

Singularity-free Treatment of Linear Bond Angles

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Using a harmonic potential energy function

$$E(\phi) = \frac{K}{2}(\phi - \phi_0)^2 \quad \text{Eqn. 1}$$

to describe valence bond angle deformations, one encounters a technical problem if the bond angle ϕ becomes 180 degrees. This normally does not happen if the equilibrium angle ϕ_0 is far away from this value. The problem is caused by the transformation of the force acting along ϕ

$$f(\phi) = -dE/d\phi = -K(\phi - \phi_0) \quad \text{Eqn. 2}$$

to Cartesian forces \mathbf{f}_i , \mathbf{f}_j and \mathbf{f}_k acting on the three atoms i , j and k defining the angle, j being the central atom. Using the chain rule, the transformation becomes

$$\mathbf{f}_i = f(\phi) \left(\frac{\partial \phi}{\partial \cos \phi} \right) \left(\frac{\partial}{\partial \mathbf{r}_i} \cos \phi \right), \quad \text{Eqn. 3}$$

and similarly for the other atoms (for details, see ref. 1). The second factor in Eqn. 3 is equal to $-1/\sin \phi$ and causes the transformation to become undefined for $\phi = \pi$. The problem has been overcome in many forcefields by using a bond angle interaction term harmonic in $\cos \phi$, rather than in ϕ

$$E(\cos \phi) = \frac{K'}{2}(\cos \phi - \cos \phi_0)^2, \quad \text{Eqn. 4}$$

in which case the factor $\left(\frac{\partial \phi}{\partial \cos \phi} \right)$ disappears from Eqn. 3.

However, for $\phi_0 = \pi$, there is a simpler solution: The sine function is linear around π to a very good approximation, so we can rewrite Eqn. 2

$$f(\phi) = K \sin \phi \quad \text{for } \phi_0 = \pi. \quad \text{Eqn. 5}$$

(In fact, Eqn. 2 is just the first non-zero term in a Taylor expansion of $\sin\phi$ around $\phi_0 = \pi$.) The $\sin\phi$ term in Eqn. 5 exactly cancels the $1/\sin\phi$ term arising in the transformation (Eqn. 3). Integrating Eqn. 5 gives the expression for the potential energy

$$E(\phi) = K(1 + \cos\phi) \quad \text{for } \phi_0 = \pi. \quad \text{Eqn. 6}$$

The force constant K has the same numerical value in the trigonometrical form of the interaction terms (Eqn. 5 and Eqn. 6) as in the harmonic form (Eqn. 1 and Eqn. 2), under the condition that its unit in the trigonometric form is an energy unit (i.e. kJ mol^{-1}) and in the harmonic form it is the same energy unit per radians squared (i.e. $\text{kJ mol}^{-1} \text{rad}^{-2}$). This equivalence is sometimes more convenient than the more complicated relationship between K (Eqn. 1) and K' (Eqn. 4).

I decided to report this little technical trick in this place for three reasons: (i) I believe it has not been described before. (ii) My original description is hidden in the appendix of a paper dealing with something completely different [2]. (iii) It has been implemented in the latest version of the YASP program [3].

References

1. E. B. Wilson, J. C. Decius and P. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
2. F. Müller-Plathe, J. Chem. Phys. (submitted).
3. F. Müller-Plathe, Comput. Phys. Commun. **78**, 77 (1993).