3805ICT - Assignment 2 - Gradient

July, 2018

1 Model Molecular Structure

To implement the BFGS local optimiser (for an N atom model) we require $V_{\alpha_1}, \ldots, V_{\alpha_{N-2}}$, where α_i is as defined in Figure 1.

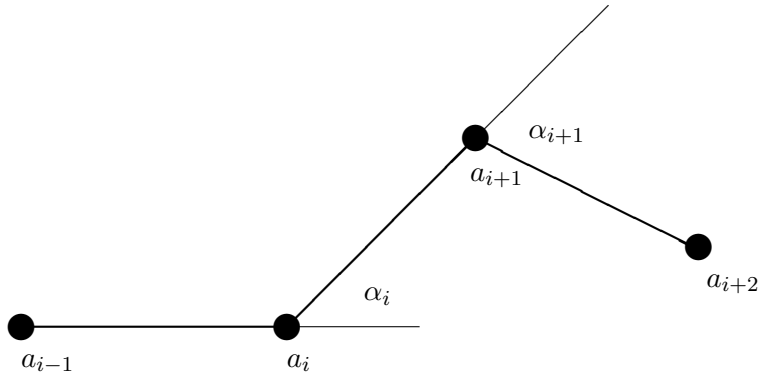

Figure 1: Bond angles (α) used to encode the model molecular structure.

The total potential energy of the system is given by

$$V = \sum_{i<j}^{N} (1/r_{ij}^{12} - 2/r_{ij}^{6})$$

where

$$r_{ij}^2 = x_{ij}^2 + y_{ij}^2$$

Let

$$\Psi_k = \sum_{i=1}^{k} \alpha_i$$

and $(x_0, y_0) = (0, 0)$ and $\Psi_0 = 0$. Then

$$\begin{aligned} x_i &= \sum_{k=0}^{i-1} \cos(\Psi_k) \\ y_i &= \sum_{k=0}^{i-1} \sin(\Psi_k) \end{aligned}$$

Now

$$V_{\alpha_m} = -12 \sum_{i<j} (1/r_{ij}^{13} - 1/r_{ij}^{7}) r_{ij_{\alpha_m}}$$

and

$$(r_{ij})_{\alpha_m} = ((x_i - x_j)(x_i - x_j)_{\alpha_m} + (y_i - y_j)(y_i - y_j)_{\alpha_m})/r_{ij}$$

Assuming that $j > i$ we have

$$\begin{aligned} (x_i - x_j)_{\alpha_m} &= -\sum_{k=i}^{j-1} (\cos(\Psi_k))_{\alpha_m} = \sum_{k=max(i,m)}^{j-1} \sin(\Psi_k) \\ (y_i - y_j)_{\alpha_m} &= -\sum_{k=i}^{j-1} (\sin(\Psi_k))_{\alpha_m} = -\sum_{k=max(i,m)}^{j-1} \cos(\Psi_k) \end{aligned}$$

Therefore

$$(r_{ij})_{\alpha_m} = ((x_i - x_j)(\sum_{k=max(i,m)}^{j-1} \sin(\Psi_k)) + (y_i - y_j)(-\sum_{k=max(i,m)}^{j-1} \cos(\Psi_k)))/r_{ij}$$

which is zero when $m \leq i$. Assuming that $m > i$, we have

$$\begin{aligned} -\sum_{k=m}^{j-1} \cos(\Psi_k) &= x_j - x_m \\ \sum_{k=m}^{j-1} \sin(\Psi_k) &= y_m - y_j \end{aligned}$$

and

$$(r_{ij})_{\alpha_m} = ((x_i - x_j)(y_m - y_j) + (y_i - y_j)(x_j - x_m))/r_{ij}$$

Combining terms we have

$$V_{\alpha_m} = -12 \sum_{i=0}^{m-1} \sum_{j=m+1}^{n} (1/r_{ij}^{14} - 1/r_{ij}^{8})((x_i - x_j)(y_m - y_j) + (y_i - y_j)(x_j - x_m))$$