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ORIGINAL PAPER

A power series potential energy function with adjustable index

Teik-Cheng Lim

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Abstract A power-series potential energy function that is analogous to that of the Molski potential is proposed herein such that reductions to the Dunham and Simons-Parr-Finlan (SPF) potential functions are obtained by prescribing numerical values of 0 and 1 respectively to a type parameter. The type parameter takes the form of an index instead of a multiplier in the case of the Molski potential. Verification of the proposed potential function was performed by comparing it alongside the Dunham, SPF and Ogilvie potentials in being fitted to the RKR results of CO diatomic molecule. The proposed potential with the selection of central value to its type parameter is a geometric mean analogy to the Ogilvie potential's arithmetic mean of the Dunham and SPF potential functions. Although prescription of any numerical value to the type parameter allows good curve fit within the range of RKR data, the extent of convergence is influenced by the choice of type parameter. Having shown the validity of the proposed potential, further studies is proposed in order to establish the comparative advantages of this potential with other power-series potential energy function.

Keywords Generalized potential · Potential energy function · Power-series

1 Introduction

The quest for quantifying the molecular interaction energy in the past century is paving a way for understanding the behavior of materials and structures at the molecular and nano-scale level. It follows that accurate molecular potential energy quantification, by means of potential energy functions, contributes towards more accurate and reliable simulation. Potential energy functions may well be broadly categorized into (a)

T.-C. Lim (✉)
School of Science and Technology, SIM University, 461 Clementi Road, Singapore 599491, Singapore
e-mail: alan_tc_lim@yahoo.com

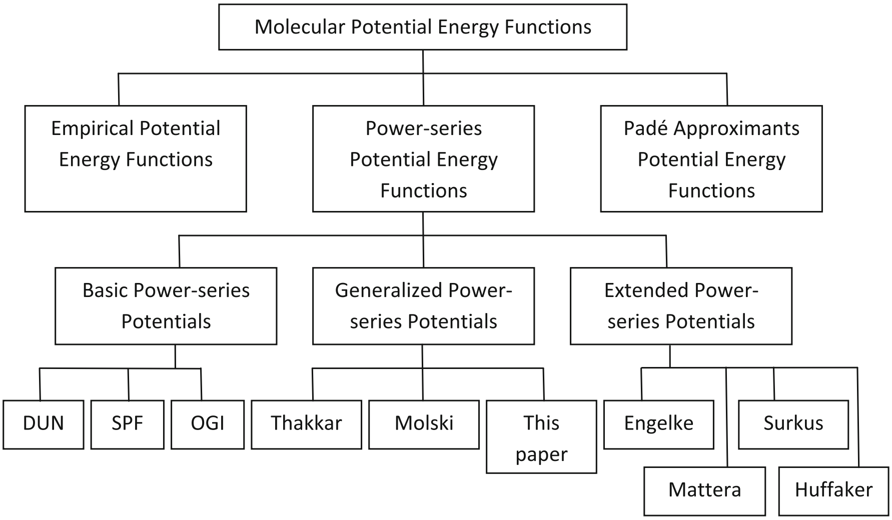

Fig. 1 Categorization of power-series potential energy functions

empirical potential functions [1–16], (b) Padé approximants [17], and (c) the power series expansions. The power-series expansion potential functions, in turn, can be classified into 3 types: (i) basic power-series potentials, (ii) generalized power-series potentials, and (iii) extended power-series potentials. Figure 1 shows the breakdown of these potential energy functions with special emphasis on the power-series expansion, which are known to give very accurate potential energy curve near the minimum well-depth zone.

The power series potential takes the form

$$U_{PS} = C_0\lambda^2\left(1 + \sum_{i=1}^{\infty} C_i\lambda^i\right) \tag{1}$$

whereby the basis function, λ is a function of the internuclear distance, r and the equilibrium bond length, R for the basic power-series potential function. In addition to r and R, λ is also a function of the type parameter and/or other fitting parameters in the case of generalized and extended potential functions. The basis functions of the Dunham [18,19], Simons-Parr-Finlan (SPF) [20] and Ogilvie [21] potentials are

$$\lambda_{DUN} = \frac{r-R}{R}, \tag{2}$$

$$\lambda_{SPF} = \frac{r-R}{r} \tag{3}$$

and

$$\lambda_{OGI} = \frac{r-R}{\frac{1}{2}(r+R)} \tag{4}$$

respectively. As the name suggests, the generalized power-series potentials possess type parameters such that prescribing specific numerical values into these parameters reduce the generalized power-series into the basic ones. The basis functions of Thakkar [22] and the Molski [23] are

$$\lambda_{THA} = sign(p)\left[1 - \left(\frac{R}{r}\right)^{p}\right] \tag{5}$$

and

$$\lambda_{MOL} = \frac{r - R}{ar + (1-a)R} \tag{6}$$

respectively. Substitutions of $p = -1$ and $p = 1$ into Eq. (5) reduce it to the basis functions of Dunham and SPF respectively, while substitutions of $a = 0, a = 1$ and $a = 0.5$ reduce Eq. (6) into the basis functions of Dunham, SPF and Ogilvie respectively. The basis functions of the extended power-series, on the other hand, generally possess additional parameter(s) with p [24–27] or without p [28–30]. Although additional parameters in general aid curve fitting by the provision of functional flexibility, the coefficients C_i (i = 0, 1, 2, ...) in the basic power-series potentials are sufficient to provide very good fitting. Any further refinement can be meaningfully and sufficiently be achieved by means of adjusting the type parameters. As such, this paper proposes a new basis function for a generalized power-series potential to complement the existing generalized power-series potentials [22,23], which are few in comparison to the extended power-series potentials [24–30].

2 Proposed potential function

A power-series potential energy function is proposed herein in the form given by Eq. (1) with a basis function, λ that complements the Thakkar and Molski basis functions. As a trial, a basis function is proposed in the form

$$\lambda_{TRIAL} = \left(\frac{R}{r}\right)^{\frac{p-1}{2}} - \left(\frac{R}{r}\right)^{\frac{p+1}{2}} \tag{7}$$

which, upon substitution of $p = -1$ and $p = 1$ leads it to the Dunham and SPF basis functions respectively, as would the Thakkar basis function. An obvious advantage that this trial basis function has over the Thakkar basis function is in its stability at $p = 0$. Thakkar's basis function is undefined when $p = 0$. However, substitution of $p = 0$ does not reduce it to the Ogilvie function. Instead, it takes the form

$$(\lambda_{TRIAL})_{p=0} = \sqrt{\frac{r}{R}} - \sqrt{\frac{R}{r}}. \tag{8}$$

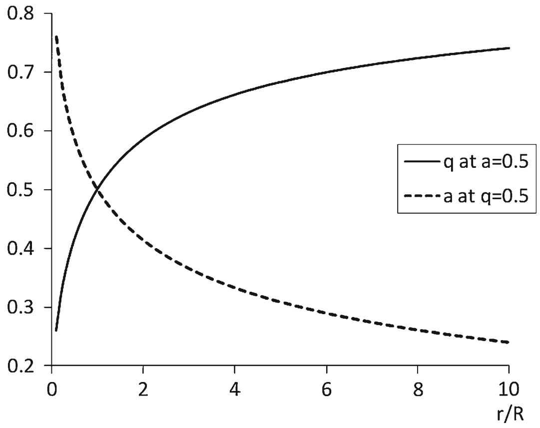

Fig. 2 Plots of q at $a = 0.5$ and of a at $q = 0.5$ against the dimensionless internuclear distance

It follows that this trial form of basis function leads one to conceive a new basis function of the form

$$\lambda = \left(\frac{r}{R}\right)^{1-q} - \left(\frac{R}{r}\right)^{q} \tag{9}$$

in which $\lambda = \lambda_{TRIAL}$ when $q = 0.5$. The basis function given in Eq. (9) can be rewritten in an alternate form

$$\lambda = \frac{r - R}{r^{q} R^{1-q}}. \tag{10}$$

Substitution of $q = 0$ and $q = 1$ gives the Dunham and SPF basis functions respectively, thereby implying an analogy between the Molski type parameter, a and the present type parameter, q. For the range $q \in (0, 1)$, an understanding on the relation between type parameters a and q can be sought by equating $\lambda = \lambda_{MOL}$ to give

$$a = \frac{\left(\frac{r}{R}\right)^{q} - 1}{\frac{r}{R} - 1} \tag{11}$$

and

$$q = \frac{\ln\left[1 + a\left(\frac{r}{R} - 1\right)\right]}{\ln\left(\frac{r}{R}\right)}. \tag{12}$$

For illustration, a curve of q at $a = 0.5$ and a curve of a at $q = 0.5$ were plotted against the dimensionless internuclear distance (r/R) in Fig. 2.

An analogy between the present basis function with that of Ogilvie can be obtained by substituting $q = 0.5$ to give

$$\lambda = \frac{r - R}{\sqrt{rR}}, \tag{13}$$

which bears remarkable resemblance to, as well as complimenting, Eqs. (2)–(4). Hence the Molski basis function at $a = 0.5$ (i.e. the Ogilvie basis function) and the presently investigated basis function at $q = 0.5$ have, at their denominator, an arithmetic mean and a geometric mean respectively. For a power-series potential energy function to be valid, it must fulfill at least two criteria, namely:

$$\lim_{r \to 0} U = \infty \tag{14}$$

and

$$U|_{r=R} = 0. \tag{15}$$

Reference to Eq. (9) shows that

$$\lim_{r \to 0} \lambda = \infty \tag{16}$$

and

$$\lambda|_{r=R} = 0, \tag{17}$$

which fulfill the conditions spelt out in Eqs. (14) and (15) respectively. The third criterion,

$$\lim_{r \to \infty} \lambda = D, \tag{18}$$

whereby D is the dissociation energy, is not readily met by power-series potentials. Nevertheless the power-series potentials are applicable for accurately describing small change in internuclear distance about the equilibrium bond length if a few coefficients are sufficient for providing reasonable curve fitting up to a desired change in the internuclear distance. As a test of validity over intermediate range, the presently proposed potential is compared with other results in the next section.

3 Results and discussion

Table 1 lists the RKR potential-energy data for the $\mathrm{X}^1\Sigma^+$ state of $^{12}C^{16}O$ adapted from Camacho et al. [31]. From this set of data, coefficients of the power-series potential function, i.e. C_i $(i = 0, 1, 2, 3, 4)$, were obtained by performing curve-fitting to the Dunham, SPF, Ogilvie and the presently proposed power-series potential at $q = 0.5$. Results of the coefficients are furnished in Table 2. The validity of the proposed power-series potential at $q = 0.5$ is attested in Fig. 3, which shows how this potential fare in comparison with other power-series being curve fitted to the RKR results. The good fit between the present power-series (at $q = 0.5$) and the RKR result is not surprising since the Dunham and SPF potentials form the extreme ends of the proposed potential at $q = 0$ and $q = 1$ respectively.

Table 1 RKR potential energy data for the $X^1\Sigma^+$ state of $^{12}C^{16}O$ (adapted from Camacho et al. [31]) whereby $R = 1.128$ Å

r/Å	U/cm^{-1}	r/Å	U/cm^{-1}	r/Å	U/cm^{-1}
0.862	68,044	0.941	26,899	1.491	28,704
0.863	66,903	0.946	25,069	1.509	30,483
0.865	65,738	0.952	23,213	1.526	32,237
0.867	64,549	0.958	21,331	1.544	33,965
0.868	63,335	0.964	19,424	1.561	35,668
0.87	62,098	0.971	17,490	1.578	37,346
0.872	60,836	0.979	15,531	1.596	38,999
0.874	59,551	0.987	13,546	1.613	40,627
0.876	58,241	0.997	11,534	1.631	42,230
0.879	56,907	1.007	9,496	1.648	43,808
0.881	55,549	1.019	7,432	1.666	45,362
0.883	54,167	1.034	5,342	1.683	46,891
0.885	52,761	1.053	3,225	1.701	48,395
0.888	51,330	1.083	1,082	1.719	49,874
0.891	49,874	1.179	1,082	1.737	51,330
0.893	48,395	1.22	3,225	1.755	52,761
0.896	46,891	1.25	5,342	1.773	54,167
0.899	45,362	1.276	7,432	1.792	55,549
0.902	43,808	1.3	9,496	1.81	56,907
0.905	42,230	1.322	11,534	1.829	58,241
0.908	40,627	1.342	13,546	1.848	59,551
0.912	38,999	1.363	15,531	1.868	60,836
0.915	37,346	1.382	17,490	1.887	62,098
0.919	35,668	1.401	19,424	1.906	63,335
0.923	33,965	1.419	21,331	1.927	64,549
0.927	32,237	1.438	23,213	1.947	65,738
0.932	30,483	1.456	25,069	1.968	66,903
0.936	28,704	1.474	26,899	1.989	68,044

Table 2 Coefficients of the Dunham, SPF, Ogilvie and the present potential function (at $q = 0.5$) based on curve fitting to the $X^1\Sigma^+$ state of $^{12}C^{16}O$ [31]

	DUN	SPF	OGI	Present
C_0/cm^{-1}	614,097	609,345	608,934	609,382
C_1	−2.843	−0.7018	−1.705	−1.699
C_2	4.679	−0.5723	1.255	0.9843
C_3	−4.432	−0.04225	−0.4904	0.1169
C_4	1.773	0.3290	0.08703	−0.2919

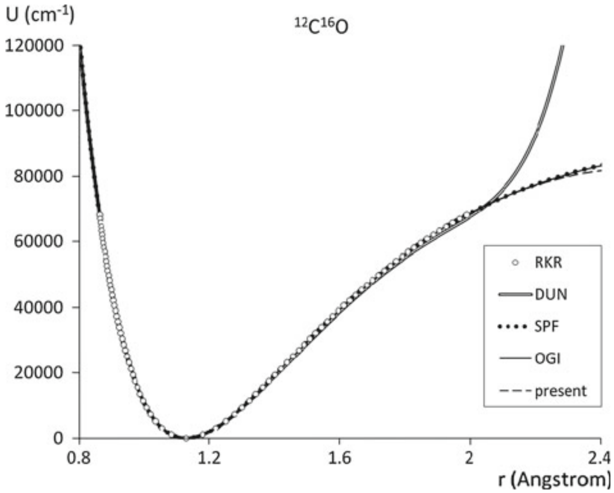

Fig. 3 Comparison between the RKR results of the $X^1\Sigma^+$ state of $^{12}C^{16}O$ with the power-series potential energy functions of Dunham, SPF, Ogilvie and the presently proposed model

Table 3 Coefficients of the present potential function based on curve fitting to the $X^1\Sigma^+$ state of $^{12}C^{16}O$ [31] at $q = 0.2$, 0.4, 0.6 and 0.8.

	$q = 0.2$	$q = 0.4$	$q = 0.6$	$q = 0.8$
C_0/cm^{-1}	609,413	609,740	608,804	608,516
C_1	−2.323	−1.895	−1.504	−1.104
C_2	2.912	1.517	0.5378	−0.1562
C_3	−2.196	−0.4179	0.4014	0.3818
C_4	0.7693	−0.08787	−0.3053	0.08791

As an example to observe how the curve fitting is influenced by the parameter q, the same RKR results for at $^{12}C^{16}O$ is being fitted by the proposed potential at $q = 0.2$, 0.4, 0.6 and 0.8. The obtained coefficients as a result of fitting are listed in Table 3. Based on these coefficients, the corresponding potential energy curves were plotted in Fig. 4. As one would expect, certain values of q give more realistic or better convergence than others. Whilst greater number of coefficients provide better fitting, a judicious choice of q aids the fitting performance for a given number of coefficients.

4 Conclusion

Although a recent series-type potential energy function aims to increase the flexibility by generalizing from the Lennard-Jones, Morse, Buckingham and Linnett potentials, and is hence generalized enough for quantifying a large range of interaction from interatomic covalent bond to intermolecular interaction [32], the presently proposed potential provides a form of generalization that is less inclusive but more accurate for describing covalent bond stretching energy. The proposed power series potential

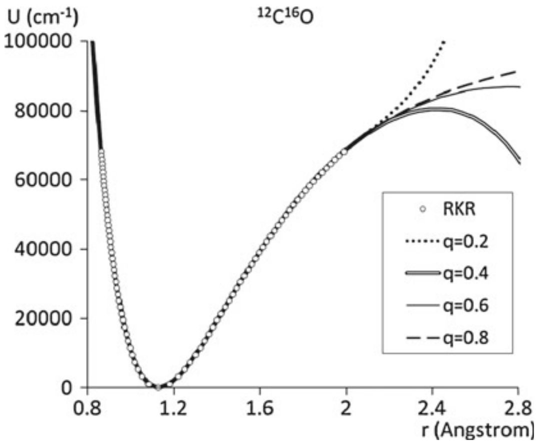

Fig. 4 Comparison between the RKR results of the $X^1\Sigma^+$ state of $^{12}C^{16}O$ with the presently proposed power-series model for various q

energy function, being analogous to the Molski potential function, which offers a mathematical alternate. While the Molski potential function changes between the Dunham and SPF potentials by the shift in the weighted multiplier of r and R at the denominator of its basis function, the functional change is effected in the proposed potential through the shift in the weighted indices of r and R in the denominator of the corresponding basis function. The "central" value of the proposed potential is analogous to the Ogilvie potential—the denominator of the former's basis function being a geometric mean while that of the latter being an arithmetic mean of r and R. Comparison with the Dunham, SPF and Ogilvie potentials by means of curve fitting to a sample RKR results verifies the validity of the proposed potential function. Further investigation on the proposed potential, especially in its comparative advantages with other power-series potential functions, is suggested. The proposed power-series expansion provides an additional choice of potential function for accurate description of molecular potential energy near the minimum well-depth. Although not intended for obtaining the exact solution within the framework of non-relative equation, the parameters of this potential can be easily extracted via curve-fitting to any given set of potential energy data, including those that have been obtained by exact solution and by experimental approach. In view of its suitability, the proposed potential energy function can be adopted as a covalent bond stretching energy for incorporation into the total molecular interaction energy as quantified by the generic molecular force field [33,34]

$$U_{Total} = \sum U_{2b} + \sum U_{3b} + \sum U_{4b} + U_{Nb} \tag{19}$$

whereby the 2-body, 3-body and 4-body interaction energy refers to bond stretching, bond bending and bond torsion respectively, while the non-bonded interaction

$$U_{Nb} = \sum U_{vdW} + \sum U_{ele} \tag{20}$$

consists of van der Waals and Coulombic (or electrostatic) interactions.

References

1. J.E. Lennard-Jones, Proc. R. Soc. Lond. A **106**, 463 (1924)
2. P.M. Morse, Phys. Rev. **34**, 57 (1929)
3. R.A. Buckingham, Proc. R. Soc. Lond. A **168**, 264 (1938)
4. J.W. Linnett, Trans. Faraday Soc. **36**, 1123 (1940)
5. J.W. Linnett, Trans. Faraday Soc. **38**, 1 (1942)
6. N. Rosen, P.M. Morse, Phys. Rev. **42**, 210 (1932)
7. R. Rydberg, Z. Phys. **73**, 21 (1933)
8. G. Poschl, E. Teller, Z. Phys. **83**, 143 (1933)
9. H.M. Hulburt, J.O. Hirschfelder, J. Chem. Phys. **9**, 61 (1941)
10. E.R. Lippincott, J. Chem. Phys. **21**, 2070 (1953)
11. E.R. Lippincott, J. Chem. Phys. **23**, 603 (1955)
12. A.A. Frost, B. Musulin, J. Am. Chem. Soc. **76**, 2045 (1964)
13. Y.P. Varshni, Rev. Mod. Phys. **29**, 664 (1957)
14. Y.P. Varshni, Rev. Mod. Phys. **31**, 839 (1959)
15. I.N. Levine, J. Chem. Phys. **45**, 827 (1966)
16. H. Hellmann, W.C. Stwalley, J. Chem. Phys. **77**, 883 (1982)
17. G.A. Baker, J.L. Gammel, *The Padé Approximant in Theoretical Physics* (Academic Press, NY, 1970)
18. J.L. Dunham, Phys. Rev. **41**, 713 (1932)
19. J.L. Dunham, Phys. Rev. **41**, 721 (1932)
20. G. Simons, R.G. Parr, J.M. Finlan, J. Chem. Phys. **59**, 3229 (1973)
21. J.F. Ogilvie, Proc. R. Soc. Lond. A **378**, 287 (1981)
22. A.J. Thakkar, J. Chem. Phys. **62**, 1693 (1975)
23. M. Molski, J. Mol. Spectrosc. **193**, 244 (1999)
24. R. Engelke, J. Chem. Phys. **68**, 3514 (1978)
25. R. Engelke, J. Chem. Phys. **70**, 3745 (1979)
26. L. Mattera, C. Salvo, S. Terreni, F. Tommasini, J. Chem. Phys. **72**, 6815 (1980)
27. A.A. Surkus, R.J. Rakauskas, A.B. Bolotin, Chem. Phys. Lett. **105**, 291 (1984)
28. J.N. Huffaker, J. Chem. Phys. **64**, 3175 (1976)
29. J.N. Huffaker, J. Chem. Phys. **64**, 4564 (1976)
30. J.N. Huffaker, J. Chem. Phys. **74**, 1217 (1981)
31. J.J. Camacho, A. Pardo, J.M.L. Poyato, J. Chem. Soc. Faraday Trans. **90**, 23 (1994)
32. T.C. Lim, J. Math. Chem. **49**, 1180 (2011)
33. A.R. Leach, *Molecular Modeling: Principles and Applications*, 2nd edn. (Prentice Hall, NJ, 2001)
34. T. Schlick, *Molecular Modeling and Simulation: An Interdisciplinary Guide*, 2nd edn. (Springer, NY, 2010)