

Quantum Chemistry

Lecture 26

Geometry Optimization

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The Born-Oppenheimer approximation permits the separation of electronic and nuclear coordinates. The reason for the separation is the very different time scales for motion of the nuclei and the electrons. In practice, this means that we calculate the electronic structure of a molecule at a fixed nuclear position. The initial configuration is not necessarily the optimum, i.e. lowest energy geometry. Thus, it is important to find the minimum energy structure. At the nuclear position of the minimum energy structure the potential energy surface has positive curvature for all of the $3N-6$ vibrational modes. Thus, a vibrational frequency calculation is meaningful at this point in nuclear coordinate space since it gives the normal modes of vibration.

Overview of a geometry optimization

In general, the nuclear position is adjusted and energies are calculated. However, the program also uses search criteria to systematically move towards lower energy and ultimately to find the minimum. Geometry optimization has three general stages,

1. Steepest Descent
2. Conjugate Gradient
3. Newton-Raphson

These are considered in an illustrative example in the following sections.

The potential energy surface

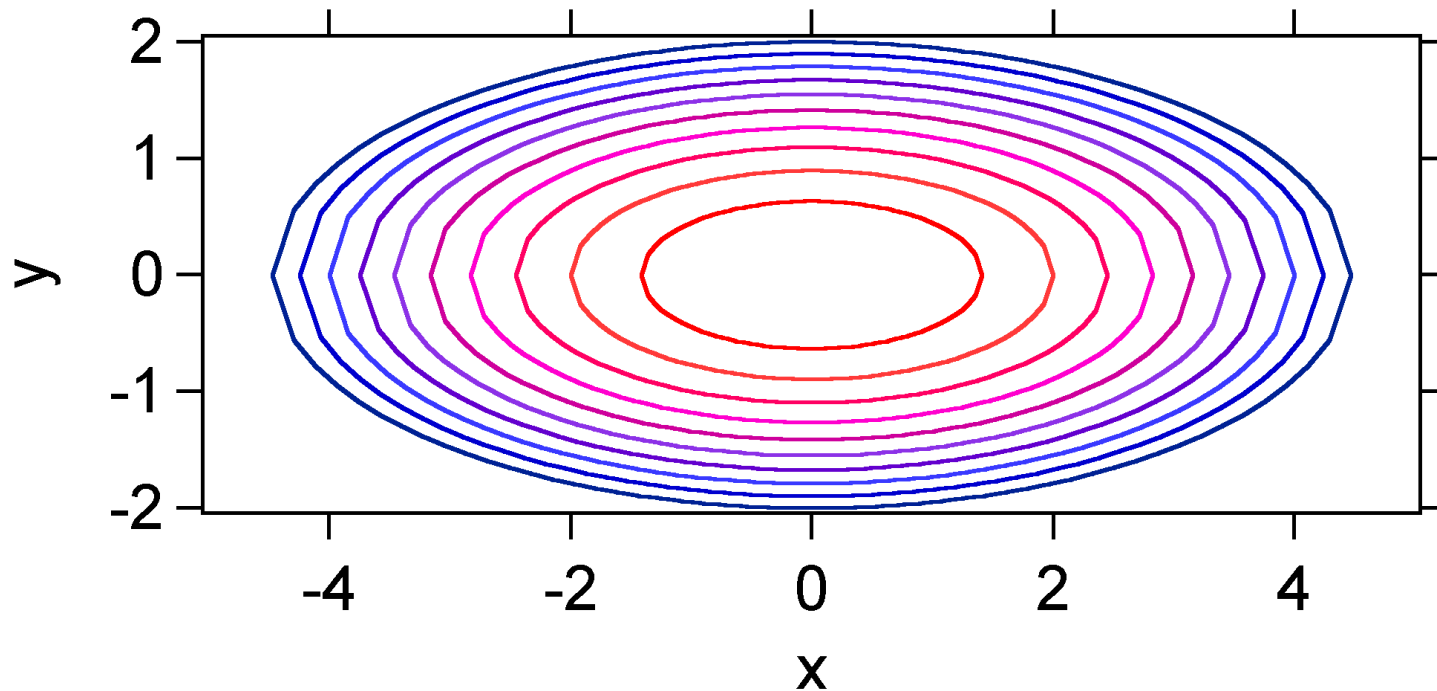


Figure. Representation of a potential energy surface. The minimum in this case is (0.0).

The contours represent various energies from red (lowest energy, $E = 2$) to blue (highest energy, $E = 20$).

Steepest Descent method

For this example, a two-dimensional harmonic potential energy surface can be represented by $E(x,y) = x^2 + 5y^2$ as shown in the Figure.

The first derivative is

$$\nabla E(x, y) = (2x, 10y)$$

The line used for a search is

$$x' = x_0 + \alpha \left(\frac{\partial E(x, y)}{\partial x} \right)_{x_0, y_0} = x_0(1 + 2\alpha)$$

$$y' = y_0 + \alpha \left(\frac{\partial E(x, y)}{\partial y} \right)_{x_0, y_0} = y_0(1 + 10\alpha)$$

Steepest Descent method

If we choose $x_0 = 3.22$, $y_0 = 1.39$ as the starting point (structure) represented by the black dot on the figure, the black line shown in Figure represents the direction for a line search.

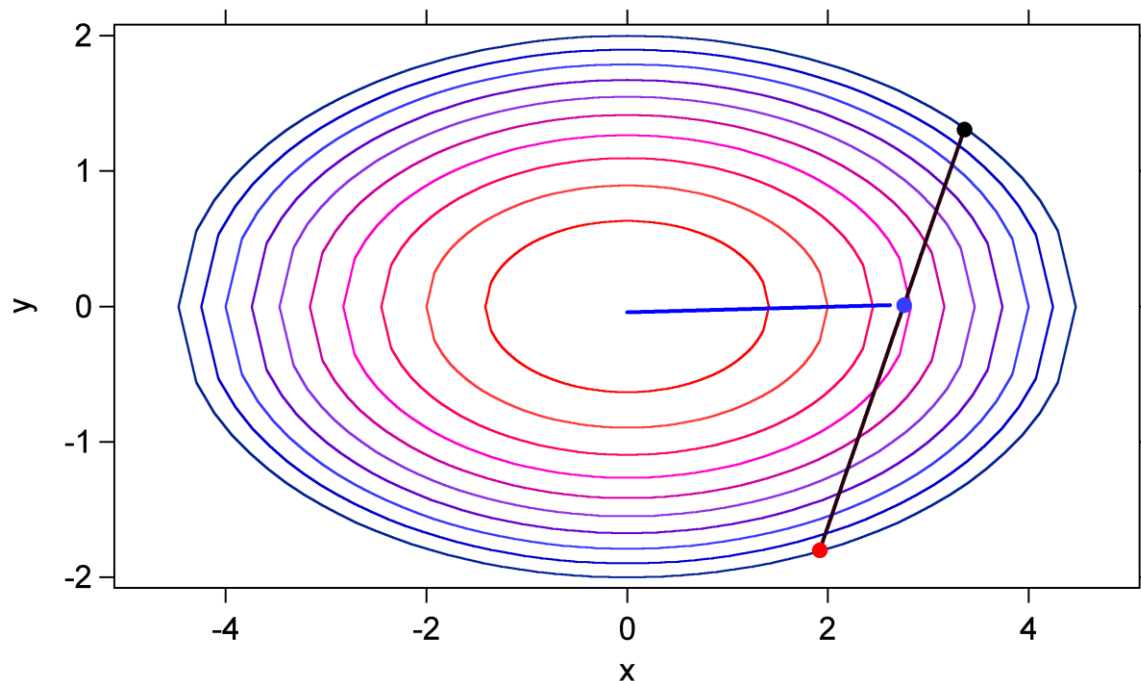


Illustration of the line search in the steepest descent method.

The line search

The line search conducted along the black line finds a second point (the red dot) also at $E = 20$ and perhaps intermediate points with lower energies demonstrating that there will be a minimum between the black and red dots. This turns out to be the blue dot. After the first iteration the blue dot is the starting point (structure) for a second iteration. The gradient now follows the blue line and this intersects the minimum at (0,0).

This example is trivial, however, it illustrates the principle of energy minimization by steepest descent. The fact that the minimum was found so quickly is attributable to the choice of a harmonic (quadratic) potential energy surface.

Conjugate Gradient

We demonstrate conjugate gradient with the above example (even though it is not needed for the harmonic surface shown). In conjugate gradients, the new direction vector, h_{i+1} leading from point $i+1$ is computed by adding a term to the gradient, g_{i+1} used by steepest descent. The addition term is a constant, γ times the old direction h_i .

$$h_{i+1} = g_{i+1} + \gamma h_i$$

where γ is a scalar defined by

$$\gamma = \frac{g_{i+1} \cdot g_{i+1}}{g_i \cdot g_i}$$

Conjugate Gradient

Since g_i and g_{i+1} are the gradients (first derivatives) calculated at points i and $i + 1$, in the above example this would have the form

$$\gamma = \frac{\left(\frac{\partial E_{i+1}}{\partial x}\right)^2 + \left(\frac{\partial E_{i+1}}{\partial y}\right)^2}{\left(\frac{\partial E_i}{\partial x}\right)^2 + \left(\frac{\partial E_i}{\partial y}\right)^2} = \frac{4x_{i+1}^2 + 100y_{i+1}^2}{4x_i^2 + 100y_i^2}$$

The new direction vector is

$$h_{i+1} = (2x_{i+1}, 10y_{i+1}) + \gamma(2x_i, 10y_i)$$

No matter what the initial point is, γ times the old direction always provides a correction to the gradient that produces a direction conjugate to all previous directions. A line search is still required as in steepest descent.

Newton-Raphson method

The Newton-Raphson method uses the gradient (first derivative) to establish a direction and curvature (second derivative) to predict where along the gradient the function will change directions (pass through a minimum). Since the second derivative matrix defines the curvature in each gradient direction, the invers of the second-derivative matrix can be multiplied by the gradient to obtain a vector that translates directly to the nearest minimum.

$$r_{\min} = r_0 - H^{-1} \tilde{\nabla} E(r_0)$$

To illustrate how this works, we return to the elliptical PES used above. We have already seen that the first derivatives are

$$\left(\frac{\partial E(x, y)}{\partial x} \right)_{x_0, y_0} = 2x_0 \quad \left(\frac{\partial E(x, y)}{\partial y} \right)_{x_0, y_0} = 10y_0$$

Using the Hessian matrix

The second derivative of Hessian matrix is

$$H = \begin{vmatrix} \left(\frac{\partial^2 E(x, y)}{\partial x^2} \right) & \left(\frac{\partial^2 E(x, y)}{\partial x \partial y} \right) \\ \left(\frac{\partial^2 E(x, y)}{\partial y \partial x} \right) & \left(\frac{\partial^2 E(x, y)}{\partial y^2} \right) \end{vmatrix}$$

Or numerically in this instance

$$H = \begin{vmatrix} 2 & 0 \\ 0 & 10 \end{vmatrix}$$

The inverse Hessian matrix is easy in this case

$$H^{-1} = \begin{vmatrix} 1/2 & 0 \\ 0 & 1/10 \end{vmatrix}$$

Newton-Raphson method

Thus we have

$$(x_{\min}, y_{\min}) = (x_0, y_0) - \begin{vmatrix} 1/2 & 0 \\ 0 & 1/10 \end{vmatrix} (2x_0, 10y_0)$$

which simplifies to

$$(x_{\min}, y_{\min}) = (x_0, y_0) - (x_0, y_0) = (0, 0)$$

Thus, we arrive at the minimum in one step. Since the Newton-Raphson method depends on second derivatives it works well only near the minimum. It is used as the last step in a multi-stage refinement process to locate the minimum energy point. It has the advantage of great efficiency in terms of the number of steps. The example shows that in the limit that the potential energy surface is quadratic in form, Newton-Raphson can find the minimum in a single step.