

Combination of pi and golden ratio in Lennard–Jones-type and Morse-type potential energy functions

Teik-Cheng Lim

*Faculty of Engineering, Nanoscience and Nanotechnology Initiative, 9 Engineering Drive 1, National
University of Singapore, S 117576, Republic of Singapore*
E-mail: alan.tc.lim@yahoo.com

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This paper tests the validity of a Lennard–Jones-type and Morse-type potential functions, consisting a combination of pi and golden ratio constants, for describing intermolecular and interatomic interaction energy. The adjustable parameter, n , can be obtained based on experimental data near the minimum well-depth or by parametric conversion from other established potential functions. The remarkably good correlation of the proposed potential functions with experimental data and other potential functions reveal an intriguing property of the relationship between pi and golden ratio within the context of chemistry.

KEY WORDS: Golden ratio, Lennard–Jones, Morse, pi, potential function, mathematical constants

AMS subject classification: 51N20, 92E99

1. Introduction

The concept of mathematical constant potentials is defined herein as interatomic and intermolecular potential energy functions that employ mathematically important constants, numbers, series or functions in a significant manner. In this paper, the mathematical constants of $\pi=3.141593$ and $\phi=1.618034$, correct up to six decimal places, are simultaneously incorporated into the Lennard–Jones-type and Morse-type functions. The schematic definitions of π and ϕ are shown in figure 1, whereby the former is the ratio of a circle's circumference to its diameter, as shown in figure 1(a), whilst the latter is the ratio of a rectangle, shown in figure 1(b), that possess the side dimensions x and y in such a manner that

$$\phi = \frac{x+y}{x} = \frac{x}{y} = \frac{y}{x-y}. \quad (1)$$

The Lennard–Jones [1–3] and the Morse [4] potential functions were selected for the combined incorporation of π and ϕ due to their widespread adoption in computational chemistry softwares. For example, the Lennard–Jones(12-6) function

$$\frac{U_{\text{LJ}(12-6)}}{D} = \left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^6 \quad (2)$$

has been adopted by OPLS [5], UFF [6], AMBER [7] and ECEPP [8] while Lennard–Jones (14-7) function

$$\frac{U_{\text{LJ}(14-7)}}{D} = \left(\frac{R}{r}\right)^{14} - 2\left(\frac{R}{r}\right)^7 \quad (3)$$

is employed by MMFF [9] software. The Morse function is either written as

$$\frac{U_{\text{Morse}}}{D} = \left(1 - e^{-\alpha(r-R)}\right)^2 \quad (4)$$

or

$$\frac{U_{\text{M}}}{D} = \frac{U_{\text{Morse}}}{D} - 1 = e^{2\alpha R(1-\frac{r}{R})} - 2e^{\alpha R(1-\frac{r}{R})} \quad (5)$$

and has been adopted in computational chemistry softwares such as UFF [6], CVFF [10], DREIDING [11] and ESFF [12] for describing bond stretching energy, and also in COSMIC [13] software for quantifying van der Waals interaction energy. Here, r is the internuclear distance while the parameters D and R refer to the dissociation energy and the equilibrium internuclear distance, respectively. In this paper, we consider the Morse function defined by equation (5) in order to conform with equations (2) and (3) whereby

$$(U)_{r=R} = -D. \quad (6)$$

Although previous studies on interatomic potentials have been largely confined to parametric connections amongst the various functions [14–28], recently a functionally flexible potential function was introduced from the chemical physics view point [29]. In this paper, two novel potential functions are proposed from the mathematical chemistry stand point with the incorporation of the two most geometrically important mathematical constants, i.e. the Lennard–Jones-type and Morse-type functions as

$$\frac{U_{\pi\phi}^{\text{LJ}}}{D} = \frac{\phi}{\pi - \phi} \left(\frac{R}{r}\right)^{n\pi} - \frac{\pi}{\pi - \phi} \left(\frac{R}{r}\right)^{n\phi} \quad (7)$$

and

$$\frac{U_{\pi\phi}^{\text{M}}}{D} = \frac{\phi}{\pi - \phi} e^{n\pi(1-\frac{r}{R})} - \frac{\pi}{\pi - \phi} e^{n\phi(1-\frac{r}{R})}, \quad (8)$$

respectively, where n , which appears at the indices of both the repulsive and attractive terms, is an adjustable constant.

2. Analysis

The adjustable parameter n can be obtained by curve-fitting using data from experimental results. To aid comparative study, we obtain n in this paper by fitting the potential function on the minimum well-depth data and two data beside it. For a set of interatomic energy data U and interatomic distance data r , the curvature at any point i is

$$\kappa = \frac{\partial^2 U_i}{\partial r^2} = \frac{U_{i-1} - 2U_i + U_{i+1}}{(\Delta r)^2} \quad (9)$$

for a fixed interatomic distance interval $\Delta r = r_{i+1} - r_i = r_i - r_{i-1}$. For a more general case where the distance is not constant, we let

$$\Delta r = \frac{1}{2} (r_{i+1} - r_{i-1}). \quad (10)$$

Expressions for the curvatures of both equations (7) and (8) are the same at the minimum well depth, i.e.

$$\left(\frac{\partial^2 U_{\pi\phi}^{\text{LJ}}}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_{\pi\phi}^{\text{M}}}{\partial r^2} \right)_{r=R} = \pi\phi D \left(\frac{n}{R} \right)^2. \quad (11)$$

Hence the adjustable parameter is

$$n = R \sqrt{\frac{\kappa_{r=R}}{\pi\phi D}}. \quad (12)$$

It is worth obtaining a set of n values for a group of diatomic molecules. Based on the Rydberg function [30,31]

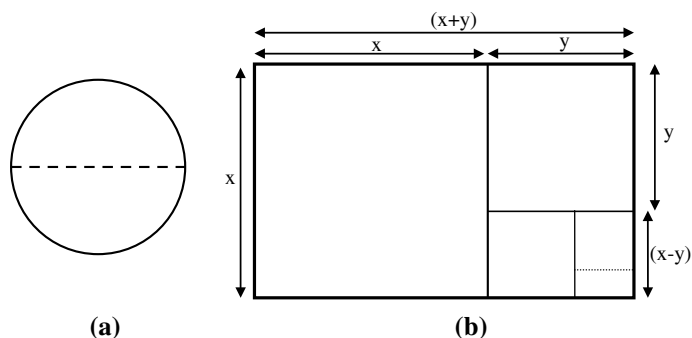
$$\frac{U_{\text{Ryd}}}{D} = -(1 + a\rho) e^{-a\rho}, \quad (13)$$

where

$$\rho = r - R, \quad (14)$$

Murrell and Sorbie [32] proposed an extended version of the Rydberg potential as

$$\frac{U_{\text{MS}}}{D} = - \left(\sum_{i=0}^3 a_i \rho^i \right) \exp(-a_1 \rho), \quad (15)$$

Figure 1. Graphical representations of (a) π and (b) ϕ .

whereby $a_0 = 1$ and that the second-order derivative with reference to the inter-nuclear distance at the minimum well-depth is

$$\left(\frac{\partial^2 U_{MS}}{\partial r^2} \right)_{r=R} = (a_1^2 - 2a_2) D. \quad (16)$$

For obtaining n in terms of the Murrell–Sorbie function, we equate

$$\left(\frac{\partial^2 U_{\pi\phi}}{\partial r^2} \right)_{r=R} = \left(\frac{\partial^2 U_{MS}}{\partial r^2} \right)_{r=R} \quad (17)$$

to give

$$n = R \sqrt{\frac{a_1^2 - 2a_2}{\pi\phi}}. \quad (18)$$

Finally, the proposed potential can be compared with the Lennard–Jones(12-6) and Lennard–Jones(14-7) functions by taking average of the repulsive and attractive indices, i.e. $n(\pi + \phi) = 12 + 6$ and $n(\pi + \phi) = 14 + 7$. This gives $n = 3.782$ and $n = 4.412$ in relation to Lennard–Jones(12-6) and Lennard–Jones(14-7) functions, respectively.

3. Results and discussion

The validity of the proposed potentials can be established by comparing their plots with established data or other theoretical curves. Figure 2 shows the Lennard–Jones (thin curve) and Morse (bold curve) functions that incorporate both π and ϕ for comparison with the Rydberg–Klein–Rees data (circles) for the H–H covalent bond [33,34], as reported by Murrell et al. [35]. It is not surprising

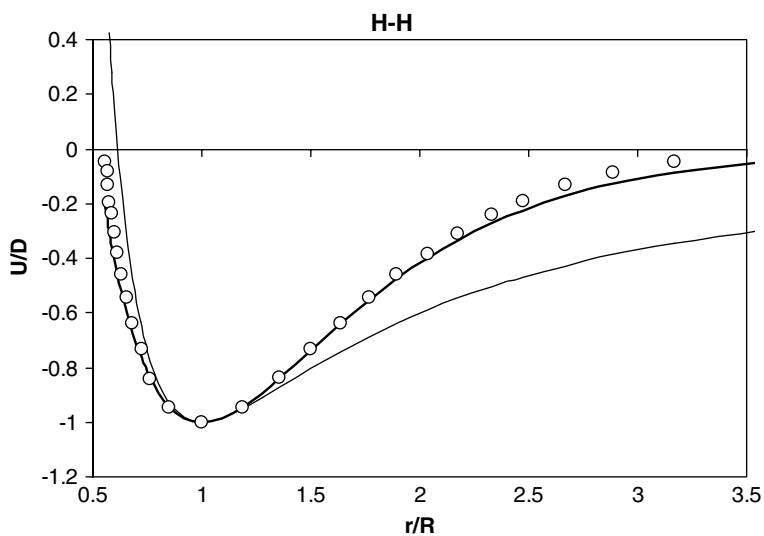


Figure 2. Comparison of the Morse (bold curve) and Lennard–Jones (thin curve) potential function based on π and ϕ parameters, with the Rydberg–Klein–Rees data (circles) for H–H diatomic molecule.

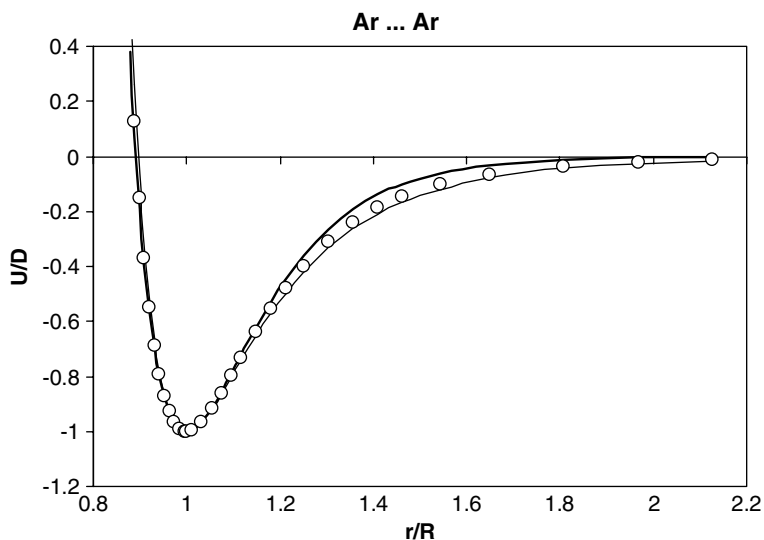


Figure 3. Comparison of the Morse (bold curve) and Lennard–Jones (thin curve) potential function based on π and ϕ parameters, with the experimental results for Ar–Ar intermolecular interaction.

that the Morse function with π and ϕ gives better agreement than that of Lennard–Jones. This observation is attributed to the nature of covalent bond. Figure 3 shows the Lennard–Jones (thin curve) and Morse (bold curve) functions

Table 1
 Values for the adjustable parameter n for a group of diatomic molecules.

Diatomic molecule	n	Diatomic molecule	n
AlAl	2.696367	FMg	3.449299
AlCl	3.40256	FN	3.630322
AlF	3.768995	FNa	2.832367
AlH	2.323694	FO	3.418327
AlO	4.268812	FP	3.928042
AlS	4.073772	FS	4.295199
BB	3.333025	FSi	3.92551
BCl	3.542736	HH	1.970144
BeCl	3.463627	HLi	1.790913
BeF	3.569848	HMg	2.164031
BeH	2.241305	HN	2.804655
BeO	4.04276	HNa	1.848445
BeS	3.920218	HO	3.002037
BF	3.97476	HP	2.827224
BH	2.384576	HS	3.057175
BN	4.096425	HSi	2.60342
BO	4.932794	LiLi	1.51475
BS	4.622959	LiNa	1.422302
CC	4.803253	MgMg	0.58437
CCl	3.624324	MgO	3.6182
CF	3.837236	MgS	3.542698
CH	2.625237	NaNa	1.431142
ClCl	3.956248	NN	5.826913
ClF	3.819801	NO	5.093588
ClH	3.208424	NP	5.265033
ClLi	2.673963	NS	4.832934
ClNa	1.483347	NSi	4.701606
ClO	3.776491	OO	4.577396
ClSi	3.695778	OP	5.028546
CN	5.241037	OS	4.727019
CO	5.453076	OSi	5.086505
CP	4.84344	PP	4.948783
CS	4.955725	SiSi	3.651316
FF	3.392785	SS	4.661095
FH	3.157099	SSi	4.750118
FLi	2.741581		

that possess both π and ϕ for comparison with the intermolecular interaction of argon gas (circles) [36,37]. It can be seen that the experimental result is bounded by both curves. However, the experimental data moves towards the Lennard–Jones-type function instead of that of Morse due to the van der Waals interaction nature in the considered inert gas. In both figures 2 and 3, the values of $n = 4$ and $n = 0.9$ were obtained using equations (9), (10) and (12).

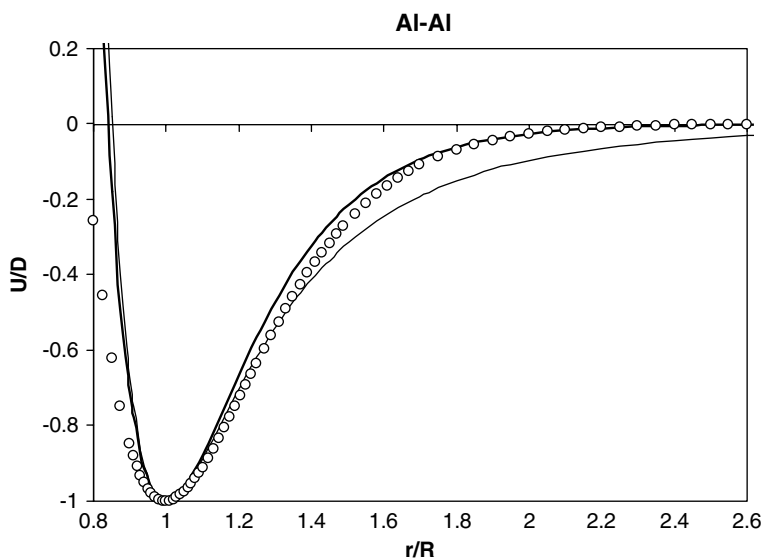


Figure 4. Comparison of the Morse (bold curve) and Lennard-Jones (thin curve) potential function based on π and ϕ parameters, with the Murrell-Sorbie result (circles) for Al-Al diatomic molecule.

The values of n in terms of the Murrell-Sorbie parameters were obtained from the parametric data furnished by Huxley and Murrell [38]. Table 1 lists a total of 71 diatomic values of n calculated using equation (18) from the Murrell-Sorbie parameters. As an illustration, we plot the first set of data, i.e. the potential energy curve of Al-Al diatomic molecule, based on equation (9) using data by Huxley and Murrell [38] and also based on equations (7) and (8) using the calculated data for Al-Al shown in table 1. Figure 4 shows that the Murrell-Sorbie potential function agrees well with the Lennard-Jones-type function within short range, but shifts towards the Morse-type function at greater interatomic separation. This discrepancy is due to the neglect of a_3 , which drops off for the second order derivative at the minimum well-depth.

Finally, substitution of $n = 3.782$ and $n = 4.412$ into equation (7) exhibits excellent correlation with equations (2) and (3), respectively, thereby validating the extraction of n using the average values of the repulsive and attractive indices (figure 5).

4. Conclusions

The incorporation of mathematical constants π and ϕ into Lennard-Jones-type and Morse-type functions has shown the versatility of such potentials in describing both covalent and van der Waals interaction energy. That the math-

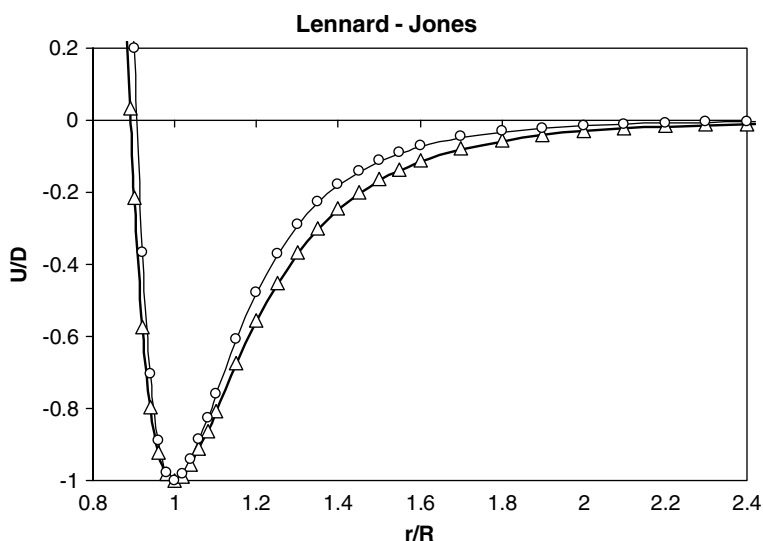


Figure 5. Comparison of the Lennard–Jones (LJ) data based on the π and ϕ for $n = 4.412$ (circles) and $n = 3.782$ (triangles) with LJ(14-7) (thin curve) and LJ(12-6) (bold curve), respectively.

ematical constants π and ϕ can be readily combined in quantifying interatomic and intermolecular potential energy shows their significance and relatedness in both mathematics and chemistry.

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