

# Relationships among potential-energy functions

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We analyse recently proposed connection formulas between potential-energy functions for bond stretching, bond bending and molecular interactions, and propose more convenient and practical expressions. For example, our mathematical relationships between Morse and Murrell—Mottram potential parameters yield much closer agreement between such potential-energy functions.

**KEY WORDS:** bond stretching, bond bending, molecular interactions, potential-energy functions, molecular mechanics, mathematical relationships

**AMS subject classification:** 70C20, 74B15, 74E40

## 1. Introduction

In a series of papers Lim discussed mathematical connections between potential-energy functions for bond torsion, bond bending and bond stretching [1–3]. The author points out that such relationships may be useful for users of commercial software for molecular dynamics and other computational chemistry approaches.

In one of the papers Lim compares four potentials for bond stretching: the simple harmonic oscillator, the more flexible polynomial series and the more realistic Morse and Murrell—Mottram interactions [3]. A surprising result of that analysis is a noticeable discrepancy between the connected Morse and Murrell—Mottram potentials.

In this paper we analyse Lim's criteria for choosing the potential parameters, and trace back the origin of the discrepancy between Morse and Murrell—Mottram functions in order to propose alternative connective equations. We also briefly discuss Lim's connection formulas for other models [1, 2, 4].

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## 2. Bond stretching potential-energy functions

Following Lim [3], we write the Morse and Murrell–Mottram oscillators as

$$U_M(r) = D_M [1 - \exp(-\alpha x)]^2, \quad (1)$$

$$U_{MM}(r) = -D_{MM} \left( 1 + \frac{ax}{r_0} \right) \exp\left(-\frac{a}{r_0}x\right), \quad (2)$$

where  $x = r - r_0$  is the displacement from the equilibrium position  $r_0$ . Defined in this way the Morse and Murrell–Mottram oscillators are not exactly comparable because  $U_M(r_0) = 0$  and  $U_{MM}(r_0) = -D_{MM}$ ,  $U_M(r \rightarrow \infty) = D_M$  and  $U_{MM}(r \rightarrow \infty) = 0$ . Consequently, Lim introduced the modified Murrell–Mottram potential  $U_{MMM}(r) = U_{MM}(r) + D_{MM}$  that satisfies  $U_{MMM}(r_0) = 0$  and  $U_{MMM}(r \rightarrow \infty) = D_{MM}$ .

The Taylor series for those potential-energy functions are

$$U_M(r) = D_M \alpha^2 \left( x^2 - \alpha x^3 + \frac{7}{12} \alpha^2 x^4 + \dots \right), \quad (3)$$

$$U_{MMM}(r) = \frac{a^2 D_{MM}}{r_0^2} \left( \frac{1}{2} x^2 - \frac{a}{3r_0} x^3 + \frac{a^2}{8r_0^2} x^4 + \dots \right). \quad (4)$$

Comparing the coefficients of  $x$  in the exponentials of both potentials (1) and (2) Lim proposed [3]

$$\alpha = \frac{a}{r_0}. \quad (5)$$

Therefore, if we require agreement of the coefficients of the quadratic terms in equations (3) and (4) we have

$$D_{MM} = 2D_M. \quad (6)$$

The choice (5) that leads to equation (6) is most unfortunate because given a Murrell–Mottram potential parameter  $D_{MM}$  the resulting Morse oscillator predicts half the dissociation energy as shown in figures 2 and 3 of Lim's paper [3].

At first sight it seems to be more reasonable to require the agreement of the first two terms of the series (3) and (4). Proceeding accordingly we obtain

$$\alpha = \frac{2a}{3r_0}, \quad D_M = \frac{9D_{MM}}{8}, \quad (7)$$

so that the resulting Morse dissociation energy is closer to the Murrell–Mottram one.

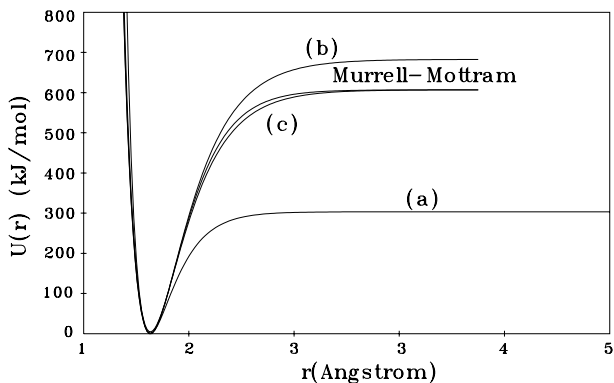


Figure 1. Murrell–Mottram and Morse potential-energy functions, the latter parametrized according to equations (5) and (6) (a), equations (7) (b) and equation (8) (c).

If we require exact agreement at infinity in addition to agreement of the coefficients of the quadratic term we have

$$D_M = D_{MM}, \quad \alpha = \frac{a}{\sqrt{2}r_0}. \tag{8}$$

We may proceed in a different way and modify the Morse oscillator as

$$V_M(r) = U_M(r) - D_M = D_M (e^{-2\alpha x} - 2e^{-\alpha x}). \tag{9}$$

If we require the agreement of the first two terms of the Taylor expansions of the potential-energy functions  $V_M(r)$  and  $U_{MM}(r)$  we obtain equation (8) from just one sensible criterion.

Figure 1 shows the Murrell–Mottram potential-energy function with the parameters

$$a = 8.2, \quad r_0 = 1.507 \text{ \AA}, \quad D_{MM} = 1.00768 \times 10^{-18} \text{ J} \tag{10}$$

chosen by Lim [3]. Figure 1 also shows the Morse function for the three connective conditions: (a) equations (5) and (6), (b) equations (7) and (c) equation (8). We appreciate that Lim’s prescription (a) produces the largest discrepancy, that case (b) gives a good agreement about equilibrium but leads to different dissociation energies (although the discrepancy is smaller than for the preceding case), and that case (c) sacrifices agreement about equilibrium to gain exact matching at infinity.

In general, if  $U_A(r)$  and  $U_B(r)$  are two single-well potential-energy functions satisfying  $U(r \rightarrow \infty) = 0$ , then the connection equations for case (c) are a particular case of

$$U_A(r_0) = U_B(r_0), \quad \left. \frac{d^j U_A(r)}{dr^j} \right|_{r=r_0} = \left. \frac{d^j U_B(r)}{dr^j} \right|_{r=r_0}, \quad j = 1, 2, \dots, k. \tag{11}$$

### 3. Lennard—Jones and exponential functions

We can apply equations (11) in order to obtain useful relationships between the Lennard—Jones potential

$$U_{LJ}(r) = \frac{D}{m-n} \left[ n \left( \frac{r_0}{r} \right)^m - m \left( \frac{r_0}{r} \right)^n \right], \quad m > n, \quad (12)$$

and the exponential- $n$  interaction [4]

$$U_E(r) = Ae^{-Br} - \frac{C}{r^n}. \quad (13)$$

A straightforward calculation shows that

$$A = \frac{nDe^\xi}{\xi - n}, \quad C = \frac{\xi Dr_0^n}{\xi - n}, \quad \xi = br_0 = \frac{m+n+1}{2} + \frac{\sqrt{(m+n+1)^2 - 4mn}}{2}, \quad (14)$$

and

$$U_E(r) = \frac{D}{\xi - n} \left[ ne^{-b(r-r_0)} - \xi \left( \frac{r_0}{r} \right)^n \right]. \quad (15)$$

Notice that the role of  $\xi > n$  in the exponential- $n$  potential is equivalent to the role of  $m$  in the Lennard—Jones one. This result generalises the one derived by Lim for the exponential-6 interaction [4].

### 4. Potential-energy functions for bond bending

Lim [2] also discussed the connection between potential-energy functions in the form of Fourier series

$$U_F(\theta) = k_F \sum_{n=0}^m C_n \cos(n\theta), \quad (16)$$

for  $m = 2$ , and the harmonic cosine function

$$U_C(\theta) = \frac{k_C}{2} (\cos \theta - \cos \theta_0)^2. \quad (17)$$

A straightforward calculation based on equations (11) yields

$$C_0 = C_2 [2 + \cos(2\theta_0)], \quad C_1 = -4C_2 \cos \theta_0, \quad (18)$$

and

$$U_F(\theta) = 2k_F C_2 (\cos \theta - \cos \theta_0)^2. \quad (19)$$

Notice that if we take into account this result, some of the connection equations derived by Lim [2] become trivial.

## 5. Conclusions

We think that our connection formulas are reasonable alternatives to the corresponding ones proposed by Lim [1–4], both from theoretical and practical points of view. If you are to compare results from alternative softwares for molecular dynamics or other quantum chemistry applications it is convenient to use clear and straightforward mathematical relationships that give the best agreement between the corresponding potential-energy functions. In the case of bond-stretching potential-energy functions you can choose, for example, between better agreement at equilibrium or at long interaction distances.

## References

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