

Polynomial forms of typical interatomic potential functions

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The use of polynomial functionals for describing two-body interactions in computational chemistry softwares has been surveyed and found to be prevalent. In this paper, Binomial and Maclaurin series expansions are used for expressing typical interatomic potential functions – such as Lennard-Jones, Morse, Rydberg and Buckingham potential – in a generic polynomial function, with the coefficients presented in a tabular format. Theoretical plots of these potential functions and their corresponding polynomial forms show increasing correlation with the order of polynomial, thereby validating the obtained polynomial's coefficients. Conversely, a polynomial functional obtained by curve-fitting of experimental data can be converted into Morse, Rydberg and Buckingham potentials by using the generated table.

KEY WORDS: Binomial series, interatomic potentials, Maclaurin series, polynomial functionals

AMS subject classification: 26C99, 30B10, 41A10, 70F05, 81V55, 92E99

1. Introduction

With the establishment of empirical interatomic potential functions [1–6], mathematical chemistry in recent years has taken advantage of applying mathematical functions to elucidate the relatedness of these interatomic potentials. This was verified by plots of interatomic potential energy with reference to the interatomic distance and/or angles. For example:

- (i) Coefficients of the Trigonometric Series and the Cosine Power Series, which are commonly used for bond-torsion energy, were related by merely applying elementary trigonometric identities [7];
- (ii) Coefficients of the Harmonic Angle, Harmonic Cosine, Polynomial Angle Series and Fourier Series – which are normally applied for describing bond-bending energy – were connected using Maclaurin series expansion, elementary trigonometry and elementary calculus [8];

- (iii) Parameters of bond-stretching potentials (e.g. Harmonic, Morse, Polynomial Series, etc) were related using Maclaurin series expansion and calculus [9];
- (iv) Parameters of van der Waals potentials – such as Lennard-Jones (LJ) and Buckingham potentials – were connected via calculus [10] and Maclaurin series expansion [11];
- (v) Due to significant discrepancies between the Morse and Murrell-Mottram potentials at large interatomic separation [9], an improved relationship was obtained which is valid for both small and large interatomic stretching [12].
- (vi) Relationships among 2-body portion of many-body system used in condensed matter were obtained mainly by taking multiple derivatives at the equilibrium interatomic distance [13–20].

The interatomic functions' relationships listed in (i)–(iv) were reviewed [21] and a prototype molecular potential function converter was developed in a spreadsheet format [22]. It is of interest to observe that in several cases the Maclaurin series expansion is of critical importance [23], particularly in obtaining coefficients of the polynomial forms. Obtaining polynomial forms (of which harmonic potential is a subset) of pair potentials is highly justifiable on the basis of the numerous computational chemistry softwares that adopt such functional forms for describing two-body interactions. These include, in chronological order, the EAS [24], MM2 [25], CVFF [26], CHARMM [27], GROMOS [28], TRIPOS [29], MM3 [30], DREIDING [31], COSMIC [32], SHAPES [33], UFF [34], CFF [35], AMBER [36], MOMEK [37], EFF [38], MMFF [39], MM4 [40] and OPLS [41] computational chemistry softwares. By extracting polynomial coefficients from typical potential functions, the obtained coefficients may then be incorporated into these softwares – thereby enabling greater flexibility and wider applications.

2. Analysis

Classical potential functions of LJ [42]

$$U_{\text{LJ}} = D \left[\left(\frac{R}{r} \right)^{12} - 2 \left(\frac{R}{r} \right)^6 \right], \quad (1)$$

of Morse [43]

$$U_{\text{M}} = D [\exp(-2\alpha(r - R)) - 2 \exp(-\alpha(r - R))], \quad (2)$$

of Rydberg [44]

$$U_{\text{Ryd}} = -D \left[1 + a \left(\frac{r-R}{R} \right) \right] \exp \left(-a \left(\frac{r-R}{R} \right) \right) \quad (3)$$

and of Buckingham [45]

$$U_{\text{B}} = A \exp(-Br) - \frac{C}{r^6} \quad (4)$$

were recently connected among one another [46]. In this paper these classical potentials are converted into polynomial forms by taking advantage of both the Maclaurin series expansion

$$\exp(z) = \sum_{i=0}^m \frac{z^i}{i!} \quad (5)$$

and the Binomial series expansion

$$\frac{1}{(1+z)^p} = \sum_{i=0}^m \binom{-p}{i} z^i. \quad (6)$$

By expressing the ratio

$$\frac{R}{r} = \frac{1}{(1+(\delta r/R))^p}, \quad (7)$$

whereby $\delta r = r - R$, in terms of the Binomial series expansion, a polynomial function for the Lennard-Jones potential can be obtained.

Unlike the Morse potential considered previously [9]

$$U_{\text{Morse}} = D [1 - \exp(-\alpha(r-R))]^2, \quad (8)$$

which is normally adopted in computational chemistry softwares, the functional form considered in this paper, as furnished in equation (2), is the original version that gives $(U_{\text{M}})_{r=R} = -D$ and $(U_{\text{M}})_{r \rightarrow \infty} = 0$ instead of $(U_{\text{Morse}})_{r=R} = 0$ and $(U_{\text{Morse}})_{r \rightarrow \infty} = D$ respectively. It is clear that $U_{\text{M}} = U_{\text{Morse}} - D$, and therefore the polynomial form of U_{M} can be easily obtained by subtracting D from the polynomial form of U_{Morse} [9].

By substituting equation (5) into equations (3) and (4), polynomial forms of Rydberg and Buckingham potentials can be obtained respectively. Special mention, however, needs to be made for the latter. To simplify the polynomial coefficients of Buckingham potential function, we let

$$\left(\frac{\partial U_{\text{B}}}{\partial r} \right)_{r=R} = 0 \quad (9)$$

Table 1
Dimensionless coefficients for the polynomial forms of typical interatomic potentials.

Coefficients	Lennard-Jones	Morse	Rydberg	Buckingham
a_0	-1	-1	-1	-1
a_1	0	0	0	0
a_2	+36	$+(\alpha R)^2$	$+\frac{1}{2}a^2$	$+\frac{3(BR)-21}{1} \left(\frac{BR}{BR-6}\right)$
a_3	-252	$-(\alpha R)^3$	$-\frac{1}{3}a^3$	$-\frac{(BR)^2-56}{1} \left(\frac{BR}{BR-6}\right)$
a_4	+1113	$+\frac{7}{12}(\alpha R)^4$	$+\frac{1}{8}a^4$	$+\frac{(BR)^3-504}{4} \left(\frac{BR}{BR-6}\right)$
a_5	-3864	$-\frac{1}{4}(\alpha R)^5$	$-\frac{1}{30}a^5$	$-\frac{(BR)^4-5040}{20} \left(\frac{BR}{BR-6}\right)$
a_6	+11452	$+\frac{31}{360}(\alpha R)^6$	$+\frac{1}{144}a^6$	$+\frac{(BR)^5-55440}{120} \left(\frac{BR}{BR-6}\right)$

such that the repulsive A and the attractive C coefficients can be related as

$$(BR) = \frac{6CR^{-6}}{A \exp(-BR)}. \tag{10}$$

Suppose the polynomials of the LJ, Morse, Rydberg and Buckingham were to be written in the following general form

$$U = D \sum_{i=0}^m a_i \left(\frac{\delta r}{R}\right)^i, \tag{11}$$

then the dimensionless coefficients a_i ($i = 0, 1, \dots, m$) are as listed in Table 1.

3. Results and discussion

In order to provide a graphical verification on the validity of the generalized polynomial form of the four potential functions, graphs of dimensionless potential energy (U/D) versus the dimensionless interatomic distance (r/R) were plotted. Figures 1 through 4 correspond to plots of (U/D) against (r/R) for the LJ, Morse, Rydberg and Buckingham potentials respectively. To show the extent of validity, the even orders of the polynomials ($m = 2, 4, 6$) were also plotted based on equation (11) and Table 1. To do so, the non-dimensional terms (αR), a and (BR) shown in Table 1 need to be assigned numerical values for illustration purposes. As such, we select

$$(BR) = 2(\alpha R) = \sqrt{2}a = 12, \tag{12}$$

from previous and present work (e.g. [10,14] and Table 1) in order to provide reasonably realistic plots. As can be seen in all the four figures, the second-order polynomials ($m = 2$, or harmonic forms) give reasonable accuracy at and near $r \cong R$, while fourth-order polynomials ($m = 4$) result in reasonable correlation for $r/R < 1.1$. As expected, the sixth-order polynomials ($m = 6$) are the best

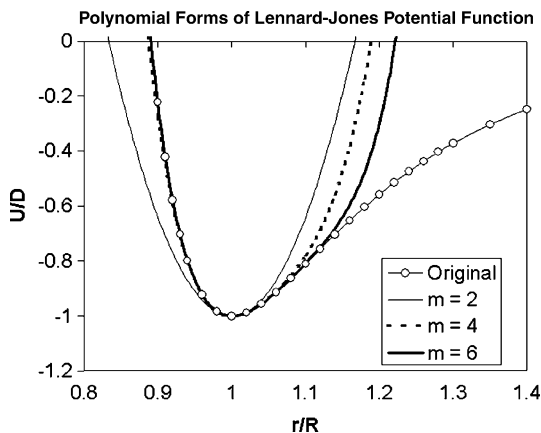


Figure 1. Lennard-Jones potential energy with its polynomial forms.

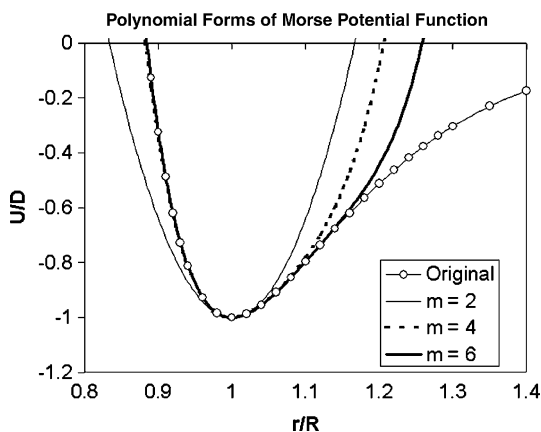


Figure 2. Morse potential energy with its polynomial forms.

among the three polynomial orders considered, as they give numerically valid agreement up to $r/R < 1.15$. Apart from enabling polynomial forms of potential functions to be generated using available parameters from typical interatomic potentials, Table 1 conversely enables the extraction of typical interatomic potential functions' parameters from polynomials functionals obtained by curve-fitting of experimental data.

4. Conclusions

Knowledge on the interconnection between the typical interatomic potential functions and their corresponding polynomial forms are relevant in view of the numerous computational chemistry softwares that adopt polynomial forms for two-body interactions [24–41]. A method for obtaining polynomial forms

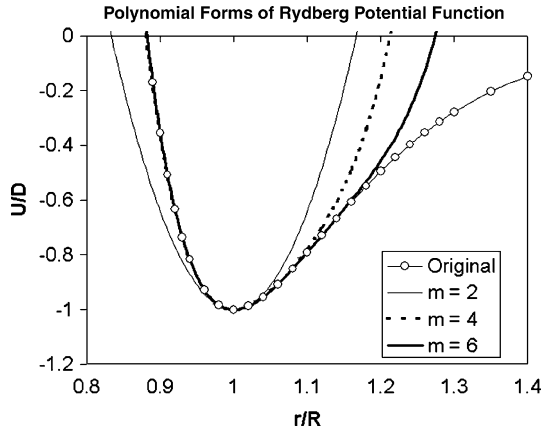


Figure 3. Rydberg potential energy with its polynomial forms.

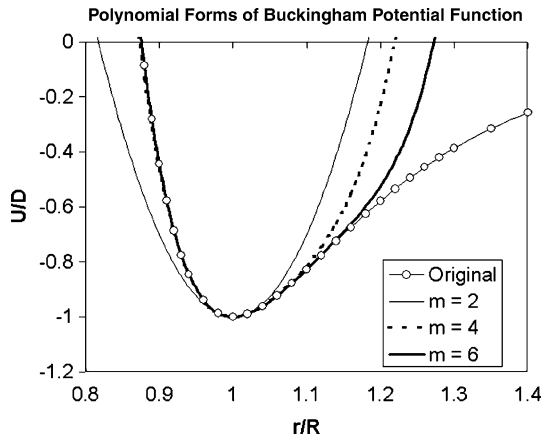


Figure 4. Buckingham potential energy with its polynomial forms.

of typical interatomic potential functions – such as LJ, Morse, Rydberg and Buckingham potentials – has been proposed by using Binomial and Maclaurin series expansions. Dimensionless coefficients for the polynomials, generated up to the sixth order, can be used for transforming the above-mentioned potentials' parameters into polynomial functionals and vice versa.

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