

Mathematical connections between bond-stretching potential functions

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Mathematical connections are useful in enabling a set of parametric data from a chemical bond-stretching potential function to be applied in a computational chemistry software that adopts a different potential function. This paper establishes connections between four potential energy functions in stretching and compression of covalent bonds. The potential functions that are mathematically connected are: (i) harmonic potential, (ii) polynomial series potential, (iii) Morse potential, and (iv) Murrell–Mottram potential. Two methods are employed in obtaining the relationships between the four potential functions. The expansion approach enables the relationships to be made at large bond-stretching, whilst the differential approach allows for the connections to be made only at infinitesimal bond-stretching. For verification, parametric data from the Murrell–Mottram potential is converted to parametric data of the harmonic, polynomial series and Morse potentials. For comparison, the bond-stretching energies for these functions are plotted. Discrepancy between the Morse and the Murrell–Mottram potentials at large bond-stretching is discussed in terms of the assumed infinitesimal deformation.

KEY WORDS: bond-stretching, potential functions, molecular mechanics, force fields, mathematical connections

1. Introduction

With recent advances in nanotechnology and molecular-scale engineering, the scientific community sees ever increasing importance of computational chemistry in simulating physical properties of nano-structured materials and working performance of nano-scale devices. Though improvement of computer speed has enabled increasing application of quantum mechanics-based computational chemistry software, the very same improvement enables faster computation by the molecular mechanics approach. The use of potential functions enables the molecular mechanics-based computational chemistry to be faster than the quantum mechanical approach due to the need to solve the Schrödinger equation in the latter. However, one drawback in the molecular mechanics approach is the diversity in potential energy functions. For N -body interaction, there exist several potential energy functions which rely on different sets of parameters. Hitherto, relationship between different potential functions for two-body interaction is

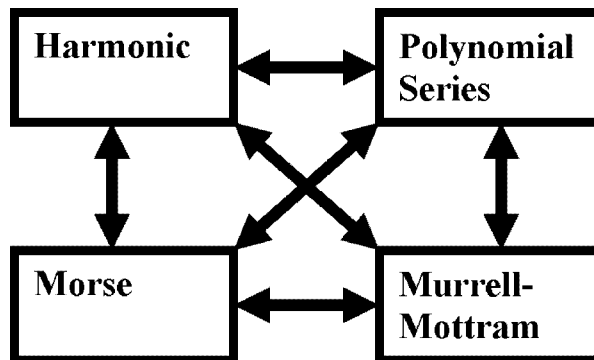


Figure 1. The four bond-stretching potentials being connected.

limited. This paper takes a mathematical approach in relating various potential energy functions of two-body interaction by establishing connections between parameters from different two-body potentials. As shown in figure 1, the two-body potential functions being connected to one another are the harmonic potential, polynomial series potential, Morse potential and Murrell–Mottram potential.

2. Analysis

Based on the Hookean spring, the simplest stretching potential energy function is known as the harmonic potential, and is written as

$$U_H = \frac{1}{2}k_H(r - r_0)^2 = \frac{1}{2}k_H(\delta r)^2, \quad (1)$$

where k_H is the “spring” stiffness between two covalently bonded atoms, whilst r and r_0 are the current and equilibrium distances, respectively. The harmonic potential is employed as the stretching energy in the following softwares: EAS [1], CVFF [2–4], CHARMM [5], TRIPOS [6,7], DREIDING [8], COSMIC [9], SHAPES [10], UFF [11–13], AMBER [14], MOMEK [15] and OPLS [16]. The harmonic potential is, however, a special case of the polynomial series potential function

$$U_S = \frac{1}{2} \sum_{n=2}^m k_{Sn} (\delta r)^n \quad (2)$$

whereby $m = 2$. Computational chemistry softwares which employ the polynomial series for bond-stretching include the MM2 [17] whereby $m = 3$; MM3 [18–21], CFF91/93/95 [22], EFF [23,24] and MMFF [25] whereby $m = 4$; and MM4 [26–29] whereby $m = 6$. Both the harmonic and the series polynomial functions give unrealistically large separation energy, instead of finite value, at large stretching that leads to

bond breaking. A finite value of potential energy at infinite bond stretching is exhibited by the Morse potential

$$U_M = D_M \{1 - \exp[-\alpha(\delta r)]\}^2, \quad (3)$$

where D_M and α are the Morse parameters. The Morse potential function is adopted by the CVFF [2–4], DREIDING [8], UFF [11–13] and ESFF [30] softwares. More recently, the Murrell–Mottram potential function [31–34] for two-body interaction,

$$U_{MM} = -D_{MM} \left[1 + \frac{a}{r_0}(\delta r) \right] \left\{ \exp \left[-\frac{a}{r_0}(\delta r) \right] \right\}, \quad (4)$$

has been developed, where D_{MM} and a are the Murrell–Mottram parameters. The Murrell–Mottram potential functions, which consists of two-body and three-body interactions, has been implemented using a suite of five FORTRAN computer programs [35], namely, the CUBEPRO, SOLIDS, SURFPRO, CLUSPRO and MELTPRO. The following analysis is a follow-up of mathematical relationships established among bond-torsion force fields [36] and those among bond-bending force fields [37].

2.1. Non-linear analysis

To relate the harmonic, series polynomial, Morse and Murrell–Mottram potential functions, we note that as $(\delta r) \rightarrow 0$,

$$\lim_{(\delta r) \rightarrow 0} \begin{Bmatrix} U_H \\ U_S \\ U_M \\ U_{MM} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \\ -D_{MM} \end{Bmatrix}. \quad (5)$$

Also, as $(\delta r) \rightarrow \infty$, we have

$$\lim_{(\delta r) \rightarrow \infty} \begin{Bmatrix} U_M \\ U_{MM} \end{Bmatrix} = \begin{Bmatrix} D_M \\ 0 \end{Bmatrix}. \quad (6)$$

To pave the way for establishing connections, the Murrell–Mottram two-body potential is written in a modified form

$$U_{MMM} = D_{MM} + U_{MM} = D_{MM} - D_{MM} \left[1 + \frac{a}{r_0}(\delta r) \right] \left\{ \exp \left[-\frac{a}{r_0}(\delta r) \right] \right\}, \quad (7)$$

so that

$$U_{MMM} = \begin{cases} 0, & (\delta r) = 0, \\ D_{MM}, & (\delta r) \rightarrow \infty. \end{cases} \quad (8)$$

Substituting the Maclaurin expansion form for the exponential term

$$\exp(\pm x) = \sum_{n=0}^{+\infty} \frac{(\pm 1)^n x^n}{n!} \quad (9)$$

into equations (3) and (7) leads to

$$U_M = D_M \left[\alpha^2 (\delta r)^2 - \alpha^3 (\delta r)^3 + \frac{7}{12} \alpha^4 (\delta r)^4 - \frac{1}{4} \alpha^5 (\delta r)^5 + \frac{31}{360} \alpha^6 (\delta r)^6 \right] \quad (10)$$

and

$$U_{MMM} = D_{MM} \left[\frac{1}{2} \left(\frac{a}{r_0} \right)^2 (\delta r)^2 - \frac{1}{3} \left(\frac{a}{r_0} \right)^3 (\delta r)^3 + \frac{1}{8} \left(\frac{a}{r_0} \right)^4 (\delta r)^4 - \frac{1}{30} \left(\frac{a}{r_0} \right)^5 (\delta r)^5 + \frac{1}{144} \left(\frac{a}{r_0} \right)^6 (\delta r)^6 \right], \quad (11)$$

respectively. Hence, comparing terms in equations (2), (10) and (11) gives simultaneous connections between polynomial series, Morse and Murrell–Mottram parameters as

$$\begin{Bmatrix} k_{S2} \\ k_{S3} \\ k_{S4} \\ k_{S5} \\ k_{S6} \end{Bmatrix} = 2D_M \alpha^2 \begin{Bmatrix} 1 \\ -\alpha \\ \frac{7}{12} \alpha^2 \\ -\frac{1}{4} \alpha^3 \\ \frac{31}{360} \alpha^4 \end{Bmatrix} = D_{MM} \left(\frac{a}{r_0} \right)^2 \begin{Bmatrix} 1 \\ -\frac{2}{3} \left(\frac{a}{r_0} \right) \\ \frac{1}{4} \left(\frac{a}{r_0} \right)^2 \\ -\frac{1}{15} \left(\frac{a}{r_0} \right)^3 \\ \frac{1}{72} \left(\frac{a}{r_0} \right)^4 \end{Bmatrix}. \quad (12)$$

For infinitesimal bond stretching, higher orders can be neglected, thereby giving parametric connections among the harmonic, polynomial series, Morse and Murrell–Mottram potential functions as

$$k_H = k_{S2} = 2D_M \alpha^2 = D_{MM} \left(\frac{a}{r_0} \right)^2. \quad (13)$$

2.2. Linearized analysis

As an alternative to the expansion approach demonstrated in section 2.1, the differential approach is applicable in obtaining mathematical connections between all four bond-stretching potential functions. Taking double differentials for equations (1)–(4), we arrive at

$$\frac{\partial^2 U_H}{\partial (\delta r)^2} = k_H, \quad (14)$$

$$\frac{\partial^2 U_S}{\partial (\delta r)^2} = \sum_{n=2}^m \frac{n(n-1)}{2} k_{Sn} (\delta r)^{n-2}, \quad (15)$$

$$\frac{\partial^2 U_M}{\partial(\delta r)^2} = 2D_M\alpha^2 \{2 \exp[-2\alpha(\delta r)] - \exp[-\alpha(\delta r)]\}, \quad (16)$$

and

$$\frac{\partial^2 U_{MM}}{\partial(\delta r)^2} = D_{MM} \left(\frac{a}{r_0}\right)^2 \left[1 - \frac{a}{r_0}(\delta r)\right] \exp\left[-\frac{a}{r_0}(\delta r)\right], \quad (17)$$

respectively. Taking the limit $(\delta r) \rightarrow 0$ reduces equations (15)–(17) into

$$\lim_{(\delta r) \rightarrow 0} \frac{\partial^2 U_S}{\partial(\delta r)^2} = k_{S2}, \quad (18)$$

$$\lim_{(\delta r) \rightarrow 0} \frac{\partial^2 U_M}{\partial(\delta r)^2} = 2D_M\alpha^2, \quad (19)$$

and

$$\lim_{(\delta r) \rightarrow 0} \frac{\partial^2 U_{MM}}{\partial(\delta r)^2} = D_{MM} \left(\frac{a}{r_0}\right)^2, \quad (20)$$

respectively. Comparing equations (14), (18), (19) and (20) thereby leads to the connection given in equation (13). To relate parameters of the Morse and Murrell–Mottram potentials to one another, we express equations (3) and (7) in dimensionless form:

$$1 - \frac{U_M}{D_M} = \{1 + [1 - \exp(-\alpha(\delta r))]\} \exp(-\alpha(\delta r)) \quad (21)$$

and

$$1 - \frac{U_{MM}}{D_{MM}} = \left\{1 + \left[\left(\frac{a}{r_0}\right)(\delta r)\right]\right\} \exp\left(-\frac{a}{r_0}(\delta r)\right). \quad (22)$$

Comparing indices of the exponential terms in equations (21) and (22) gives

$$\alpha = \frac{a}{r_0}, \quad (23)$$

which agrees well with the infinitesimal deformation, whilst comparison of terms in the square parenthesis shows that

$$1 - \exp(-\alpha(\delta r)) = \frac{a}{r_0}(\delta r). \quad (24)$$

Writing equation (24) in summation series,

$$\frac{a}{r_0} = \sum_{n=0}^{+\infty} \frac{(-1)^n \alpha^{n+1} (\delta r)^n}{(n+1)!}, \quad (25)$$

then, upon consideration of very small bond-stretching, equation (25) simplifies to equation (23). Under this special condition of infinitesimal deformation, we note that

$$D_{MM} = 2D_M, \quad (26)$$

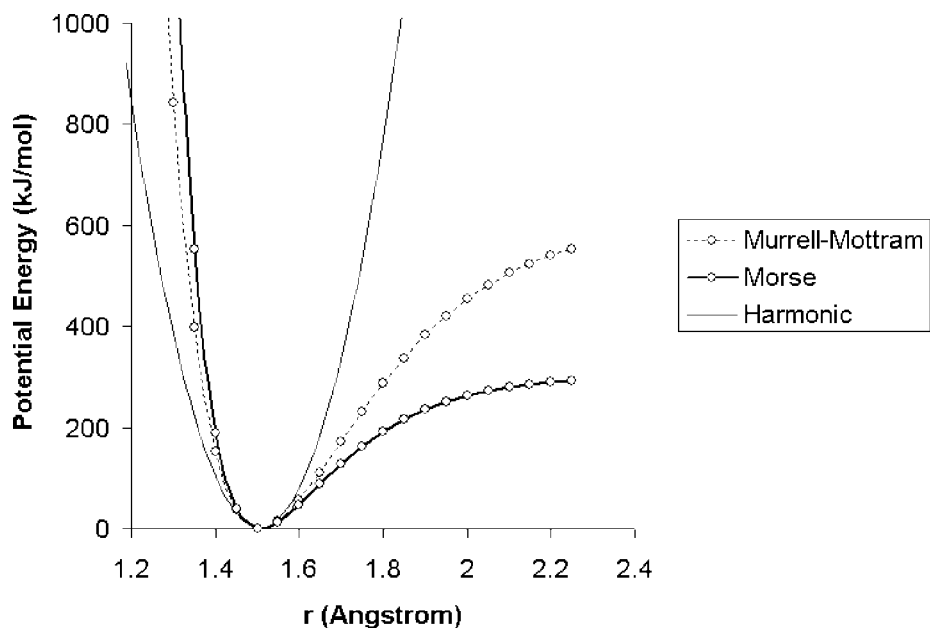


Figure 2. Comparison of harmonic, Morse and Murrell–Mottram potentials, equated at infinitesimal deformation.

Table 1
Equivalent sets of parameters.

	Murrell–Mottram [36] data	Morse parameters
	$a = 8.2$	$\alpha = 5.441 \times 10^{10} \text{ m}^{-1}$
	$r_0 = 1.507 \text{ \AA}$	
	$D_{\text{MM}} = 1.00768 \times 10^{-18} \text{ J}$	$D_{\text{M}} = 5.038 \times 10^{-19} \text{ J}$
$k_{\text{S}2} = k_{\text{H}} (\text{kJ mol}^{-1} \text{ m}^{-2})$	2979.7	2983.5
$k_{\text{S}3} (\text{kJ mol}^{-1} \text{ m}^{-3})$	-1.0809×10^{14}	-1.6234×10^{14}
$k_{\text{S}4} (\text{kJ mol}^{-1} \text{ m}^{-4})$	2.2055×10^{24}	5.1528×10^{24}
$k_{\text{S}5} (\text{kJ mol}^{-1} \text{ m}^{-5})$	-3.2002×10^{34}	-12.0162×10^{34}
$k_{\text{S}6} (\text{kJ mol}^{-1} \text{ m}^{-6})$	3.6278×10^{44}	22.5209×10^{44}

that is, if the two-body interaction potentials according to Morse and Murrell–Mottram are equated only for infinitesimal bond-stretching, then the predicted dissociation energy (at infinite separation) for covalent bonds according to Morse potential is half of that according the Murrell–Mottram potential.

3. Results and discussion

To verify the mathematical connections described in section 2, we plot the variation in bond-stretching potential energy (in kJ/mol) with respect to the interatomic

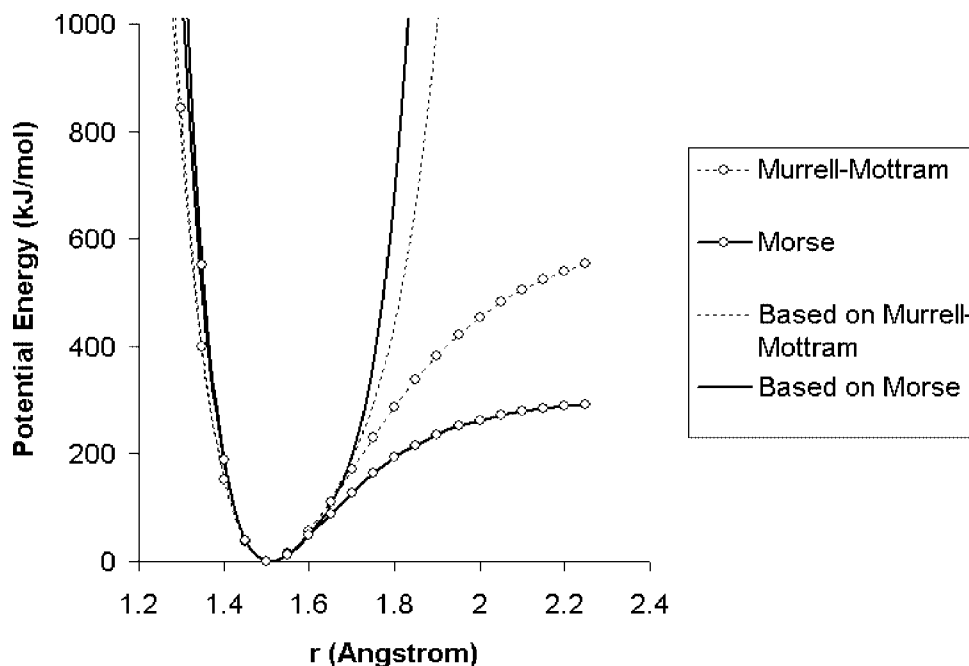


Figure 3. Comparison between Morse and Murrell–Mottram potentials, with corresponding polynomial series solution at fourth order.

distance, r , in angstroms. Adopting the Murrell–Mottram parameters for tetrahedral carbons [38], the various bond-stretching parameters are obtained on the basis of equations (12), (13), (23) and (26). The Morse parameters are obtained from those of Murrell–Mottram based on equations (23) and (26). Two sets of polynomial series potential function parameters are thus obtained, each from the Murrell–Mottram parameters and the Morse parameters, on the basis of equation (12). For infinitesimal deformation whereby the harmonic function is valid, both k_{S2} from either the Murrell–Mottram parameters or the Morse parameters converge into a common value, as shown in table 1 and equation (13).

Figure 2 shows that the change in potential energy of a two-body system with respect to the interatomic distance. As expected, the harmonic potential gives a symmetric distribution about the equilibrium bond length. The Morse potential, being an empirical form of the *ab initio* approach, gives a more realistic energy distribution whereby the potential rises in a steep manner for bond-compression but rises with a decreasing slope terminating at an asymptotic constant value. This terminal energy of D_M signifies the energy required for bond-dissociation. The Murrell–Mottram potential, on the other hand, is shown to be bounded by the harmonic and the Morse potentials, with a dissociating energy twice of that predicted by the Morse function. For small change in bond length, the three potential functions agree well with one another.

Figure 3 shows the polynomial series approximation at $m = 4$ to the Morse and Murrell–Mottram potentials. Not surprisingly, with three terms the polynomial series

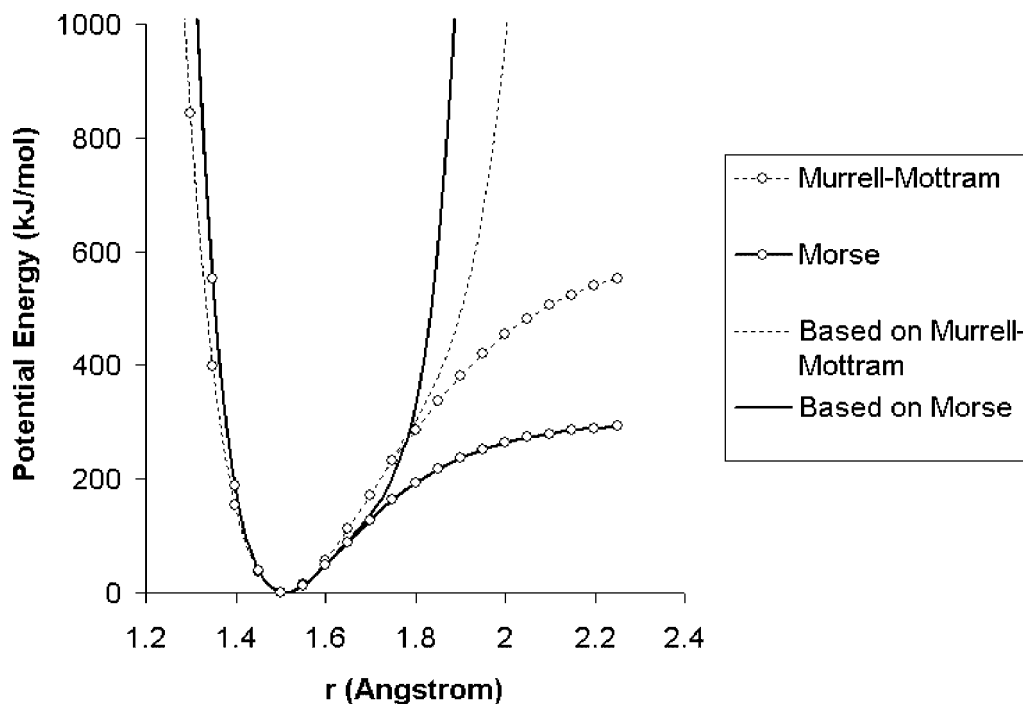


Figure 4. Comparison between Morse and Murrell–Mottram potentials, with corresponding polynomial series solution at sixth order.

function gives better agreement than the harmonic function. Needless to say, the polynomial series function at $m = 6$ gives better approximation than that at $m = 4$, as evident from figure 4.

The relation in equation (26), which describes the discrepancy between the Morse and Murrell–Mottram functions, is clearly shown in figures 2–4. This discrepancy may well be attributed to the assumption of infinitesimal deformation described in equation (23). It is due to this discrepancy that gives rise to two sets of polynomial series potential parameters.

4. Conclusions and suggestion

A set of relationship quantifying the connections between the harmonic, polynomial series, Morse and Murrell–Mottram potential functions for bond-stretching has been derived. The expansion approach enables good approximation to be made for large bond-stretching, whilst the differential approach gives parametric connections valid only at infinitesimal atomic separation. To deal with the discrepancy between the Morse and Murrell–Mottram potentials at large deformation, it is suggested that both sets of parameters be related exactly or in terms of a series summation. An exact relationship

between parameters of the Morse and Murrell–Mottram potentials is expected to give common polynomial series potential parameters.

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