## Geometry Corresponding to the Minimum Energy

An important problem in Quantum Chemistry is to find the point on a molecules potential energy surface that corresponds to the lowest energy because if the molecular vibrations were harmonic this point would define its equilibrium structure. Since anharmonic effects are often small the geometry corresponding to this minimum is a good approximation to the equilibrium structure.

Let's suppose that we have the energy of an N nuclei molecule as a function of the coordinates of each nucleus.

$$E = E\left(x_1, x_2, x_3, \cdots x_{3N}\right)$$

and we want to find the minimum energy. Let's expand this function around a point

 $x_1^o, x_2^o, x_3^o, \cdots x_{3N}^o$ 

in the 3N dimensional space that we think is a reasonable approximation to the minimum energy point.

$$E = E\left(x_1^o, x_2^o, \cdots, x_{3N}^o\right) + \sum_{K=1}^{3N} \left(\frac{\partial E}{\partial x_K}\right)_o \left(x_K - x_K^o\right) + \frac{1}{2} \sum_{L=1}^{3N} \sum_{K=1}^{3N} \left(\frac{\partial^2 E}{\partial x_K \partial x_L}\right)_o \left(x_K - x_K^o\right) \left(x_L - x_L^o\right) + \cdots$$

Let's define the first and second derivatives of the energy at the expansion point as

$$E_K^o = \left(\frac{\partial E}{\partial x_K}\right)_o$$
 and  $E_{KL}^o = \left(\frac{\partial^2 E}{\partial x_K \partial x_L}\right)_o$  and the distance  $\left(x_K - x_K^o\right) = \Delta x_K$ . Truncating the

expansion after quadratic terms results in

$$E = E^{o} + \sum_{K=1}^{3N} E^{o}_{K} \Delta x_{K} + \frac{1}{2} \sum_{K=1}^{3N} \sum_{L=1}^{3N} E^{0}_{KL} \Delta x_{K} \Delta x_{L}$$

Which we can write as

$$E = E^o + \vec{q}_o^+ \Delta \vec{x} + \frac{1}{2} \Delta \vec{x}^+ \ \boldsymbol{F}^o \Delta \vec{x}$$

Where  $\vec{q}_o$  is a column vector containing the first derivatives,  $\Delta \vec{x}$  is a column vector containing the displacements and  $F^o$  is a matrix containing the second derivatives.  $F^o$  is called the Hessian matrix.

$$\vec{q}_{0} = \begin{pmatrix} E_{1}^{o} \\ E_{2}^{o} \\ \vdots \\ E_{3N}^{0} \end{pmatrix}, \qquad \Delta \vec{x} = \begin{pmatrix} \Delta x_{1} \\ \Delta x_{2} \\ \vdots \\ \Delta x_{3N} \end{pmatrix}; \qquad \boldsymbol{F}^{o} = \begin{pmatrix} E_{11}^{0} & E_{12}^{0} & \cdots & E_{1,3N}^{0} \\ E_{12}^{0} & E_{22}^{0} & \cdots & E_{1,3N}^{0} \\ \vdots & \ddots & \vdots \\ E_{1,3N}^{0} & \cdots & E_{3N,3N}^{0} \end{pmatrix}$$

If this quadratic approximation is a reasonable approximation in the vicinity of the minimum we may approximate the minimum by taking the derivative and setting it equal to zero. This results in the 3N equations

$$\frac{\partial E}{\partial x_{K}} = \left(\vec{q}_{o}\right)_{K} + \left(\boldsymbol{F}^{o}\Delta\vec{x}\right)_{K} = 0$$

and so

$$\vec{q}_o = -\boldsymbol{F}^o \Delta \vec{x}_{min}$$

where  $(\Delta \vec{x}_{min})_{k} = x_{k}^{min} - x_{k}^{o}$ 

So we can calculate  $\Delta \vec{x}_{min}$  from  $-(F^o)^{-1} \vec{q}_o = \Delta \vec{x}_{min}$  and estimate the minimum point from

 $x_{K}^{min} = x_{K}^{o} + (\Delta \vec{x}_{min})_{K}$ . We then use this updated estimate as the new expansion point and repeat the procedure until the input estimate and the output estimate are equal to within a prescribed tolerance. At this point  $\vec{q}_o \square o$ .

The effort required to find the minimum energy geometry depends on the initial estimate and the way the derivatives are computed. The worst case is when the first and second derivatives are computed numerically. The first derivative  $E_K^o$  requires 2 separate energy calculations and is evaluated as

$$E_{K}^{o} \approx \frac{E\left(x_{K}^{o}+\delta\right)-E\left(x_{K}^{o}-\delta\right)}{2\delta} \text{ and there are 3N of these to evaluate. The second}$$
  
derivatives would be  $E_{KL}^{o} \approx \frac{E_{K}^{o}\left(x_{L}^{o}+\delta\right)-E_{K}^{o}\left(x_{L}^{o}-\delta\right)}{2\delta}$  and there are 3N(3N+1)/2 of these.

Clearly this could become very impractical!

One of the most significant developments in Quantum Chemistry was the development of a method by Pulay (Adv. Chem. Phys., 1987, 69, 241) to evaluate the first derivative of the energy of an SCF wavefunction analytically. This technique typically takes 1-3 times more than the energy calculation and makes the derivative calculation practical. Also its often necessary to have a reasonable estimate of the Hessian and improve it by various

numerical methods as the geometry improves. As we will see latter there are analytic gradients for many correlated wavefunctions and these have lead to the ability to calculate very accurate equilibrium geometries.