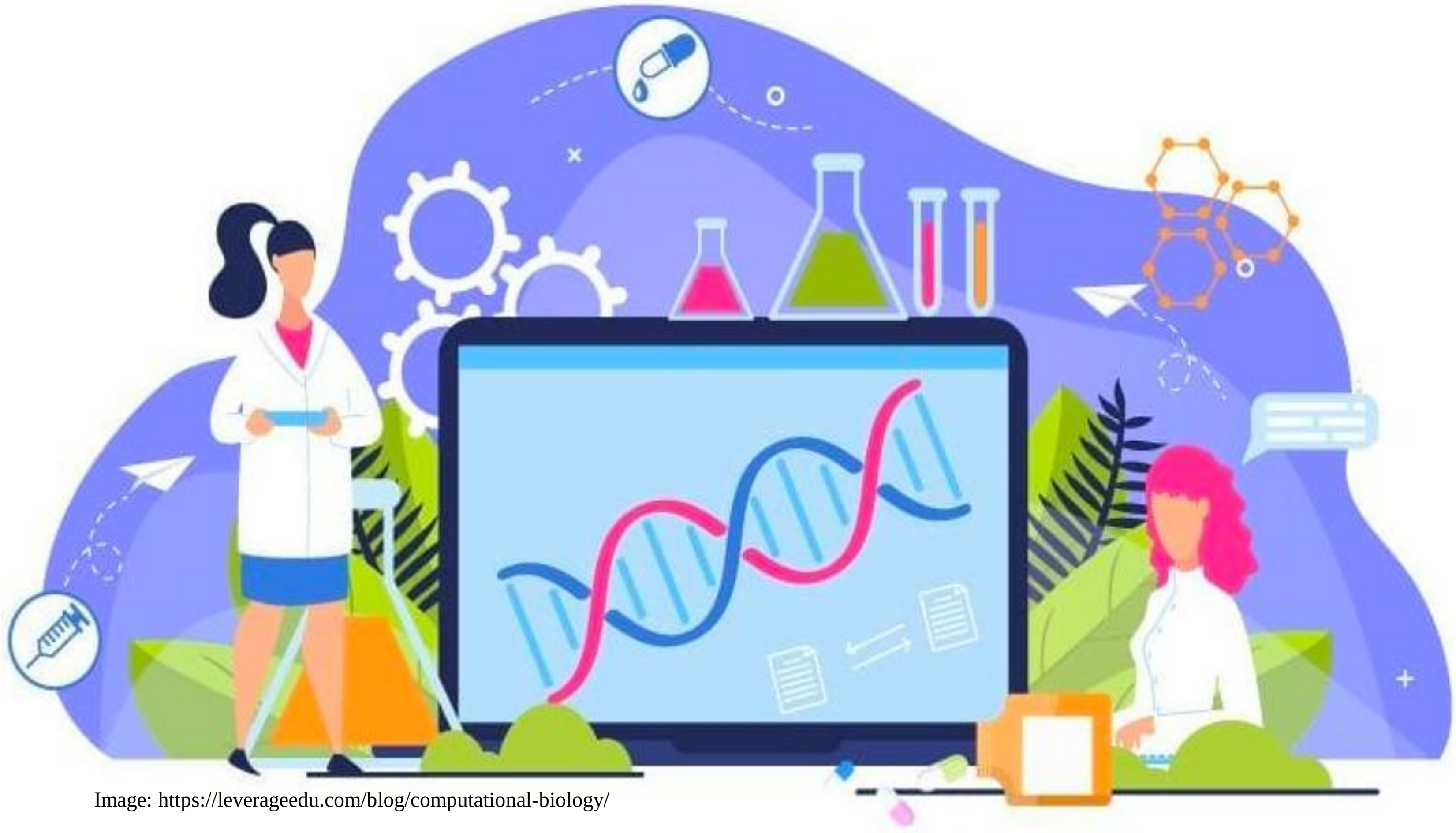


Image: https://leverageedu.com/blog/computational-biology/