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Application of the Four-Parameter Diatomic Potential in Molecular Mechanics Force Fields

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Abstract

Motivation. Parameters from a four-parameter diatomic potential (FPDP) are herein converted into Morse parameters for application in molecular mechanics force fields that adopt the Morse potential for describing the bond-stretching energy.

Method. Three methods for converting the FPDP parameters, *i.e.* (*a*) imposition of equal bond stiffness, (*b*) imposition of equal equilibrium–to–dissociation energy integral, and (*c*) imposition of equal limits of bond dissociation, give the Morse shape parameter for near, intermediate and far range respectively.

Results. The validity of these methods has been supported through comparison of FPDP energy and the Morse energy using FPDP parameters. Because FPDP can be converted into the Morse potential, it is possible to use FPDP parameters for Morse potential. This property may be applied to molecular mechanics code that use Morse potential to increase the accuracy of the bond–stretching energy without drastic change in the source code.

Conclusions. The use of three Morse shape parameters for various dimensionless bond length (r/R) ranges enables the FPDP accuracy to be approached by the Morse function.

Keywords. Four-parameter potential; Morse; parameter conversion; potential energy.

Abbreviations and notations	
FPDP, Four parameter Diatomic Potential	<i>R</i> , equilibrium bond length
D, bond dissociation energy	r, internuclear distance of bond

1 INTRODUCTION

Molecular mechanics force fields consist of the summation of bond-stretching (2-body), bondbending (3-body), bond-torsion (4-body), and non-bonded (van der Waals and Coulombic) interaction energies,

$$U = U_{2b} + U_{3b} + U_{4b} + U_{vdW} + U_{ionic}$$
(1)

A survey of commonly used force fields reveals most molecular mechanics softwares, such as EAS [1], CHARMM [2], GROMOS [3], TRIPOS [4], COSMIC [5], SHAPES [6], AMBER [7], MOMEC [8], and OPLS [9], adopt the harmonic potential:

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$$U_{2b} = \frac{1}{2}k(r-R)^2$$
(2)

which consists of 2 parameters, for describing bond–stretching. Although higher orders polynomials with the formula:

$$U_{2b} = \frac{1}{2} \sum_{i=2}^{n} k_i (r - R)^i$$
(3)

have been introduced – such as in MM2 (n = 3) [10], MM3 (n = 4) [11], CFF (n = 4) [12], EFF (n = 4) [13], MMFF (n = 4) [14], and MM4 (n = 6) [15], these functions do not converge as $r \rightarrow \infty$. Molecular mechanics softwares such as CVFF [16], DREIDING [17], UFF [18] and ESFF [19] adopt the 3–parameter Morse [20] potential function:

$$U_M = D\left(e^{-2\alpha(r-R)} - 2e^{-\alpha(r-R)}\right) \tag{4}$$

which converges as $r \to \infty$, for describing the 2-body energy. A four-parameter diatomic potential (FPDP)

$$U_{F} = D \left(\frac{e^{a} - \lambda}{e^{\frac{a^{r}}{R}} - \lambda} \right)^{2} - 2D \left(\frac{e^{a} - \lambda}{e^{\frac{a^{r}}{R}} - \lambda} \right)$$
(5)

which resembles the Morse function, was introduced by Sun [21], and was used by Gang [22] for solving the Dirac equation. When $\lambda = 0$, the FPDP reduces to the Morse potential. The existence of an additional parameter undoubtedly allows better curve–fitting by FPDP in comparison to the Morse function.

Any replacement of the Morse potential with the FPDP, in the interest of improving the bond stretching energy accuracy, however, would require hard–coding of existing softwares that adopt Morse function. Developing new softwares that incorporate FPDP, on the other hand, would not be cost effective. This paper proposes the use of the FPDP parameters for application in Morse function. Force fields that adopt Morse potential for quantifying bond–stretching energy (e.g. [16–19]) can then be refined without changing the functional form of the 2–body portion, thereby improving accuracy with insignificant cost. Accordingly, 3 methods for converting FPDP parameters are developed herein, and are suggested for different (r/R) range.

2 ANALYSIS

Although the Morse and FPDP functions consist of 3 and 4 parameters respectively, writing them in terms of dimensionless ratio

$$\frac{U_M}{D} = e^{2\alpha R \left(1 - \frac{r}{R}\right)} - 2e^{\alpha R \left(1 - \frac{r}{R}\right)}$$
(6)

and

$$\frac{U_F}{D} = \left(\frac{e^a - \lambda}{e^{\frac{a^r}{R}} - \lambda}\right)^2 - 2\left(\frac{e^a - \lambda}{e^{\frac{a^r}{R}} - \lambda}\right)$$
(7)

reduces them to one and two parameters respectively, with (U/D) and (r/R) being dimensionless. The near range relation between Morse and FPDP can be obtained by imposition of equal curvatures [23–25] at the minimum well–depth

$$\frac{1}{D} \left(\frac{\partial^2 U_M}{\partial r^2} \right)_{r=R} = \frac{1}{D} \left(\frac{\partial^2 U_F}{\partial r^2} \right)_{r=R}$$
(8)

Substituting

$$\frac{1}{D} \left(\frac{\partial^2 U_M}{\partial r^2} \right)_{r=R} = 2\alpha^2 \tag{9}$$

and

$$\frac{1}{D} \left(\frac{\partial^2 U_F}{\partial r^2} \right)_{r=R} = 2(a/R)^2 e^{2a} (e^a - \lambda)^{-2}$$
(10)

into Eq.(8) gives the Morse shape parameter in terms of FPDP parameters

$$\alpha = \frac{a}{R} \left(\frac{e^a}{e^a - \lambda} \right) \tag{11}$$

The intermediate range parameter relationship can be obtained by equating energy integral [26–28] from bond equilibrium to bond dissociation,

$$\frac{1}{D} \int_{\mathbb{R}}^{\infty} U_M dr = \frac{1}{D} \int_{\mathbb{R}}^{\infty} U_F dr$$
(12)

The Morse potential can be easily integrated to give

$$\frac{1}{D} \int_{\mathbb{R}}^{\infty} U_M dr = -\frac{3}{2\alpha} \tag{13}$$

where the negative sign results from $U_M < 0$ in the integral range. The FPDP energy integral can be performed by modifying the integral

$$\frac{1}{D} \int_{R}^{\infty} U_{F} dr = \int_{R}^{\infty} \left\{ \left(\frac{e^{a} - \lambda}{e^{\frac{a^{r}}{R}} - \lambda} \right)^{2} - 2 \left(\frac{e^{a} - \lambda}{e^{\frac{a^{r}}{R}} - \lambda} \right) \right\} dr$$
(14)

into an equivalent form

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$$\frac{1}{D}\int_{R}^{\infty}U_{F}dr = \frac{\left(e^{a}-\lambda\right)^{2}R}{a}\int_{\exp\left(a\right)}^{\infty}\frac{1}{x\left(-\lambda+x\right)^{2}}dx - 2\frac{\left(e^{a}-\lambda\right)R}{a}\int_{\exp\left(a\right)}^{\infty}\frac{1}{x\left(-\lambda+x\right)}dx$$
(15)

The integrals shown in Eq.(15) can be evaluated as

$$\int_{\exp(a)}^{\infty} \frac{1}{x(-\lambda+x)^2} dx = \left[\frac{1}{\lambda(\lambda-x)} + \frac{1}{\lambda^2} \ln \left|\frac{x}{x-\lambda}\right|\right]_{\exp(a)}^{\infty}$$
(16)

and

$$\int_{\exp(a)}^{\infty} \frac{1}{x(-\lambda+x)} dx = \left[\frac{1}{-\lambda} \ln \left| \frac{x}{x-\lambda} \right| \right]_{\exp(a)}^{\infty}$$
(17)

As such,

$$\frac{1}{D} \int_{\mathbb{R}}^{\infty} U_F dr = \frac{(e^a - \lambda)^2 R}{a\lambda} \left[\frac{1}{e^a - \lambda} - \frac{a - \ln(e^a - \lambda)}{\lambda} \right] - 2 \frac{(e^a - \lambda)R}{a} \left(\frac{a - \ln(e^a - \lambda)}{\lambda} \right)$$
(18)

Hence substitution of Eqs. (13) and (18) into Eq. (12) leads to

$$\alpha = \frac{3}{2} \frac{(a/R)}{e^a - \lambda} \left[\frac{e^a + \lambda}{\lambda^2} \left(a - \ln(e^a - \lambda) \right) - \frac{1}{\lambda} \right]^{-1}$$
(19)

The far range parameter relation can be obtained by equating

$$\left(\frac{U_M}{D}\right)_{r \to \infty} = \left(\frac{U_F}{D}\right)_{r \to \infty}.$$
(20)

Substituting

$$\left(\frac{U_M}{D}\right)_{r \to \infty} = e^{-2\alpha r} - 2e^{-\alpha r}$$
(21)

and

$$\left(\frac{U_F}{D}\right)_{r\to\infty} = (1-\lambda)^2 e^{-2a\frac{r}{R}} - 2(1-\lambda)e^{-a\frac{r}{R}}$$
(22)

into Eq. (20) implies

$$\ell = 0 \tag{23}$$

and

$$\alpha = \frac{a}{R} \tag{24}$$

Equation (24) can also be obtained by comparing the indices of Eqs. (6) and (7) when $\lambda = 0$. This comparison of indices is analogous to the equating the indices for the attractive terms of Lennard–

Jones and Buckingham potential functions used for quantifying van der Waals interaction [17,18].

Hence we generally write the Morse shape parameter as

$$\alpha = \frac{a}{R}f(a,\lambda) \tag{25}$$

where $f(a, \lambda)$, the refinement factor, is summarized in Table 1 (see also Fig.1).





3 RESULTS AND DISCUSSION

To verify the validity of the developed relations, we plot the potential energy curves of ClCl, CO and HH using the FPDP potential function with their corresponding parameters given by Sun [21]. For comparison, we plot the Morse potential energy curves using the converted shape parameter. The equilibrium bond lengths were obtained from Huxley and Murrell [29]. Table 2 summarizes all the parameters used for the plotting of FPDP and the corresponding Morse curves.

Table 2. FPDP parameters and the Morse parameter converted from the former							
Diatoms	R (Angstrom)	а	λ	αR (near)	αR (mid)	αR (far)	
ClCl	1.9879	4.3914	-7.8323	4.003135	4.215951	4.3914	
CO	1.1283	2.4784	0.53295	2.594375	2.529519	2.4784	
HH	0.7414	1.1967	0.56278	1.441923	1.302028	1.1967	

Figures 2 to 4 show the FPDP potential energy of ClCl (circles), CO (crosses) and HH (triangles) with sub–figures (a), (b) and (c) showing the converted Morse curves based on Eqs. (11), (19) and (24), respectively.



Figure 2. FPDP potential energy for ClCl (circles), CO (crosses), and HH (triangles) for $0.7 \le r/R \le 1.3$ and Morse potential energy curves converted from FPDP parameters based on (*a*) near range, Eq. (11), (*b*) intermediate range, Eq. (19), and (*c*) far range, Eq. (24).



Figure 3. FPDP potential energy for ClCl (circles), CO (crosses), and HH (triangles) for $0.8 \le r/R \le 2.6$ and Morse potential energy curves converted from FPDP parameters based on (*a*) near range, Eq. (11), (*b*) intermediate range, Eq. (19), and (*c*) far range, Eq. (24).



Figure 4. FPDP potential energy for ClCl (circles), CO (crosses), and HH (triangles) for $2.5 \le r/R \le 6$ and Morse potential energy curves converted from FPDP parameters based on (*a*) near range, Eq. (11), (*b*) intermediate range, Eq. (19), and (*c*) far range, Eq. (24).

Figure 2, which shows the comparison of both potential functions very near to the minimum well–depth, confirms that Eq. (11) is suitable for converting FPDP into Morse energy for small change in bond length. Figure 3 shows the change in energy over intermediate change in internuclear distance. This confirms the validity of Eq. (19) for converting FPDP into Morse energy in the case of intermediate range of bond stretching. Figure 4 shows that Eq. (24) gives the best agreement between FPDP and the Morse energy converted from the former, for very large bond stretching. A clear presentation of all new results should be given, followed by a discussion of their significance and relationships with previous knowledge in the field.

Table 5. Comparative advantages of different parameter conversion under different conditions						
λ sign	r / R	Near range, Eq. (11)	Mid range, Eq. (19)	Far range, Eq. (24)		
1 . 0	$r \leq R$	Good agreement	Slight overestimation	Large overestimation		
$\lambda < 0$	r > R	Slight underestimation	Good agreement	Slight overestimation		
	r >> R	Large underestimation	Slight underestimation	Good agreement		
	$r \leq R$	Good agreement	Slight underestimation	Large underestimation		
$\lambda > 0$	r > R	Slight overestimation	Good agreement	Slight underestimation		
	r >> R	Large overestimation	Slight overestimation	Good agreement		

Table 3. Comparative advantages of different parameter conversion under different condition

Table 3 summarizes the comparative advantages of the three sets of FPDP to Morse parameter conversion, for various internuclear ranges with respect to the bond length, and the influence of λ sign.

4 CONCLUSIONS

A Morse–like four–parameter diatomic potential (FPDP) has been shown to be easily converted into the conventional Morse potential, which is commonly used in molecular mechanics softwares. The Morse shape parameter, α , can be converted from the FPDP parameters using three methods outlined herein for different (r/R) range. Through this conversion, the accuracy of bond– stretching potential energy is enhanced without the need of modifying existing Morse function into the FPDP. Consequently, the advantage of a more accurate bond stretching energy can be attained without performing hard–coding on the softwares. As such, an improved accuracy can be attained without significant increase of the computation time.

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