Some further notes on linear bond angles

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Introduction

This note is a follow up to the article by Florian Müller-Plathe from the previous issue. [1] It describes an alternative procedure for dealing with the problem of linear bonds in molecular mechanics and dynamics programs, and also gives detail of the mathematics which is not included in the original literature reference. [2] Most of this article will be concerned with the case where the equilibrium angle ϕ_0 is not equal to π. The analysis is also extended to consider second derivatives of the energy function with respect to particle positions. This energy function has been included in the CCP5 static lattice simulation programs for a number of years.

For simplicity the valence bond angle deformation energy is assumed to be a function of the bond angle ϕ only; i.e. cross terms with the bond lengths are omitted.

Starting from this energy expression

$$E = f(\phi) \tag{1}$$

the first and second derivatives with respect to particle coordinates are found using the chain rule

$$\frac{\partial E}{\partial r_{i\alpha}} = \frac{dE}{d\cos\phi}\frac{\partial\cos\phi}{\partial r_{i\alpha}} \tag{2}$$

$$\frac{\partial^2 E}{\partial r_{i\alpha}\partial r_{j\beta}} = \frac{d^2 E}{d\,(\cos\phi)^2}\frac{\partial\cos\phi}{\partial r_{i\alpha}}\frac{\partial\cos\phi}{\partial r_{j\beta}} + \frac{dE}{d\cos\phi}\frac{\partial^2\cos\phi}{\partial r_{i\alpha}\partial r_{j\beta}} \tag{3}$$

where i, j, k label the three particles in the bond and α, β, γ the Cartesian axes. i is the label of the particle about which there is a bond angle ϕ.

First and second derivatives of $\cos\phi$ are easily found by the chain rule using bond length derivatives. Also, this part of the calculation does not depend on the functional form of $f(\phi)$. Thus:

$$\begin{aligned}\frac{\partial\cos\phi}{\partial r_{i\alpha}} &= 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}} + 2\frac{\partial\cos\phi}{\partial r_{ik}^2}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}} \\ &= 2\frac{\partial\cos\phi}{\partial r_{ij}^2}r_{ij\alpha} + 2\frac{\partial\cos\phi}{\partial r_{ik}^2}r_{ik\alpha} \end{aligned} \tag{4}$$

$$
\begin{aligned}
\frac{\partial^2 \cos\phi}{\partial r_{i\alpha}\partial r_{j\beta}} &= \left\{\left[\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{ij}^2} + \frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{jk}^2}\right]2\frac{\partial\cos\phi}{\partial r_{ij}^2}\right\}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}} + 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\frac{\partial}{\partial r_{j\beta}}r_{ij\alpha} \\
&\quad + \left\{\left[\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{ij}^2} + \frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{jk}^2}\right]2\frac{\partial\cos\phi}{\partial r_{ik}^2}\right\}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}} \\
&= 4\frac{\partial^2\cos\phi}{\left(\partial r_{ij}^2\right)^2}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}} + 4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{jk}^2}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}} - 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\delta_{\alpha\beta} \\
&\quad + 4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{ik}^2}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}} + 4\frac{\partial^2\cos\phi}{\partial r_{ik}^2\partial r_{jk}^2}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}} \\
&= -4\frac{\partial^2\cos\phi}{\left(\partial r_{ij}^2\right)^2}r_{ij\alpha}r_{ij\beta} + 4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{jk}^2}r_{ij\alpha}r_{jk\beta} - 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\delta_{\alpha\beta} \\
&\quad - 4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{ik}^2}r_{ik\alpha}r_{ij\beta} + 4\frac{\partial^2\cos\phi}{\partial r_{ik}^2\partial r_{jk}^2}r_{ik\alpha}r_{jk\beta}
\end{aligned}
\tag{5}
$$

Where

$$r_{ij} = r_i - r_j \tag{6}$$

The other first and second derivatives follow similarly. Derivatives of $\cos\phi$ with respect to bond lengths are found using the cosine rule; the derivation is straightforward and is left to the reader. The results are given below.

$$2\frac{\partial\cos\phi}{\partial r_{ij}^2} = \frac{1}{r_{ij}r_{ik}} - \frac{\cos\phi}{r_{ij}^2} \qquad 2\frac{\partial\cos\phi}{\partial r_{ik}^2} = \frac{1}{r_{ij}r_{ik}} - \frac{\cos\phi}{r_{ik}^2} \qquad 2\frac{\partial\cos\phi}{\partial r_{jk}^2} = -\frac{1}{r_{ij}r_{ik}} \tag{7}$$

$$4\frac{\partial^2\cos\phi}{\left(\partial r_{ij}^2\right)^2} = \frac{1}{r_{ij}^3 r_{ik}} - \frac{3}{r_{ij}^2}\left[2\frac{\partial\cos\phi}{\partial r_{ij}^2}\right] \qquad 4\frac{\partial^2\cos\phi}{\left(\partial r_{ik}^2\right)^2} = \frac{1}{r_{ij}r_{ik}^3} - \frac{3}{r_{ik}^2}\left[2\frac{\partial\cos\phi}{\partial r_{ik}^2}\right] \tag{8}$$

$$4\frac{\partial^2\cos\phi}{\left(\partial r_{jk}^2\right)^2} = 0 \qquad 4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{jk}^2} = \frac{1}{r_{ij}^3 r_{ik}} \qquad 4\frac{\partial^2\cos\phi}{\partial r_{ik}^2\partial r_{jk}^2} = \frac{1}{r_{ij}r_{ik}^3} \tag{9}$$

$$4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{ik}^2} = -\frac{\cos\phi}{r_{ij}^2 r_{ik}^2} - \frac{1}{r_{ik}^2}2\frac{\partial\cos\phi}{\partial r_{ij}^2} - \frac{1}{r_{ij}^2}2\frac{\partial\cos\phi}{\partial r_{ik}^2} \tag{10}$$

Difficulties arise with the cosine derivatives of the energy from equations (1) and (2), $\frac{dE}{d\cos\phi}$ and $\frac{d^2E}{d(\cos\phi)^2}$. These may be calculated as follows:

$$\frac{dE}{d\cos\phi} = \frac{dE}{d\phi}\frac{d\phi}{d\cos\phi} \qquad = -\frac{dE}{d\phi}\frac{1}{\sin\phi} \tag{11}$$

$$\frac{d^2E}{d(\cos\phi)^2} = \frac{1}{\sin^2\phi}\left[\frac{d^2E}{d\phi^2} - \frac{dE}{d\phi}\frac{\cos\phi}{\sin\phi}\right] \tag{12}$$

Problems will arise with the appearance of $\frac{1}{\sin\phi}$ and $\frac{1}{\sin^2\phi}$ in the denominators of the above expressions, and their behaviour as $\phi \to \pi$. Conventionally the explicit form of the function f will be

$$E = \frac{1}{2}k\left(\phi - \phi_0\right)^2 \tag{13}$$

where k is the force constant and ϕ_0 is an assumed equilibrium angle. The overall derivative of E with respect to particle coordinates in this case may be either singular or indeterminate. A Cartesian axis system may be defined with respect to the directions of the bonds with x along ij, y in the plane of the three atoms and z normal to the plane. In this reference frame it is possible to show that the first derivatives with respect to particle positions all tend to finite limits as $\phi \to \pi$, i.e. the method used to calculate the first derivatives leads to an indeterminate. However, the second derivatives involving two z directions diverge. So there is a singularity in the function only in its second derivatives. This derivation is left to the reader.

It is possible instead to use a quartic function for E [2] of this form:

$$E = \frac{1}{4}AB^2 \tag{14}$$

where

$$A = \frac{1}{2}\frac{k}{\left(\phi_0 - \pi\right)^2} \qquad B = \left(\phi_0 - \pi\right)^2 - \left(\phi - \pi\right)^2 \tag{15}$$

This function has the following properties.

1. There is a minimum at $\phi = \phi_0$ (and also at $2\pi - \phi_0$)
2. The second derivative of E with respect to ϕ at this point is k, i.e. the same as the conventional expression.
3. There is a maximum, not a cusp, at $\phi = \pi$
4. As shown below all the first and second derivatives are easily calculable.
5. As $\phi \to 0$ difficulties arise with singularities, although this situation is unlikely to occur in real systems which are treated by molecular mechanics or dynamics.

The first and second derivatives will now be obtained.

$$\frac{dE}{d\phi} = -ABC \qquad \frac{d^2E}{d\phi^2} = A\left(2C^2 - B\right) \qquad \text{where} \quad C = \phi - \pi \tag{16}$$

The appearance of $C = \phi - \pi$ in the numerator make the calculation tractable. From (11),

$$\frac{dE}{d\cos\phi} = \frac{ABC}{\sin\phi} \tag{17}$$

Now

$$\begin{aligned} \frac{C}{\sin\phi} &= -\frac{\phi - \pi}{\sin(\phi - \pi)} \\ &= -\frac{\sin^{-1} S}{S} \qquad \text{where} \qquad S = \sin(\phi - \pi) \\ &= -\frac{1}{S}\left[S + 1/6S^3 + 3/40S^5 + \frac{(2n)!S^{2n+1}}{2^{2n}(n!)^2(2n+1)} + \ldots\right] \qquad \text{for small S} \\ &= -\left[1 + 1/6S^2 + 3/40S^4 + \ldots\right] \\ &= -\left[1 + 1/6\sin^2\phi + 3/40\sin^4\phi + \ldots\right] \\ &= T_1 \end{aligned} \tag{18}$$

where the expansion for $\sin^{-1} S$ for small S has been used and may be calculated to the necessary accuracy. Hence

$$\frac{dE}{d\cos\phi} = ABT_1 \tag{19}$$

From (12),

$$\begin{aligned} \frac{d^2E}{d(\cos\phi)^2} &= \frac{1}{\sin^2\phi}\left[A\left(2C^2 - B\right) - \frac{\cos\phi}{\sin\phi}(-ABC)\right] \\ &= \frac{A}{\sin^2\phi}\left[2C^2 - B\left(1 - \frac{C}{\tan\phi}\right)\right] \end{aligned} \tag{20}$$

Now

$$\begin{aligned} & -\frac{1}{\sin^2\phi}\left[1 - \frac{\phi - \pi}{\tan\phi}\right] \\ &= -\frac{1}{\sin^2(\phi - \pi)}\left[1 - \frac{\phi - \pi}{\tan(\phi - \pi)}\right] \\ &= -\frac{1}{S^2}\left[1 - \frac{\tan^{-1} T}{T}\right] \qquad \text{where} \qquad T = \tan(\phi - \pi) \\ &= -\frac{1}{S^2}\left[1 - \frac{1}{T}\left(T - 1/3T^3 + 1/5T^5 + \frac{(-1)^n T^{(2n+1)}}{(2n+1)} + \ldots\right)\right] \qquad \text{for small T} \\ &= -\frac{1}{S^2}\left[1 - \left(1 - 1/3T^2 + 1/5T^4 - \ldots\right)\right] \end{aligned}$$

$$
\begin{aligned}
&= -\frac{1}{S^2}\left[+1/3T^2 - 1/5T^4 + \ldots\right] \\
&= -\frac{1}{3\cos^2(\phi-\pi)} + \frac{\sin^2(\phi-\pi)}{5\cos^4(\phi-\pi) - \ldots} \\
&= -\frac{1}{3\cos^2(\phi)} + \frac{\sin^2(\phi)}{5\cos^4(\phi)} - \ldots \\
&= T_2 \qquad (21)
\end{aligned}
$$

where the expansion for $\tan^{-1} T$ for small T has been used and may be calculated to the necessary accuracy. Hence

$$\frac{d^2E}{d\left(\cos\phi\right)^2} = A\left[2T_1^2 + BT_2\right] \qquad (22)$$

This procedure breaks down if the equilibrium angle ϕ_0 is π as in this case A is infinite. However, a similar procedure may be followed using a harmonic potential of the form

$$E = \frac{1}{2}k\left(\phi-\pi\right)^2 \qquad (23)$$

Now

$$\frac{dE}{d\phi} = kC \qquad \frac{d^2E}{d\phi^2} = k \qquad \text{where} \quad C = \phi - \pi \qquad (24)$$

and

$$\frac{dE}{d\cos\phi} = -k\frac{C}{\sin\phi} \qquad (25)$$

which may be expanded as above. Also

$$\frac{d^2E}{d\left(\cos\phi\right)^2} = \frac{k}{\sin^2\phi}\left[1 - \frac{\phi-\pi}{\tan\phi}\right] \qquad (26)$$

which again may be expanded in the same way as above.

References

[1] F. Müller-Plathe CCP5 Newsletter No. 44, July 1995 Page 40.

[2] M. Leslie Physica **131B** (1985) 145-150