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ORIGINAL PAPER

Approximation of the Dymond-Rigby-Smith potential function using the Lennard-Jones form

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Abstract Due to the mathematical similarities between the Dymond-Rigby-Smith (DRS) function with the conventional Lennard-Jones (LJ) functions, modification to the LJ indices is made herein in order to approximate the DRS energy curve. It is herein shown that the LJ(9-6) potential approximates well the DRS curve for interatomic distance shorter than the equilibrium distance. For interatomic distance longer than the equilibrium distance, a pair of LJ indices, based on the equal mean stretching energy, was found to give very good agreement with the DRS curve. Modification to the conventional LJ functions for describing the DRS energy, rather than the replacement of the LJ potentials with DRF function, allows numerous computational chemistry softwares to quantify the DRS energy with minimal hard-coding of their algorithms.

Keywords Dymond-Rigby-Smith · Lennard-Jones · Inert gases

1 Introduction

Where stretching of covalent bonds are concerned, the polynomial series

$$U_{2-b} = \frac{1}{2}k_2(r-R)^2 + \frac{1}{2}k_3(r-R)^3 + \cdots = \frac{1}{2}\sum_{i=2}^{n} k_i(r-R)^i \tag{1}$$

is a general form which has been adopted by computational chemistry softwares such as EAS [1], CVFF [2], CHARMM [3], GROMOS [4], TRIPOS [5], DREIDING [6],

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COSMIC [7], SHAPES [8], UFF [9], AMBER [10], MOMEC [11] and OPLS [12] with $n = 2$, by MM2 [13] with $n = 3$, by MM3 [14], CFF [15], EFF [16] and MMFF [17] with $n = 4$, and by MM4 [18] with $n = 6$. Here, r is the internuclear distance while R is the distance at the minimum well depth, and k_i $(i = 2, 3, \ldots)$ are the fitted coefficients. Less well-known is the use of series

$$U_{\mathrm{vdW}} = D \sum_{i=1}^{\infty} C_i \left(\frac{R}{r}\right)^i \tag{2}$$

for describing van der Waals interaction energy whereby D is the dissociation energy and C_i $(i = 1, 2, \ldots)$ are the coefficients. The conditions $C_i = 0$ (for $i \neq 6,\ 12$), $C_6 = -2$ and $C_{12} = 1$ reduce Eq. 2 into a conventional Lennard-Jones (12-6) function [2–6,8–10,12], while the conditions $C_i = 0$ (for $i \neq 6,\ 9$), $C_6 = -3$ and $C_9 = 2$ simplify Eq. 2 into another conventional Lennard-Jones (9-6) function [15,19]. Substituting $C_i = 0$ (for $i \neq 6,\ 8,\ 18,\ 24,\ 28$), $C_6 = -0.3359$, $C_8 = -1.74452$, $C_{18} = 2.07151$, $C_{24} = -1.2584$ and $C_{28} = 0.331$ into Eq. 2 converts it into the Dymond-Rigby-Smith (DRS) potential [20] that was developed for describing interaction energy of inert gases.

Unlike Eq. 1, the form in Eq. 2 converges since every term in the latter converges as $r \to \infty$. While it is obvious that the incorporation of greater number of terms allow better flexibility (e.g. [20]), most computational chemistry softwares adopt the simpler potentials, such as the conventional LJ(12-6) and LJ(9-6) functions for describing the van der Waals energy of interaction. The use of simpler potentials is nonetheless justified, especially in molecular dynamics modeling of macromolecules in order to reduce the computation time and cost. This paper proposes a minor adjustment to the LJ indices in such a way that the implementation of these index adjustments allows molecular modeling softwares to accurately quantify the DRS potential energy by using the modified Lennard-Jones function. Without addition of terms to the potential function, the Lennard-Jones function with the modified indices would retain almost the same computation speed.

2 Analysis

In recent years the conversion of potential function (e.g. U_1) parameters into those of another function (e.g. U_2) were performed by imposing equal force constant via equating the well-depth curvatures [21–23]

$$\left.\frac{\partial^2 U_1}{\partial r^2}\right|_{r=R} = \left.\frac{\partial^2 U_2}{\partial r^2}\right|_{r=R}. \tag{3}$$

Where more than one shape parameters exist, equating of higher order derivatives was imposed. Although such approach gives valid correlation near the well-depth and for internuclear compression, the discrepancies become salient for internuclear separation of the range $1.2 < (r/R) < 2.4$. These parameter conversions appear to be valid for $(r/R) > 2.5$, but the correlation is a result of independently converging functions.

In an attempt to minimize the discrepancies for $(r/R) > 1$, equal mean stretching energy was imposed [24–26]

$$\lim_{S\to\infty}\left(\frac{1}{S-R}\int_R^S U_1 \mathrm{d}r\right) = \lim_{S\to\infty}\left(\frac{1}{S-R}\int_R^S U_2 \mathrm{d}r\right). \tag{4}$$

By relaxing the imposition of equal well-depth curvature, the algebraic error between the connected functions is reduced to zero. This, however, was attained at the expense of accuracy for internuclear compression. As a result of their comparative advantages and limitation, we herein adopt both approaches. Hence the imposition of equal well-depth curvature and equal mean stretching energy on the general Lennard-Jones function

$$\frac{U_{\mathrm{LJ}}}{D} = \frac{n}{m-n}\left(\frac{R}{r}\right)^m - \frac{m}{m-n}\left(\frac{R}{r}\right)^n \tag{5}$$

and the DRS function

$$\begin{aligned}\frac{U_{\mathrm{DRS}}}{D} = 0.331\left(\frac{R}{r}\right)^{28} - 1.2584\left(\frac{R}{r}\right)^{24} + 2.0751\left(\frac{R}{r}\right)^{18}\\ -1.74452\left(\frac{R}{r}\right)^{8} - 0.39959\left(\frac{R}{r}\right)^{6}\end{aligned} \tag{6}$$

gives

$$mn = 79.8002 \tag{7}$$

and

$$\frac{1-m-n}{(m-1)(n-1)} = -0.2497354. \tag{8}$$

Solving Eqs. 7 and 8 for the generalized Lennard-Jones parameters leads to a pair of solution in complex numbers

$$\begin{Bmatrix} m \\ n \end{Bmatrix} = \frac{1}{2}\begin{bmatrix} +1 & +1 \\ +1 & -1 \end{bmatrix}\begin{Bmatrix} 17 \\ \sqrt{-30} \end{Bmatrix}. \tag{9}$$

Since these indices cannot be solved for their real numbers, they are solved separately from Eqs. 7 and 8 with an additional condition

$$m = 2n \tag{10}$$

in order to enable Eqs. 7 and 8 to be solved. Since the implementation of Eq. 10 allows Eqs. 7 and 8 to be solved independently from each other, two sets of solutions

Table 1 Possible Lennard-Jones indices for approximating the DRS potential

Method	m	n
Equal force constant	12.6333	6.3167
Equal mean energy	14.3135	7.1567
Average	13.4734	6.7367

exists: (a) $m = 2n = 12.6333$ based on Eqs. 7 and 10, and (b) $m = 2n = 14.3135$ based on Eqs. 8 and 10. A third set of solution can be obtained by taking average of (a) and (b) to give $m = 2n = 13.4734$. Table 1 summarizes the three pairs of adjusted Lennard-Jones indices for approximating the DRS potential. The next section investigates the performance of these proposed Lennard-Jones indices with reference to the conventional Lennard-Jones(12-6) and Lennard-Jones(9-6) potentials.

3 Results and discussion

To compare the performance of the developed Lennard-Jones indices with the conventional Lennard-Jones potentials currently used in computational chemistry softwares, the DRS, LJ(12-6) and LJ(9-6) potential energy curves were plotted in the first instance. Perusal to Fig. 1 shows that the LJ(9-6) potential approximates the DRS curve better than the LJ(12-6) potential for $r < R$, but the trend reverses for $r > R$. The use of LJ(9-6) for approximating the DRS potential for $r < R$ is therefore a possible option if the obtained indices do not provide better correlation with the DRS curve. The performance of the three pairs of LJ indices for approximating the DRS function can be seen in Fig. 2. Amongst the three "new" LJ functions, the LJ curve based on equal force constant is best for $r < R$. For the case where $r > R$, the LJ curve based on equal mean energy gives a very good agreement with the DRS energy. Comparison between the conventional LJ functions (Fig. 1) with the adjusted LJ functions (Fig. 2) reveals that the conventional LJ(9-6) function works best for approximating the DRS potential for $r < R$, while one of the new pair of parameters, based on equal mean energy, gives very good agreement with the DRS potential for $r > R$. Hence it is herein suggested that computational chemistry softwares that adopt the LJ(12-6) or LJ(9-6) can be minimally re-coded such that a two part LJ function can be used for describing the DRS function as

$$\frac{U_{\mathrm{LJ}}}{D} = \begin{cases} 2(R/r)^9 - 3(R/r)^6 & ; r \leq R \\ (R/r)^{14.31} - 2(R/r)^{7.157} & ; r \geq R \end{cases} \tag{11}$$

4 Conclusions

A cost effective method for quantifying the interatomic energy of inert gases in computational chemistry softwares has been proposed in this paper. This was achieved by enabling the DRS potential, which was developed for describing interacting energy

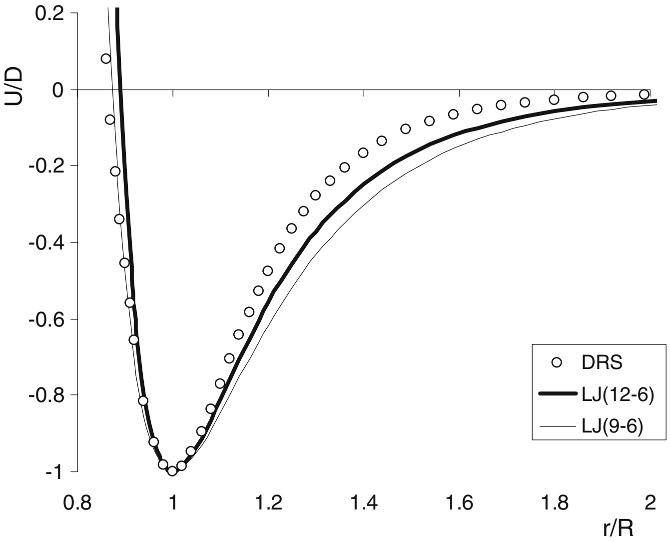

Fig. 1 Comparison between the DRS potential with the conventional Lennard-Jones potential used in computational chemistry softwares: LJ(12-6) and LJ(9-6)

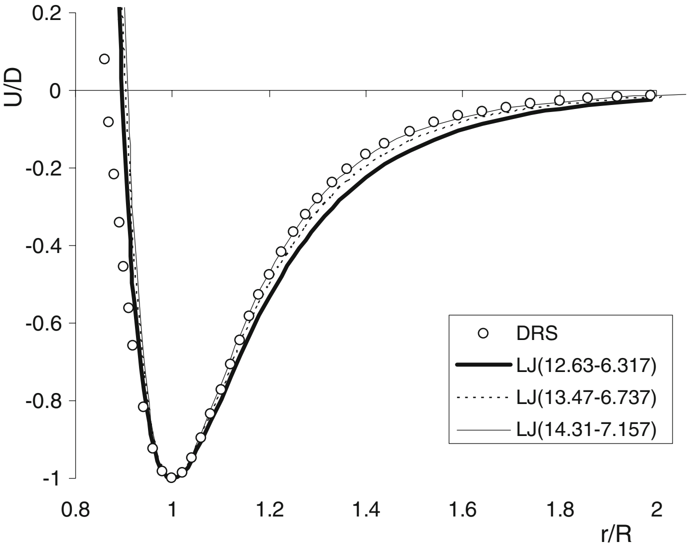

Fig. 2 Comparison between the DRS potential and the Lennard-Jones potentials with the ndices obtained via equal force constant (*bold curve*), equal mean energy (*fine curve*) and their average (*dashed curve*)

of inert gases, to be satisfactorily described by the Lennard-Jones potential, which is commonly incorporated in computational chemistry softwares. The conventional Lennard-Jones (12-6) potential has been shown not to give good agreement with the DRS function. It was found that the DRS energy can be well approximated by the

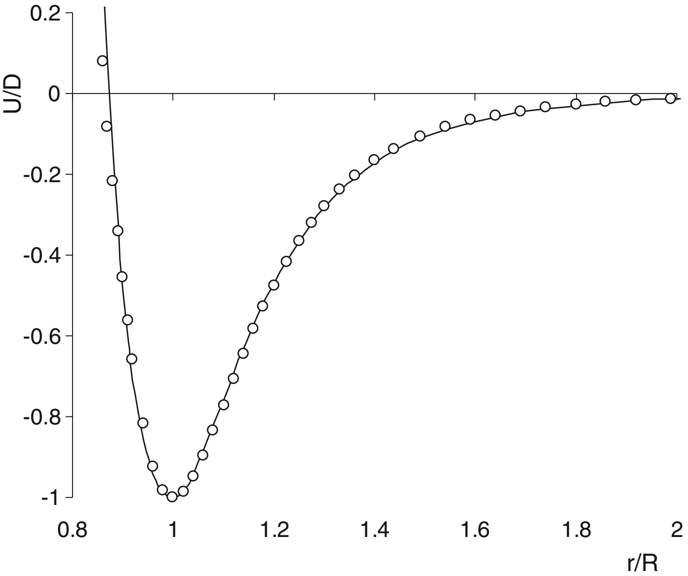

Fig. 3 Proposed piecewise Lennard-Jones function for approximating the DRS potential with $2m = 3n = 18$ for $r \leq R$ and $m = 2n = 14.3135$ for $r \geq R$

Lennard-Jones potential with $2m = 3n = 18$ and $m = 2n = 14.3135$ for interatomic distance shorter than and longer than the equilibrium distances, respectively (Fig. 3).

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