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On the applicability of mathematical constants and sequences in intermolecular potential energy functions

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Six intermolecular potential energy functions incorporating mathematical functions such as the Golden ratio, Euler number and Pi, and three consecutive numbers in the Half Square, Lucas and Fibonacci sequences are proposed herein. It is shown that the Lucas potential function exhibits reasonable agreement with the Lennard-Jones(12-10) function, whilst the Golden ratio potential function describes the argon gas potential energy and the Lennard-Jones(14-7) function excellently. Both the Euler and Pi potential functions agree well with the Lennard-Jones(12-6) function, whilst the Fibonacci potential function exhibits very good correlation with the Lennard-Jones(9-6) function. The relatedness of the mathematical constants and sequences examined in this paper with application to intermolecular potential functions suggests their additional significance in the field of chemistry.

KEY WORDS: Euler constant, Fibonacci sequence, golden ratio, intermolecular energy, Lucas sequence, Pi, potential functions

AMS subject classification: 51N20, 11B68, 11B39, 92E99

1. Motivation

In the pages that follow, it will be shown that there exists an intriguing applicability of mathematical constants and other mathematically significant sequences for generating simple, yet reliable, intermolecular potential energy functions. The mathematical constants considered herein are some transcendental numbers such as pi $\pi = 3.141593\cdots$, the base of natural logarithm $e = 2.718282\cdots$ (also known as Napier number and one of Euler's numbers), and the golden ratio $\phi = 1.618034\cdots$ (also known as golden section, golden mean and divine proportion). The sequences considered herein are the Half Squares $H(n)$, Lucas numbers $L(n)$ and Fibonacci numbers $F(n)$. Various mathematical techniques have recently been applied for furthering the understanding of the relationships amongst interatomic potential energy functions – with the purpose of developing a potential function converter (e.g. [1]) – either by the derivative methodology [2–10] or by the series expansion approach [11–15]. Recently a functionally flexible interatomic potential has been proposed [16], which can be reduced to the Lennard-Jones function [17–19], Morse function [20], Buckingham function [21,22] and the Linnett function [23,24] as special cases or as an interlace of these four functions. Based on the observation of the coefficients and the indices for both the repulsive and the attractive terms in a recent paper [16], we herein conceptualize and test six intermolecular potential energy functions, namely the Euler potential function

$$U_{\mathrm{e}} = D\left[\frac{1}{e-1}\left(\frac{R}{r}\right)^{ne} - \frac{e}{e-1}\left(\frac{R}{r}\right)^{n}\right] \tag{1}$$

the Pi potential function

$$U_{\pi} = D\left[\frac{1}{\pi-1}\left(\frac{R}{r}\right)^{n\pi} - \frac{\pi}{\pi-1}\left(\frac{R}{r}\right)^{n}\right] \tag{2}$$

the golden ratio potential function

$$U_{\phi} = D\left[\phi\left(\frac{R}{r}\right)^{n\phi} - \phi^{2}\left(\frac{R}{r}\right)^{n}\right] \tag{3}$$

the Half of Square potential function

$$U_{\mathrm{H}} = D\left[\frac{H(n-1)}{H(n)}\left(\frac{R}{r}\right)^{H(n+1)} - \frac{H(n+1)}{H(n)}\left(\frac{R}{r}\right)^{H(n-1)}\right] \tag{4}$$

the Lucas potential function

$$U_{\mathrm{L}} = D\left[\frac{L(n-1)}{L(n)}\left(\frac{R}{r}\right)^{L(n+1)} - \frac{L(n+1)}{L(n)}\left(\frac{R}{r}\right)^{L(n-1)}\right] \tag{5}$$

and the Fibonacci potential function

$$U_{\mathrm{F}} = D\left[\frac{F(n-1)}{F(n)}\left(\frac{R}{r}\right)^{F(n+1)} - \frac{F(n+1)}{F(n)}\left(\frac{R}{r}\right)^{F(n-1)}\right], \tag{6}$$

where n is an adjustable parameter in equations (1)–(3), with $n = 4, 5, 6$ for equations (4)–(6), respectively, whilst D and R are the magnitude of the minimum well-depth and the corresponding intermolecular equilibrium distance.

2. Conception

It is well known that a potential function of the form

$$U = D\left[\frac{n}{m-n}\left(\frac{R}{r}\right)^m - \frac{m}{m-n}\left(\frac{R}{r}\right)^n\right] \tag{7}$$

fulfills the following criterion for an acceptable intermolecular energy

$$\lim_{r\to 0} U = \infty, \tag{8}$$

$$(U)_{r=R} = -D, \tag{9}$$

$$\left(\frac{\partial U}{\partial r}\right)_{r=R} = \lim_{r\to\infty} U = \lim_{r\to\infty}\frac{\partial U}{\partial r} = 0. \tag{10}$$

Indeed, substitution of $m = 2n = 12$, $5m = 6n = 60$, $2m = 3n = 18$ and $m = 2n = 14$ into equation (7) gives rise to Lennard-Jones(12-6), Lennard-Jones(12-10), Lennard-Jones(9-6) and Lennard-Jones(14-7), respectively. The practicality of these functions is undoubted. This can be inferred from the use of Lennard-Jones(12-6) function in OPLS [25] and UFF [26], AMBER [27] and ECEPP [28] computational chemistry softwares for describing van der Waals interaction energy. The Lennard-Jones(12-10) function is also incorporated in AMBER and ECEPP [27,28] as an option. The ESFF [29] and CFF [30] softwares adopt the Lennard-Jones(9-6) whilst MMFF [31] employ the Lennard-Jones(14-7) for quantifying the van der Waals interaction.

Since, it is a requirement that $m > n$, we let a general mathematical constant $C > 1$ be assigned the following ratio

$$C = \frac{m}{n}, \tag{11}$$

such that equation (7) can be rewritten as

$$U_{\mathrm{C}} = D\left[\frac{1}{C-1}\left(\frac{R}{r}\right)^{nC} - \frac{C}{C-1}\left(\frac{R}{r}\right)^n\right]. \tag{12}$$

The adjustable parameter, n, can be obtained as

$$n = R\sqrt{\frac{\kappa}{CD}}, \tag{13}$$

where κ is the curvature at the well-depth's minimum

$$\kappa = \left(\frac{\partial^2 U}{\partial r^2}\right)_{r=R}. \tag{14}$$

It can be easily seen that substituting $C = e$ and $C = \pi$ into equation (12) gives equations (1) and (2), respectively.

From the definition of the golden ratio, we have

$$\phi = 1 + \frac{1}{\phi} = \frac{1}{\phi - 1}. \tag{15}$$

By virtue of equation (15), substitution of $C = \phi$ into equation (12) leads to equation (3).

Equations (4)–(6) were conceived, not by analysis, but via observation. It has been noted that the product of the coefficient and the index of the repulsive term must be equal to that of the attractive term in order to fulfill the condition of minimum point at equilibrium intermolecular distance [16]. We further note that the repulsive index is in the order of 10^1 with the attractive index being a fraction of the former, as shown in table 1, for the four Lennard-Jones potentials [25–31] and the Buckingham potential [26,32–35]. The attractive coefficients are in the order of 10^0 and are greater than the corresponding repulsive coefficients by 1. As such we introduce the Half of Square sequence written as

$$H(n) = \frac{n^2}{2}, \tag{16}$$

Table 1

Coefficients and indices of repulsive and attractive terms in the proposed and some common intermolecular potentials.

Repulsive coefficient	Attractive coefficient	Repulsive index	Attractive index	Remark(s)
5	6	12	10	Lennard-Jones(12-10)
2	3	9	6	Lennard-Jones(9-6)
1.618034	2.618034	11.83741	7.31592	Golden (this paper)
1	2	14	7	Lennard-Jones(14-7)
1	2	12	6	Lennard-Jones(12-6)
0.772	1.772	13.772	6	Buckingham [26,32-34]
0.636364	1.636364	18	7	Lucas (this paper)
0.625	1.625	13	5	Fibonacci (this paper)
0.6119	1.6119	13.772	5.228	[16,35]
0.581977	1.581977	15.34299	5.644371	Euler (this paper)
0.5625	1.5625	12.5	4.5	Half Square (this paper)
0.466942	1.466942	16.49445	5.250345	Pi (this paper)
0.3488	1.3488	16.685	4.315	[16]

Note: Unlike the rest, the repulsive term for the Buckingham potential is an exponential function.

where n is a non-negative integer. Based on $H(3) = 4.5$ and $H(5) = 12.5$ one may write the following potential function

$$U_{\mathrm{H}} = D\left[\frac{4.5}{12.5-4.5}\left(\frac{R}{r}\right)^{12.5} - \frac{12.5}{12.5-4.5}\left(\frac{R}{r}\right)^{8.5}\right], \tag{17}$$

which is similar to the form shown in equation (7). Additionally,

$$H(n+1) - H(n-1) = H(n) \quad \text{iff } n = 4, \tag{18}$$

which gives

$$U_{\mathrm{H}} = D\left[\frac{4.5}{8.0}\left(\frac{R}{r}\right)^{12.5} - \frac{12.5}{8.0}\left(\frac{R}{r}\right)^{8.5}\right], \tag{19}$$

which is equation (4) with $n = 4$. Hence, equation (19) is a potential function that adopts three consecutive Half Square numbers $H(n) = 4.5, 8.0, 12.5$ corresponding to $n = 3, 4, 5$.

On the basis of the Lucas numbers $L(4) = 7$ and $L(6) = 18$ and the Fibonacci numbers $F(5) = 5$ and $F(7) = 13$, we conceptualize the Lucas potential function

$$U_{\mathrm{L}} = D\left[\frac{7}{18-7}\left(\frac{R}{r}\right)^{18} - \frac{18}{18-7}\left(\frac{R}{r}\right)^{7}\right] \tag{20}$$

and the Fibonacci potential function

$$U_{\mathrm{F}} = D\left[\frac{5}{13-5}\left(\frac{R}{r}\right)^{13} - \frac{13}{13-5}\left(\frac{R}{r}\right)^{5}\right], \tag{21}$$

respectively, which are similar to the form described by equation (7). Since the Lucas and the Fibonacci sequences are defined as

$$L(n+1) = L(n) + L(n-1), \quad L(0) = 2,\ L(1) = 1 \tag{22}$$

and

$$F(n+1) = F(n) + F(n-1), \quad F(0) = 0,\ F(1) = 1, \tag{23}$$

respectively, it follows that

$$U_{\mathrm{L}} = D\left[\frac{7}{11}\left(\frac{R}{r}\right)^{18} - \frac{18}{11}\left(\frac{R}{r}\right)^{7}\right] \tag{24}$$

Table 2
The first few numbers in the mathematical sequences considered herein.

n	0	1	2	3	4	5	6	7	8
$H(n)$	0	0.5	2	4.5	8	12.5	18	24.5	32
$L(n)$	2	1	3	4	7	11	18	29	47
$F(n)$	0	1	1	2	3	5	8	13	21

and

$$U_{\mathrm{F}} = D\left[\frac{5}{8}\left(\frac{R}{r}\right)^{13} - \frac{13}{8}\left(\frac{R}{r}\right)^{5}\right] \tag{25}$$

as proposed in equations (5) and (6) with $n = 5$ and $n = 6$, respectively. Hence, the use of three consecutive Lucas numbers $L(n) = 7, 11, 18$ corresponding to $n = 4, 5, 6$ and three consecutive Fibonacci numbers $F(n) = 5, 8, 13$ corresponding to $n = 5, 6, 7$ for their potential energy functions. Table 2 gives the first few numbers in the Half Square, Lucas and Fibonacci sequences.

3. Results and discussion

To verify the validity of the intermolecular potential functions proposed herein, we plot these functions on a non-dimensionalized intermolecular energy (U/D) versus non-dimensionalized intermolecular distance (r/R) axes for comparison with a set of established potential function curves as reference. These reference functions include the well-known and frequently adopted Lennard-Jones(12-6) function, as well as the Lennard-Jones(9-6) and the Lennard-Jones(12-10) which are used for fitting softer and harder intermolecular interactions, respectively, as compared to Lennard-Jones(12-6). Another reference function is the Lennard-Jones(14-7), which is known to give good fit for inert gases. In addition, the argon intermolecular energy data by Aziz and Chen [36], as reported by Maitland et al. [37], are incorporated for a more comprehensive comparison.

The Lennard-Jones(12-6), Lennard-Jones(9-6), Lennard-Jones(12-10), Lennard-Jones(14-7), Half Square, Lucas and Fibonacci potential energy functions as well as the experimental data [36,37] can be plotted directly. However, the Golden ratio, Euler and Pi potential energy functions were not readily plotted due to the need to obtain the adjustable parameter, n. Based on three coordinate points at the minimum well-depth of the experimental data, the curvature can be numerically calculated using

$$\kappa = 4\frac{U_{i+1} - 2U_i + U_{i-1}}{\left(r_{i+1} - r_{i-1}\right)^2} \tag{26}$$

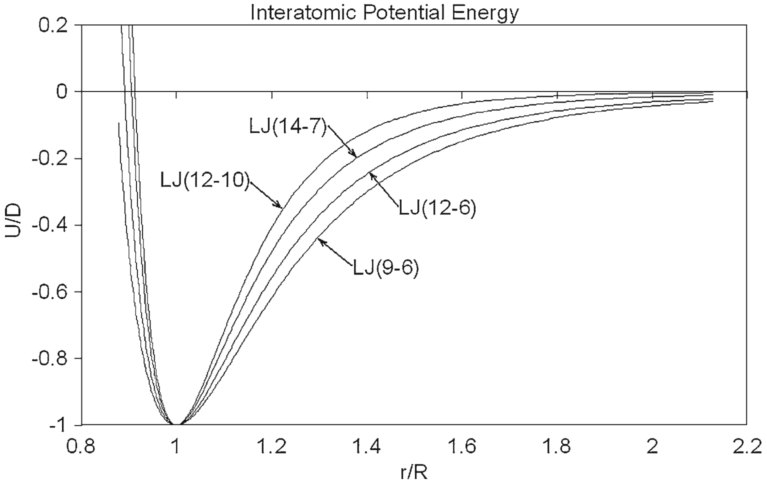

Figure 1. A comparison of the four Lennard-Jones functions used herein as reference potentials.

to give the curvature as $\kappa = 87777.78\,\mathrm{Knm}^{-2}$. This curvature and other parameters $R = 0.3759\,\mathrm{nm}$, $D = 143.22\,\mathrm{K}$ [36,37], upon substitution into equation (13) gives the adjustable parameter as

$$n = \begin{cases} 5.644371, & C = e, \\ 5.250345, & C = \pi, \\ 7.315920, & C = \phi. \end{cases} \tag{27}$$

The Euler, Pi and Golden ratio potential energy functions were then plotted based on their corresponding value of n.

Figure 1 shows the four established Lennard-Jones potential energy function plots. It can be easily seen that these four curves do not coincide due to their intended applications. As such the proposed potential functions are compared separately according to their closeness with the respective Lennard-Jones potential curves.

With reference to figure 2, we observe that the Lucas potential function agrees well with the Lennard-Jones(12-10) function for the intermolecular distance range $0.9 \leqslant (r/R) \leqslant 1.2$. Thereafter, the Lucas potential function underestimates the Lennard-Jones(12-10) function. In view of the extremely high energy of Lennard-Jones(12-10) as compared to other Lennard-Jones functions (see fig. 1), the lower value of Lucas potential function implies the latter's closeness with many other van der Waals systems as compared to the Lennard-Jones(12-10) function.

Perusal to figure 3 reveals the excellent agreement between the proposed golden ratio potential function and the experimental results for argon. The plot also reveals that the golden ratio potential function performs better than the Lennard-Jones(14-7) function, which is reputed to give good fit for inert gases.

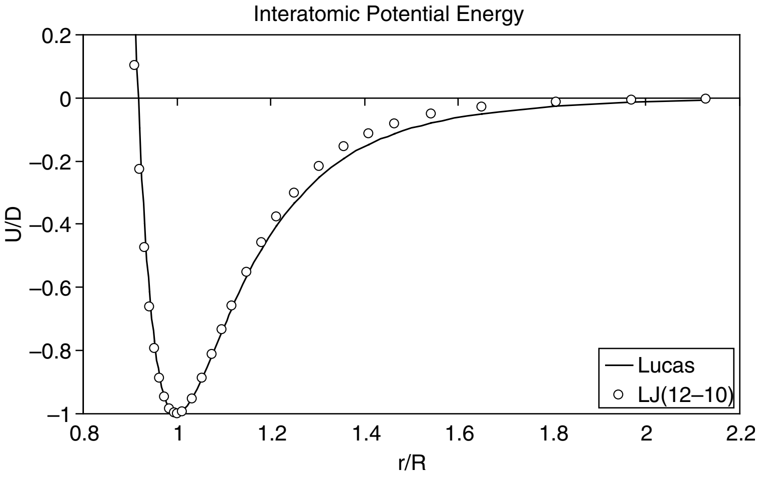

Figure 2. Comparing the proposed Lucas potential against Lennard-Jones(12-10) function.

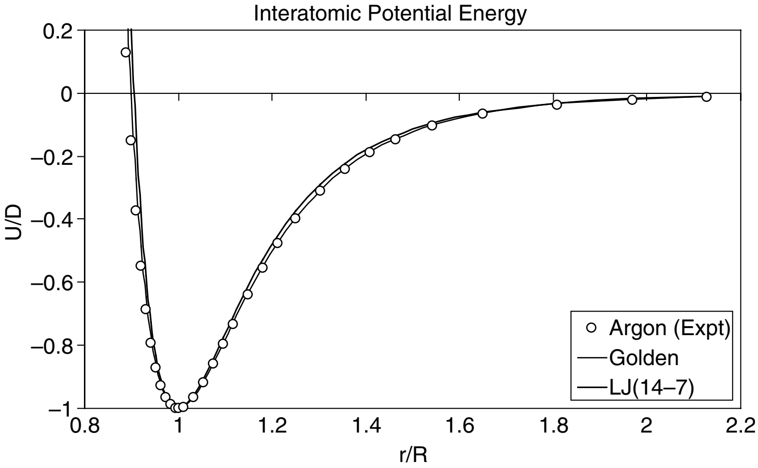

Figure 3. Comparing the proposed golden ratio potential against Lennard-Jones(14-7) function and experimental results for argon [36, 37].

The better fit exhibited by the golden ratio potential function can be attributed to the adjustable parameter n, as shown in equation (3), which is not available for the Lennard-Jones(14-7) function.

With reference to figure 4, we observe that both the Euler and the Pi potential functions agree well with the frequently employed Lennard-Jones(12-6) function. A closer scrutiny, however, reveals that (i) both the Euler and Pi potential functions coincide almost exactly for $(r/R) < 1.2$ and $(r/R) > 2$, (ii) the Euler potential slightly overestimates the Lennard-Jones(12-6) function for $1.2 < (r/R) < 1.5$, and (iii) the Pi potential function slightly underestimates the

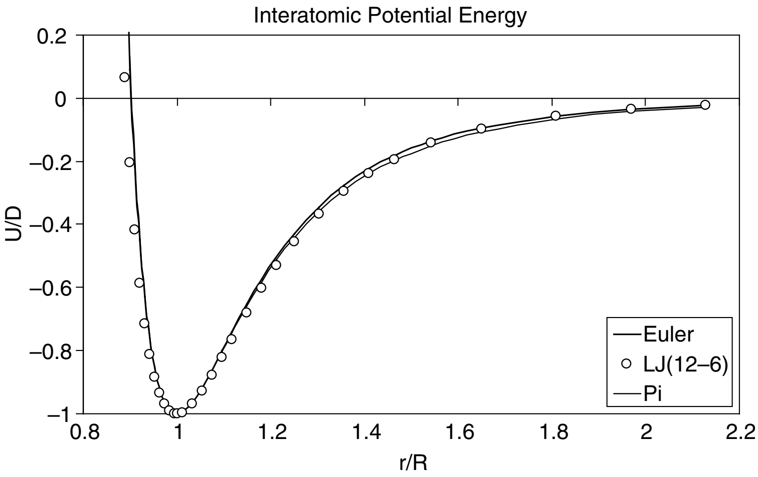

Figure 4. Comparing the proposed Euler and Pi potentials against Lennard-Jones(12-6) function.

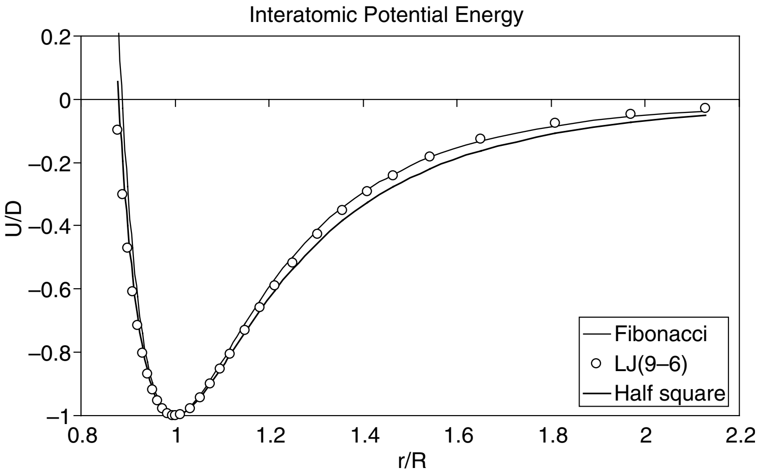

Figure 5. Comparing the proposed Fibonacci and half Square potentials against the Lennard-Jones(9-6) function.

Lennard-Jones(12-6) function for $1.5 < (r/R) < 2$. In spite if these discrepancies, the numerical difference is insignificant and that both Euler and Pi potentials are nonetheless excellent functions for any van der Waals systems that obey the Lennard-Jones(12-6) function.

Figure 5 shows a reasonable agreement between the proposed Half Square and Fibonacci potentials with the Lennard-Jones(9-6) function, thereby indicating the proposed potentials' applicability for weak van der Waals systems. Further observation shows the Fibonacci potential's overestimation and the Half

Square potential's underestimation of the Lennard-Jones(9-6) curve. This observation implies the applicability of the Fibonacci potential for modeling weak van der Waals systems that experiences stronger interaction energy in high pressure, and the usefulness of the Half Square potential for modeling weak van der Waals systems that exhibits further weakening as a result of lower pressure.

4. Conclusions

Six intermolecular potential energy functions have been proposed herein based on the mathematical constants of Golden ratio, Euler number and Pi, as well as three consecutive numbers from each of the Half Square, Lucas and Fibonacci sequences. Although any number greater than 1 can be assigned to the introduced constant C, the use of the above mentioned constants and integers have been shown to be consistent with other established intermolecular potential energy function. Furthermore, the use of consecutive numbers in some sequences in the proposed potentials reveals their relatedness to intermolecular energy. These new observations indicate additional significance of some mathematical constants and sequences in the field of chemistry.

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