

## MATHEMATICAL RELATIONSHIPS FOR DEVELOPMENT OF A MOLECULAR POTENTIAL FUNCTION CONVERTER

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### **Abstract:**

This paper gives a short review on relating molecular potential functions within the same category of interatomic interactions. The bond-stretching potentials that were related include the harmonic, polynomial series and Morse functions. The bond-bending potentials that were connected involve the harmonic angle, polynomial angle series, harmonic cosine and Fourier series functions. The bond-twisting potentials that were related are the trigonometric series and the cosine power series functions. Finally, the non-bonded potentials that were connected include the Lennard-Jones type and the Exponential-6 functional forms. The above-mentioned relationships were previously obtained using mathematical methods such as Maclaurin's series expansions, trigonometric identities and elementary calculus. These relationships are tabulated in a concise manner in preparation for the development of a potential function converter software that enables a given molecular potential function to be converted to a different functional form. The software can be further utilized as an educational tool for displaying, in a graphical manner, the similarities and discrepancies in normalized molecular potential functions.

## I. Introduction

The significance of molecular modeling in shedding insight into physical properties, chemical reactions and biological implications, is undoubted. Critical to the molecular simulation is the computational chemistry softwares that employ various forms of molecular force fields. Notwithstanding the exactness of the quantum mechanical approach, the application of empirical potential energy functions is advantageous in greatly reducing computational time and cost. As a result, there exist a good number of computational chemistry softwares that adopt empirically-based molecular force fields. Basically, force fields can be written as the summation of two-body (bond stretching), three-body (bond-bending), four-body (bond twisting) and non-bonded potential energy functions,

$$E_{Total} = E_{2b} + E_{3b} + E_{4b} + E_{Nb} \quad (1)$$

with

$$E_{2b} = \sum_{i,j} U(r_{ij}) \quad (2)$$

$$E_{3b} = \sum_{i,j,k} U(\theta_{ijk}) \quad (3)$$

$$E_{4b} = \sum_{i,j,k,l} U(\phi_{ijkl}) \quad (4)$$

$$E_{Nb} = \sum (U_{vdW} + U_{Ctb}) \quad (5)$$

where  $r_{ij}$ ,  $\theta_{ijk}$  and  $\phi_{ijkl}$  are the bond length between atoms  $i$  and  $j$ , the bond angle formed by atoms  $i$ ,  $j$  and  $k$ , and the twisted angle defined from atoms  $i$ ,  $j$ ,  $k$  and  $l$  respectively, whilst  $U_{vdW}$  and  $U_{Ctb}$  refer to van der Waals (electrodynamic) and Coulombic (electrostatic) interatomic interactions respectively.

Due to different functional forms adopted by different computational chemistry softwares, conversion of potential functions via parametric relationships are required. However, such relationships are limited. Recently a whole range of mathematical relationships was developed for relating parameters of different potential functions for describing bond-stretching [1], bond-bending [2], bond-torsion [3] and non-bonded interactions [4,5]. Mathematical relationships among parameters of the same class of interatomic interaction are updated herein. Hence the objectives of this paper are threefold:

(a) To provide a brief review of recent development in mathematical relationships between molecular potential functions of the same class;

- (b) To update on parametric relationships that were not previously covered in recent literature [1-4] and;
- (c) To pave a way toward an algorithmic development of a potential function converter.

Figure 1 summarizes the potential function conversion reviewed in this paper, with the continuous arrows describing relationships developed previously [1-4] while the dashed arrows signify relationships proposed in this paper.

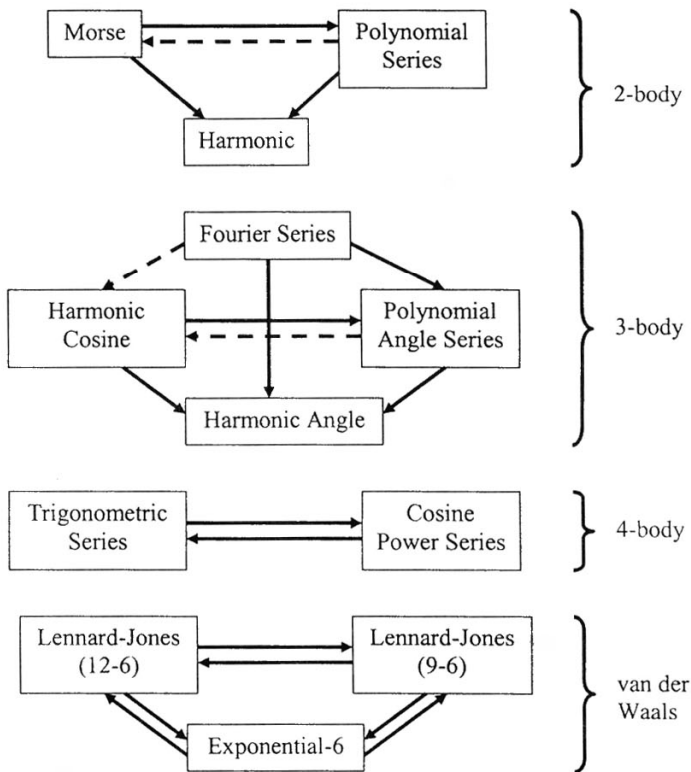


Fig.1 Inter-relationships among potential functions of the same class of interatomic interactions. (Continuous arrows refer to recently developed relationships [1-4]; dashed arrows refer to relationships given in this paper).

## II. 2-Body Interaction

Based on stretching of a spring, the harmonic potential is written as [6,7]

$$U_H = \frac{1}{2} k_H (r - r_0)^2 = \frac{1}{2} k_H (\delta r)^2 \quad (6)$$

where  $k_H$  is the structural stiffness of the “spring” that connects two covalently bonded atoms, whilst  $r$  and  $r_0$  are the current and equilibrium bond lengths respectively. Due to its simplicity, the harmonic potential has been employed by the following softwares: EAS [8], CVFF [9], CHARMM [10], GROMOS [11], TRIPOS [12], DREIDING [13], COSMIC [14], SHAPES [15], UFF [16], AMBER [17], MOMEK [18] and OPLS [19]. The harmonic potential can be considered the simplest case of the polynomial series potential function, whereby the latter is generally expressed as

$$U_S = \frac{1}{2} \sum_{n=2}^m k_{sn} (\delta r)^n \quad (7)$$

This form where  $m$  can be any integer greater than 2 enables greater flexibility during curve-fitting of experimental data. In spite of giving an infinite value of energy as the bond length increases – thereby erroneous as in the harmonic potential – the polynomial series has been adopted in various softwares such as MM2 [20] whereby  $m=3$ ; MM3 [21], CFF91/93/95 [22], EFF [23] and MMFF [24] whereby  $m=4$ ; and MM4 [25] whereby  $m=6$ . The most frequently employed 2-body potential function that gives a finite value at bond dissociation, and hence realistic for describing large change in bond length, is the Morse potential [26]

$$U_M = D_M [1 - \exp(\alpha \delta r)]^2 \quad (8)$$

where  $D_M$  is the bond dissociation energy while  $\alpha$  expresses the rate of change of the interaction energy with respect to the change of bond length. The Morse potential has been adopted in the CVFF [9], DREIDING [13], UFF [16] and ESFF [27] softwares. In view of the appropriateness of the Morse functional form in describing 2-body potentials, it has been used as the basis in obtaining the polynomial series functional form. Substituting the Maclaurin expansion for negative exponential

$$\exp(-\alpha \delta r) = \sum_{n=0}^{+\infty} (-1)^n \frac{\alpha^n (\delta r)^n}{n!} \quad (9)$$

into Eq.(8) and, upon comparing with coefficients of Eqs.(6) and (7) up to  $m=6$ , we obtain the harmonic parameter [1,13,16]

$$k_H = 2D_M \alpha^2 \quad (10)$$

and the polynomial series parameters [1]

$$\begin{Bmatrix} k_{S2} \\ k_{S3} \\ k_{S4} \\ k_{S5} \\ k_{S6} \end{Bmatrix} = 2D_M \alpha \begin{Bmatrix} 1 \\ -\alpha \\ \frac{7}{12}\alpha^2 \\ -\frac{1}{4}\alpha^3 \\ \frac{31}{360}\alpha^4 \end{Bmatrix} \quad (11)$$

in terms of the Morse parameters. Comparison between the harmonic potential and the polynomial series potential reveals that the latter can be converted to the former but not vice versa, i.e. given  $k_{S_n}$  ( $n=2,3,\dots,m$ ), the harmonic parameter is simply

$$k_H = k_{S2}. \quad (12)$$

While the harmonic parameter cannot lead to the Morse parameter, one can easily obtain the Morse parameter from the polynomial series parameter. Solving the first and second rows of Eq.(11), we have

$$\alpha = -\frac{k_{S3}}{k_{S2}} \quad (13)$$

and

$$D_M = \frac{k_{S2}^3}{2k_{S3}^2}, \quad (14)$$

which is applicable for the given polynomial of order  $m \geq 3$ , such as MM2 [20]. Alternatively when  $m \geq 4$ , such as MM3 [21], CFF91/93/95 [22], EFF [23], MMFF [24] and MM4 [25], the Morse parameters can also be obtained from the first and third rows of Eq.(11) to give

$$\alpha = \sqrt{\frac{12}{7} \left( \frac{k_{S4}}{k_{S2}} \right)} \quad (15)$$

and

$$D_M = \frac{7}{24} \left( \frac{k_{S2}^2}{k_{S4}} \right). \quad (16)$$

### III. 3-Body Interaction

As with the harmonic potential in the 2-body interaction, the harmonic angle potential function [6]

$$U_{\theta} = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2 = \frac{1}{2}k_{\theta}(\delta\theta)^2 \quad (17)$$

is simple for execution, and has been adopted in various softwares such as CVFF [9], CHARMM [10], GROMOS [11], TRIPOS [12], COSMIC [14], AMBER [17], MOMECS [18], OPLS [19] and MM2 [20].  $\theta$ ,  $\theta_0$  and  $k_{\theta}$  are the current bond angle, equilibrium bond angle and the harmonic angle stiffness respectively. To provide better curve-fitting, the harmonic angle function has been extended into a polynomial angle series potential function

$$U_{S\theta} = \frac{1}{2} \sum_{n=2}^m k_{\theta n} (\delta\theta)^n \quad (18)$$

where  $m$  is the polynomial order. The third-order polynomial ( $m=3$ ) has been applied in the following softwares: EAS [8], EFF [23] and MMFF [24]. The fourth-order polynomial ( $m=4$ ) series has been incorporated in the CFF91/93/95 [22] software while the sixth-order ( $m=6$ ) has been employed in the MM3 [21] and MM4 [25] softwares. An alternative to the above-mentioned 3-body potential functions is the harmonic cosine potential function

$$U_C = \frac{1}{2}k_c(\cos\theta - \cos\theta_0)^2, \quad (19)$$

which was adopted in the DREIDING [13] and the ESFF [27] softwares. An advantage of the harmonic cosine function is in its allowance for asymmetric curve about the equilibrium bond angle – thereby providing a more realistic and yet equally simple execution as compared to the harmonic angle potential. Another alternative is the Fourier series

$$U_F = k_F \sum_{n=0}^m C_n \cos(n\theta), \quad (20)$$

which caters for high flexibility in curve-fitting. The Fourier series has been used in the SHAPES [15] and UFF [16] softwares with  $m=2$  whereby

$$C_0 = C_2(2\cos^2\theta_0 + 1) \quad (21)$$

$$C_1 = -4C_2 \cos\theta_0 \quad (22)$$

$$C_2 = \frac{1}{4\sin^2\theta_0}. \quad (23)$$

Similar to the case of 2-body potential functions, the given polynomial angle series parameters  $k_{\theta_n}$  ( $n=2,3,\dots,m$ ) can be reduced to the harmonic angle parameter as

$$k_{\theta} = k_{\theta_2}. \quad (24)$$

Parameters from both the harmonic cosine and the Fourier series functions can be converted to parameters of the polynomial angle series by firstly expressing

$$\theta = \theta_0 + \delta\theta \quad (25)$$

in Eqs.(19) and (20), followed by substituting the Maclaurin's expansions for sine and cosine functions as

$$\sin(\delta\theta) = \sum_{n=0}^{+\infty} (-1)^n \frac{(\delta\theta)^{2n+1}}{(2n+1)!} \quad (26)$$

and

$$\cos(\delta\theta) = \sum_{n=0}^{+\infty} (-1)^n \frac{(\delta\theta)^{2n}}{(2n)!}. \quad (27)$$

respectively. Hence comparison of coefficients gives the polynomial angle series parameters in terms of the harmonic cosine parameters [2]

$$\begin{Bmatrix} k_{\theta_2} \\ k_{\theta_3} \\ k_{\theta_4} \\ k_{\theta_5} \\ k_{\theta_6} \end{Bmatrix} = k_C \begin{Bmatrix} \sin^2 \theta_0 \\ \sin \theta_0 \cos \theta_0 \\ -\frac{1}{3} \sin^2 \theta_0 + \frac{1}{4} \cos^2 \theta_0 \\ -\frac{1}{4} \sin \theta_0 \cos \theta_0 \\ \frac{2}{45} \sin^2 \theta_0 - \frac{1}{24} \cos^2 \theta_0 \end{Bmatrix}, \quad (28)$$

and in terms of the Fourier series parameters [2]

$$\begin{Bmatrix} k_{\theta_2} \\ k_{\theta_3} \\ k_{\theta_4} \\ k_{\theta_5} \\ k_{\theta_6} \end{Bmatrix} = k_C \begin{Bmatrix} -(C_1 \cos \theta_0 + 2^2 C_2 \cos 2\theta_0) \\ \frac{1}{3} (C_1 \sin \theta_0 + 2^3 C_2 \sin 2\theta_0) \\ \frac{1}{12} (C_1 \cos \theta_0 + 2^4 C_2 \cos 2\theta_0) \\ -\frac{1}{60} (C_1 \sin \theta_0 + 2^5 C_2 \sin 2\theta_0) \\ -\frac{1}{360} (C_1 \cos \theta_0 + 2^6 C_2 \cos 2\theta_0) \end{Bmatrix}. \quad (29)$$

For the case where the polynomial angle series is at least third order ( $m \geq 3$ ), the first and second rows of Eq.(28) can be solved to give the harmonic cosine angle parameter in terms of the polynomial angle series parameters

$$k_C = \frac{2(k_{\theta_2} - k_{\theta_3})}{1 - (\sin 2\theta_0 + \cos 2\theta_0)}. \quad (30)$$

For the case where the polynomial angle series are of at least fourth order ( $m \geq 4$ ), an alternative can be obtained from the first and third rows of Eq.(28) to give

$$k_C = \frac{4}{3} \left( \frac{k_{\theta_2} + k_{\theta_4}}{\cos^2 \theta_0} \right). \quad (31)$$

The harmonic cosine parameter can also be obtained from the Fourier series parameters by expanding the former and comparing its coefficients with those of the latter, which leads to

$$k_C = 4k_F C_2, \quad (32)$$

$$k_C = -\frac{k_F C_1}{\cos \theta_0} \quad (33)$$

or

$$k_C = \frac{4k_F C_0}{2 \cos^2 \theta_0 + 1}. \quad (34)$$

Considering Eq.(24) and the first rows of Eqs.(28) or (29), the harmonic angle parameter can be obtained from the harmonic cosine parameter [2,13]

$$k_\theta = k_C \sin^2 \theta_0 \quad (35)$$

or from the Fourier series parameters [2]

$$k_\theta = -k_F (C_1 \cos \theta_0 + 4C_2 \cos 2\theta_0) \quad (36)$$

respectively.

#### IV. 4-Body Interaction

Two of the most highly utilized functions for twisting of bonds are the trigonometric series potential function

$$U_\phi = \frac{1}{2} \sum_{n=1}^m k_n [1 - (-1)^n \cos n\phi] \quad (37)$$

used in CHARMM [10], DREIDING [13], UFF [16], MM3 [21], ECEPP [28] and TRIPOS [29], and the cosine power series potential function



$$U_T = \sum_{n=0}^m k_{Tn} \cos^n \phi, \quad (38)$$

that has been used by various groups with  $m=3$  [30-34] and  $m=5$  [35-38] where  $\phi$  is the amount of twisted dihedral angle. Substituting

$$\begin{cases} \cos 1\phi \\ \cos 2\phi \\ \cos 3\phi \\ \cos 4\phi \\ \cos 5\phi \end{cases} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 & 0 & 0 \\ 0 & -3 & 0 & 4 & 0 & 0 \\ 1 & 0 & -8 & 0 & 8 & 0 \\ 0 & 5 & 0 & -20 & 0 & 16 \end{bmatrix} \begin{cases} \cos^0 \phi \\ \cos^1 \phi \\ \cos^2 \phi \\ \cos^3 \phi \\ \cos^4 \phi \\ \cos^5 \phi \end{cases} \quad (39)$$

into Eq.(37) and upon comparing coefficients with Eq.(38) we arrive at the cosine power series parameters in terms of the trigonometric series parameters [3]

$$\begin{cases} k_{T0} \\ k_{T1} \\ k_{T2} \\ k_{T3} \\ k_{T4} \\ k_{T5} \end{cases} = \frac{1}{2} \begin{bmatrix} 1 & 2 & 1 & 0 & 1 \\ 1 & 0 & -3 & 0 & 5 \\ 0 & -2 & 0 & 8 & 0 \\ 0 & 0 & 4 & 0 & -20 \\ 0 & 0 & 0 & -8 & 0 \\ 0 & 0 & 0 & 0 & 16 \end{bmatrix} \begin{cases} k_{\phi 1} \\ k_{\phi 2} \\ k_{\phi 3} \\ k_{\phi 4} \\ k_{\phi 5} \end{cases}, \quad (40)$$

and vice versa [3] upon solving Eq.(40)

$$\begin{cases} k_{\phi 1} \\ k_{\phi 2} \\ k_{\phi 3} \\ k_{\phi 4} \\ k_{\phi 5} \end{cases} = \frac{1}{8} \begin{bmatrix} 16 & 0 & 12 & 0 & 10 \\ 0 & -8 & 0 & -8 & 0 \\ 0 & 0 & 4 & 0 & 5 \\ 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{cases} k_{T1} \\ k_{T2} \\ k_{T3} \\ k_{T4} \\ k_{T5} \end{cases}. \quad (41)$$

## V. Non-bonded Interaction

The non-bonded interaction due to electrostatic (or Coulombic) force is written [39] as

$$U_{cb} = \frac{q_A q_B}{\epsilon r_{AB}} \quad (42)$$

where  $q_A$  and  $q_B$  are the charge of atoms A and B respectively,  $r_{AB}$  being the distance between them and  $\epsilon$  is the dielectric constant. There being no other functional form for this point charge interaction, there exists no justification for any conversion. The earliest non-bonded

interaction due to electrodynamic (or van der Waals) force is written as the Lennard-Jones (12-6) form [40]

$$U_{12-6}^{LJ} = D_{12-6}^{LJ} \left[ \left( \frac{R}{r} \right)^{12} - 2 \left( \frac{R}{r} \right)^6 \right], \quad (43)$$

which has been applied in the CVFF [9], CHARMM [10], GROMOS [11], TRIPOS [12], DREIDING [13], SHAPES [15], UFF [16], AMBER [17], OPLS [19] and ECEPP [28] softwares. To a lesser extent the alternative Lennard-Jones (9-6) function

$$U_{9-6}^{LJ} = D_{9-6}^{LJ} \left[ 2 \left( \frac{R}{r} \right)^9 - 3 \left( \frac{R}{r} \right)^6 \right] \quad (44)$$

has been adopted by the CFF91/93/95 [22] and the ESFF [27] softwares. For the Lennard-Jones class of potential functions,  $D^{LJ}$  refers to minimum well depth. The van der Waals distance,  $R$ , refers to the non-bonded interatomic length that gives the minimum potential energy. Apart from the Lennard-Jones functional forms, the Exponential-6 potential function [41]

$$U_{x6} = A \exp(-Br) - \frac{C}{r^6} \quad (45)$$

has been employed in the EAS [8], DREIDING [13], MOMEK [18], MM2 [20], MM3 [21], EFF [23] and MM4 [25] softwares. In view of the ease by which non-bonded atoms relatively displace among themselves, two forms of potential function parametric conversions were established:

- (a) The close range (or near equilibrium) parametric conversion which is exact at and near  $r = R$  but displays gross discrepancies over long range, and;
- (b) The long range parametric conversion which is non-exact but gives good approximation throughout an entire range of interatomic distance. Mathematical relationships between a generalized Lennard-Jones ( $m$ - $n$ ) function

$$U_{m-n}^{LJ} = D_{m-n}^{LJ} \left[ \frac{n}{m-n} \left( \frac{R}{r} \right)^m - \frac{m}{m-n} \left( \frac{R}{r} \right)^n \right] \quad ; \quad m > n, \quad (46)$$

and the Exponential-6 potential function, Eq.(45), were developed [4]. By equating the corresponding zeroth, first and second differentials of both van der Waals potentials at  $r = R$ , close range relationships were obtained. By comparing the coefficients and indices of the repulsive and attractive terms, long range relationships were obtained. Given a Lennard-Jones

(12-6) potential function parameters, parameters of Exponential-6 potential can be obtained as [4,16]

$$A = 739132D_{12-6}^{LJ} \quad (47)$$

$$B = \frac{13.772}{R} \quad (48)$$

$$C = 1.772D_{12-6}^{LJ}R^6 \quad (49)$$

for close range approximation, and

$$A = 162755D_{12-6}^{LJ} \quad (50)$$

$$B = \frac{12}{R} \quad (51)$$

$$C = 2D_{12-6}^{LJ}R^6 \quad (52)$$

for long range approximation. Given a Lennard-Jones (9-6) potential function parameters, parameters of Exponential-6 potential can be obtained as [4]

$$A = 18153.1D_{9-6}^{LJ} \quad (53)$$

$$B = \frac{11.162}{R} \quad (54)$$

$$C = 2.1623D_{9-6}^{LJ}R^6 \quad (55)$$

for close range approximation, and

$$A = 16206.2D_{9-6}^{LJ} \quad (56)$$

$$B = \frac{9}{R} \quad (57)$$

$$C = 3D_{9-6}^{LJ}R^6 \quad (58)$$

for long range approximation. As such, given an Exponential-6 potential function, parameters of the Lennard-Jones (12-6) function can be obtained from Eqs.(47) and (48) for close range approximation, and Eqs.(50) and (51) for long range approximation. Similarly, given an Exponential-6 potential function, parameters of the Lennard-Jones (9-6) function can be obtained from Eqs.(53) and (54) for close range approximation, and Eqs.(56) and (57) for long range approximation. Parametric relationships between Lennard-Jones (12-6) and that of (9-6) applies only for short range, whereby

$$D_{12-6}^{LJ} = D_{9-6}^{LJ} \quad (59)$$

## VI. Conclusions and Recommendations

Based on established mathematical relations – such as Maclaurin's expansions, trigonometric identities, calculus, etc – a range of relationships between parameters of different potential functions within the same class of interatomic interactions were recently obtained [1-5] and reviewed in this paper. A summary of conversion equations for bonded and non-bonded interactions are listed in Tables 1 to 5 in preparation for the development of a potential function converter.

**Table 1** Conversion among 2-body potential functions

		To			
		Harmonic	Polynomial Series ( $m = 3$ )	Polynomial Series ( $m = 4$ )	Morse
From	Harmonic	-	nil	nil	nil
	Polynomial Series ( $m \geq 3$ )	Eq.(12)	-	-	Eqs.(13) & (14)
	Polynomial Series ( $m \geq 4$ )	Eq.(12)	-	-	Eqs.(15) & (16)
	Morse	Eq.(10)	Eq.(11)	Eq.(11)	-

**Table 2** Conversion among 3-body potential functions

		To			
		Harmonic Angle	Polynomial Angle Series	Harmonic Cosine	Fourier Series
From	Harmonic Angle	-	nil	Eq.(35)	nil
	Polynomial Angle Series	Eq.(24)	-	Eqs.(30) or (31)	nil
	Harmonic Cosine	Eq.(35)	Eq.(28)	-	nil
	Fourier Series	Eq.(36)	Eq.(29)	Eqs.(32), (33) or (34)	-

**Table 3** Conversion among 4-body potential functions

		To	
		Trigonometric Series	Cosine Power Series
From	Trigonometric Series	-	Eq.(40)
	Cosine Power Series	Eq.(41)	-

**Table 4** Close-range conversion among van der Waals potential functions

		To		
		Lennard-Jones (12-6)	Lennard-Jones (9-6)	Exponential-6
From	Lennard-Jones (12-6)	-	Eq.(59)	Eqs.(47) to (49)
	Lennard-Jones (9-6)	Eq.(59)	-	Eqs.(53) to (55)
	Exponential-6	Eqs.(47) & (48)	Eqs.(53) & (54)	-

**Table 5** Long-range conversion among van der Waals potential functions

		To		
		Lennard-Jones (12-6)	Lennard-Jones (9-6)	Exponential-6
From	Lennard-Jones (12-6)	-	nil	Eqs.(50) to (52)
	Lennard-Jones (9-6)	nil	-	Eqs.(56) to (58)
	Exponential-6	Eqs.(50) & (51)	Eqs.(56) & (57)	-

The potential function converter software can be used as a tool to enable parameters of one potential function to be made useful for generating another potential function of the same class of interatomic interaction. In addition, the software can be an educational tool for graphical display to compare the given and converted potential function curves.

## References

- [1] T.C. Lim, J. Math. Chem. **33** (2003) 29
- [2] T.C. Lim, J. Math. Chem. **32** (2002) 249
- [3] T.C. Lim, J. Math. Chem. **31** (2002) 421
- [4] T.C. Lim, J. Math. Chem. **33** (2003) 279
- [5] T.C. Lim, J. Math. Chem. (submitted)
- [6] T.L. Hill, J. Chem. Phys. **14** (1946) 465
- [7] F.H. Westheimer and J.E. Mayer, J. Chem. Phys. **14** (1946) 733
- [8] E.M. Engler, J.D. Andose, P.v.R. Schleyer, J. Am. Chem. Soc. **95** (1973) 8005
- [9] S. Lifson, A.T. Hagler and P. Dauber, J. Am. Chem. Soc. **101** (1979) 5111

- [10] R. Brooks, R.E. Bruccoleri, B.D. Olafson, D.J. States, S. Swaminathan and M. Karplus, *J. Comput. Chem.* **4** (1983) 187
- [11] W.F. van Gunsteren and H.J.C. Berendsen, *Groningen Molecular Simulation (GROMOS) Library Manual* (1987)
- [12] M. Clark, R.D. Cramer III and N. van Opdenbosch, *J. Comput. Chem.* **10** (1989) 982
- [13] S.L. Mayo, B.D. Olafson and W.A. Goddard III, *J. Phys. Chem.* **94** (1990) 162
- [14] S.D. Morley, R.J. Abraham, I.S. Haworth, D.E. Jackson, M.R. Saunders and J.G. Vinter, *J. Comput.-Aided Mol. Des.* **5** (1991) 475.
- [15] V.S. Allured, C.M. Kelly and C.R. Landis, *J. Am. Chem. Soc.* **113** (1991) 1
- [16] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard and W.M. Skiff, *J. Am. Chem. Soc.* **114** (1992) 10024
- [17] W.D. Cornell, P. Cieplak, C.I. Bayly, I.R. Gould, K.M. Merz Jr, D.M. Ferguson, D.C. Spellmeyer, T. Fox, J.W. Caldwell and P.A. Kollman, *J. Am. Chem. Soc.* **117** (1995) 5179
- [18] P. Comba and T.W. Humbley, *Molecular Modeling of Inorganic Compounds*, VCH (1995)
- [19] W. Damm, A. Frontera, J. Tirado-Rives and W.L. Jorgensen, *J. Comput. Chem.* **18** (1997) 1955
- [20] N.L. Allinger, *J. Am. Chem. Soc.* **99** (1977) 8127
- [21] N.L. Allinger, Y.H. Yuh and J.H. Li, *J. Am. Chem. Soc.* **111** (1989) 8551
- [22] M.J. Hwang, T.P. Stockfish and A.T. Hagler, *J. Am. Chem. Soc.* **116** (1994) 2515
- [23] J.L.M. Dillen, *J. Comput. Chem.* **16** (1995) 595
- [24] T.A. Halgren, *J. Comput. Chem.* **17** (1996) 490
- [25] N.L. Allinger, K. Chen, J.H. Lii, *J. Comput. Chem.* **17** (1996) 642
- [26] P.M. Morse, *Phys. Rev.* **34** (1929) 57
- [27] S. Barlow, A.H. Rohl, S. Shi, C.M. Freeman and D. O'Hare, *J. Am. Chem. Soc.* **118** (1996) 7578
- [28] G. Nemethy, K.D. Gibsen, K.A. palmer, C.N. Yoon, G. Paterlini, A. Zagari, S. Rumsey and H.A. Scheraga, *J. Phys. Chem.* **96** (1992) 6472

- [29] J.R. Maple, M.J. Hwang, F.P. Stockfisch, U. Dinur, M. Waldman, C.S. Ewig and A.T. Hagler, *J. Comput. Chem.* **15** (1994) 162
- [30] B.G. Sumpter, D.W. Noid and B. Wunderlich, *J. Chem. Phys.* **93** (1990) 6875
- [31] D.W. Noid, B.G. Sumpter and B. Wunderlich *Macromol.* **24** (1991) 4148
- [32] D. Brown and J.H.R. Clarke, *Macromol.* **24** (1991) 2075
- [33] B.G. Sumpter, D.W. Noid and B. Wunderlich, *Macromol.* **25** (1992) 7247
- [34] K. Fukui, B.G. Sumpter, B.D. Barnes and D.W. Noid, *Comput. Theor. Polym. Sci.* **9** (1999) 245
- [35] D. Rigby and R.J. Roe, *J. Chem. Phys.* **87** (1987) 7285
- [36] D. Rigby and R.J. Roe, *J. Chem. Phys.* **89** (1988) 5280
- [37] D. Rigby and R.J. Roe, *Macromol.* **22** (1989) 2259
- [38] D. Rigby and R.J. Roe, *Macromol.* **23** (1990) 5312
- [39] A.I. Kitaygorodsky, *Tetrahedron* **14** (1961) 230
- [40] J.E. Lennard-Jones, *Proc. Royal Soc. London* **A106** (1924) 463
- [41] T.L. Hill, *J. Chem. Phys.* **16** (1948) 399