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Coefficient interrelatedness among polynomial potential functions of diatomic molecules

Teik-Cheng Lim

Abstract It is shown that the diatomic potential energy functions of Dunham, SPF and Ogilvie can be easily converted from one another when their coefficients are related. Through Maclaurin expansion and comparison of terms, the coefficients can be related by using the Pascal Triangle. In this paper, the coefficients were related up to the tenth order of $\delta r/R$ for HX (X = H, Ga, Cl, I). Comparison of all three potential energy curves shows very good agreement for $r \le 1.5R$, thereby verifying the formulated relations. Observation of the plotted potential energy curves for $r > 1.5R$ shows that the difference of the three potential function definitions is not reflected as any consistent trend arising from the related potential functions.

Keywords Coefficients relationships · Diatoms · Interatomic energy · Potential function

1 Introduction

It has recently been shown that the flexible interatomic potential function [1]

$$
\frac{U}{D} = \frac{n^x S_2^{1-x}}{m^y S_1^{1-y} - n^x S_2^{1-x}} \left(\frac{R}{r}\right)^{my} \exp\left[S_1\left(1 - \frac{r}{R}\right)(1 - y)\right]
$$

$$
- \frac{m^y S_1^{1-y}}{m^y S_1^{1-y} - n^x S_2^{1-x}} \left(\frac{R}{r}\right)^{nx} \exp\left[S_2\left(1 - \frac{r}{R}\right)(1 - x)\right] \tag{1}
$$

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reduces to generalized Lennard-Jones [2–4], Morse [5], Buckingham [6,7] and Linnett [8,9] potential energy functions for $(x, y) = (1, 1), (0, 0), (1, 0)$ and $(0,1)$, respectively, whereby D is the well-depth magnitude, r and R being the varying and equilibrium interatomic distances, respectively, m and n are the repulsive and attractive indices, respectively, and S_1 and S_2 refer to the scaling factors for the repulsive and attractive indices, respectively. Although technically accurate, this interrelation possesses limited applications as it attempts to bridge potential function for van der Waals interaction, such as $(x, y) = (1, 1)$, with potential functions for covalent bonds, such as $(x, y) = (0, 0)$. A more meaningful bridging of potential functions should then be confined to those that model similar type of bonds, such as in the case of covalent bonds in diatomic molecules. In regard to the latter, interrelations have been proposed for the group of potential functions of the polynomial type

$$U_c = c_0 \xi_c^2 \left(1 + \sum_{i=1} c_i \xi_c^i\right) \tag{2}$$

in which $c = \alpha, \beta, \gamma$ refer to the Dunham [10], Simons–Parr–Finlan (SPF) [11] and Ogilvie [12] potential functions, respectively, whereby

$$\xi_\alpha = \frac{r - R}{R} \tag{3}$$

$$\xi_\beta = \frac{r - R}{r} \tag{4}$$

$$\xi_\gamma = \frac{r - R}{0.5(R + r)}. \tag{5}$$

Although Thakkar [13] proposed

$$\xi = \text{sign}(p) \left[1 - \left(\frac{R}{r}\right)^p\right] \tag{6}$$

for generalizing the Dunham ($p = -1$) and the SPF ($p = +1$) potential functions, incorporation of the Ogilvie potential function was made possible through Molski's model [14,15]

$$\xi = \frac{r - R}{ar + (1 - a)R} \tag{7}$$

which reduces to the Dunham, SPF and Ogilvie potential functions with the substitution of $a = 0, 1, 0.5$, respectively. This paper extends the earlier works [13–15] by establishing relationships among α_i, β_i and γ_i for $i = 1, 2, 3, \ldots$.

2 Analysis

In view of the ease by which the power series generation by the Maclaurin expansion can be used for relating coefficients of potential functions [16–23], we rewrite

Eqs. 3–5 in a set of different, but equivalent, forms as

$$\xi_\alpha = \frac{\delta r}{R} \tag{8}$$

$$\xi_\beta = \sum_{i=1} (-1)^{i-1} \left(\frac{\delta r}{R}\right)^i \tag{9}$$

$$\xi_\gamma = \sum_{i=1} \left(-\frac{1}{2}\right)^{i-1} \left(\frac{\delta r}{R}\right)^i \tag{10}$$

such that the Dunham, SPF and Ogilvie potentials can be expressed as

$$\frac{U_\alpha}{\alpha_0} = \left(\frac{\delta r}{R}\right)^2 + \alpha_1 \left(\frac{\delta r}{R}\right)^3 + \alpha_2 \left(\frac{\delta r}{R}\right)^4 + \alpha_3 \left(\frac{\delta r}{R}\right)^5 + \alpha_4 \left(\frac{\delta r}{R}\right)^6 + \cdots \tag{11}$$

$$\frac{U_\beta}{\beta_0} = \left(\frac{\delta r}{R}\right)^2 + (-2 + \beta_1) \left(\frac{\delta r}{R}\right)^3 + (3 - 3\beta_1 + \beta_2) \left(\frac{\delta r}{R}\right)^4$$

$$+ (-4 + 6\beta_1 - 4\beta_2 + \beta_3) \left(\frac{\delta r}{R}\right)^5$$

$$+ (5 - 10\beta_1 + 10\beta_2 - 5\beta_3 + \beta_4) \left(\frac{\delta r}{R}\right)^6 + \cdots \tag{12}$$

$$\frac{U_\gamma}{\gamma_0} = \left(\frac{\delta r}{R}\right)^2 + \left(-\frac{2}{2} + \gamma_1\right) \left(\frac{\delta r}{R}\right)^3 + \left(\frac{3}{4} - \frac{3}{2}\gamma_1 + \gamma_2\right) \left(\frac{\delta r}{R}\right)^4$$

$$+ \left(-\frac{4}{8} + \frac{6}{4}\gamma_1 - \frac{4}{2}\gamma_2 + \gamma_3\right) \left(\frac{\delta r}{R}\right)^5$$

$$+ \left(\frac{5}{16} - \frac{10}{8}\gamma_1 + \frac{10}{4}\gamma_2 - \frac{5}{2}\gamma_3 + \gamma_4\right) \left(\frac{\delta r}{R}\right)^6 + \cdots, \tag{13}$$

respectively. To obtain the relationships among coefficients of the three potential functions that give equivalent energy at the vicinity of the equilibrium point, coefficients from different potential energy functions are compared for the same index of $(\delta r/R)$. If a general expansion was to be written as

$$U = k_0 \left(\frac{\delta r}{R}\right)^2 + k_1 \left(\frac{\delta r}{R}\right)^3 + k_2 \left(\frac{\delta r}{R}\right)^4 + k_3 \left(\frac{\delta r}{R}\right)^5 + k_4 \left(\frac{\delta r}{R}\right)^6 + \cdots \tag{14}$$

which resembles the bond stretching description of some molecular mechanics force fields [24–36], then a one-to-one relation can be made possible through comparison of coefficients possessing equal order. See Table 1.

Comparison of k_0 coefficient gives

$$\alpha_0 = \beta_0 = \gamma_0. \tag{15}$$

Table 1 Comparison of coefficients for the first five terms

Coefficients	Dunham	SPF	Ogilvie
k_0	α_0	β_0	γ_0
k_1	$\alpha_0\alpha_1$	$\beta_0(-2+\beta_1)$	$\gamma_0\left(-\frac{2}{2^1}+\frac{1}{2^0}\gamma_1\right)$
k_2	$\alpha_0\alpha_2$	$\beta_0(3-3\beta_1+\beta_2)$	$\gamma_0\left(\frac{3}{2^2}-\frac{3}{2^1}\gamma_1+\frac{1}{2^0}\gamma_2\right)$
k_3	$\alpha_0\alpha_3$	$\beta_0(-4+6\beta_1-4\beta_2+\beta_3)$	$\gamma_0\left(-\frac{4}{2^3}+\frac{6}{2^2}\gamma_1-\frac{4}{2^1}\gamma_2+\frac{1}{2^0}\gamma_3\right)$
k_4	$\alpha_0\alpha_4$	$\beta_0(5-10\beta_1+10\beta_2-5\beta_3+\beta_4)$	$\gamma_0\left(\frac{5}{2^4}-\frac{10}{2^3}\gamma_1+\frac{10}{2^2}\gamma_2-\frac{5}{2^1}\gamma_3+\frac{1}{2^0}\gamma_4\right)$

while comparison of k_i ($i = 1, 2, 3, \ldots$) terms leads to

$$\alpha_i = (-1)^i (i+1) + \sum_{j=1}^{i} (-1)^{j+1} \binom{i+1}{j+1} \beta_j$$

$$= \left(-\frac{1}{2}\right)^i (i+1) + \sum_{j=1}^{i} \frac{(-1)^{j+1}}{2^{i-j}} \binom{i+1}{j+1} \gamma_j \tag{16}$$

$$\beta_i = (i+1) + \sum_{j=1}^{i} \binom{i+1}{j+1} \alpha_j$$

$$= \frac{1}{2} (i+1) + \sum_{j=1}^{i} \frac{1}{2^{i-j}} \binom{i+1}{j+1} \gamma_j \tag{17}$$

$$\gamma_i = \frac{1}{2} (i+1) + \sum_{j=1}^{i} \frac{1}{2^{i-j}} \binom{i+1}{j+1} \alpha_j$$

$$= \left(-\frac{1}{2}\right)^i (i+1) + \sum_{j=1}^{i} \frac{(-1)^{j+1}}{2^{i-j}} \binom{i+1}{j+1} \beta_j. \tag{18}$$

As a result of the binomial expression, the relations above can be easily extracted from a portion of the Pascal Triangle, as shown in Tables 2–4. These relations further suggest

Table 2 Obtaining Dunham coefficients from SPF and Ogilvie coefficients using Pascal Triangle

α	$h(\beta)$	$f(\gamma)$
α_1	$-2+1\beta_1$	$-\frac{2}{2^1}+\frac{1}{2^0}\gamma_1$
α_2	$3-3\beta_1+1\beta_2$	$\frac{3}{2^2}-\frac{3}{2^1}\gamma_1+\frac{1}{2^0}\gamma_2$
α_3	$-4+6\beta_1-4\beta_2+1\beta_3$	$-\frac{4}{2^3}+\frac{6}{2^2}\gamma_1-\frac{4}{2^1}\gamma_2+\frac{1}{2^0}\gamma_3$
α_4	$5-10\beta_1+10\beta_2-5\beta_3+1\beta_4$	$\frac{5}{2^4}-\frac{10}{2^3}\gamma_1+\frac{10}{2^2}\gamma_2-\frac{5}{2^1}\gamma_3+\frac{1}{2^0}\gamma_4$

Table 3 Obtaining SPF coefficient from Dunham and Ogilvie coefficients using Pascal Triangle

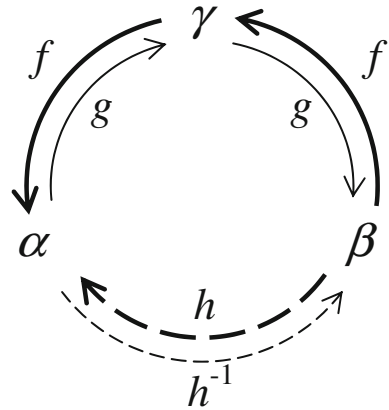| β	$h^{-1}(\alpha)$	$g(\gamma)$
β_1	$2 + 1\alpha_1$	$\frac{2}{2^1} + \frac{1}{2^0}\gamma_1$
β_2	$3 + 3\alpha_1 + 1\alpha_2$	$\frac{3}{2^2} + \frac{3}{2^1}\gamma_1 + \frac{1}{2^0}\gamma_2$
β_3	$4 + 6\alpha_1 + 4\alpha_2 + 1\alpha_3$	$\frac{4}{2^3} + \frac{6}{2^2}\gamma_1 + \frac{4}{2^1}\gamma_2 + \frac{1}{2^0}\gamma_3$
β_4	$5 + 10\alpha_1 + 10\alpha_2 + 5\alpha_3 + 1\alpha_4$	$\frac{5}{2^4} + \frac{10}{2^3}\gamma_1 + \frac{10}{2^2}\gamma_2 + \frac{5}{2^1}\gamma_3 + \frac{1}{2^0}\gamma_4$

Table 4 Obtaining Ogilvie coefficients from Dunham and SPF coefficients using Pascal Triangle

γ	$g(\alpha)$	$f(\beta)$
γ_1	$\frac{2}{2^1} + \frac{1}{2^0}\alpha_1$	$-\frac{2}{2^1} + \frac{1}{2^0}\beta_1$
γ_2	$\frac{3}{2^2} + \frac{3}{2^1}\alpha_1 + \frac{1}{2^0}\alpha_2$	$\frac{3}{2^2} - \frac{3}{2^1}\beta_1 + \frac{1}{2^0}\beta_2$
γ_3	$\frac{4}{2^3} + \frac{6}{2^2}\alpha_1 + \frac{4}{2^1}\alpha_2 + \frac{1}{2^0}\alpha_3$	$-\frac{4}{2^3} + \frac{6}{2^2}\beta_1 - \frac{4}{2^1}\beta_2 + \frac{1}{2^0}\beta_3$
γ_4	$\frac{5}{2^4} + \frac{10}{2^3}\alpha_1 + \frac{10}{2^2}\alpha_2 + \frac{5}{2^1}\alpha_3 + \frac{1}{2^0}\alpha_4$	$\frac{5}{2^4} - \frac{10}{2^3}\beta_1 + \frac{10}{2^2}\beta_2 - \frac{5}{2^1}\beta_3 + \frac{1}{2^0}\beta_4$

Fig. 1 Schematic representation of functions that relate the Dunham, SPH and Ogilvie coefficients, and the connection among these interrelations functions

a set of cyclic functions, as depicted in Fig. 1, that relate α_i, β_i and γ_i ($i = 1, 2, 3, \ldots$) as

$$\alpha_i = f(\gamma_i) \tag{19}$$
$$\gamma_i = f(\beta_i) \tag{20}$$
$$\alpha_i = f(f(\beta_i)) \tag{21}$$
$$\beta_i = g(\gamma_i) \tag{22}$$
$$\gamma_i = g(\alpha_i) \tag{23}$$
$$\beta_i = g(g(\alpha_i)) \tag{24}$$

where the functions $f(x)$ and $g(x)$ are defined as

$$f(x_i) = \left(-\frac{1}{2}\right)^i (i+1) + \sum_{j=1}^{i} \frac{(-1)^{j+1}}{2^{i-j}} \binom{i+1}{j+1} x_j \tag{25}$$

$$g(x_i) = \frac{1}{2}(i+1) + \sum_{j=1}^{i} \frac{1}{2^{i-j}} \binom{i+1}{j+1} x_j \tag{26}$$

with $f(f(x))$ and $g(g(x))$ being inverse of one another, i.e.

$$h(x) = f(f(x)) \tag{27}$$
$$h^{-1}(x) = g(g(x)). \tag{28}$$

3 Results and discussion

The validity of the obtained relations can be attested by plotting the potential energy curved of one function in comparison to the other two functions, whose coefficients are obtained from the former's coefficients. Due to the "central" nature of Ogilvie potential in comparison to the Dunham and SPF potentials, as shown in Eqs. 3–5, we herein select Ogilvie coefficients for conversion into coefficients of Dunham and SPF potential functions. Based on Ogilvie coefficients γ_i—for HH [37], HGa [38], HCl [39] and HI [40]—the Dunham coefficients α_i and SPF coefficients β_i were calculated (see Table 5) using Eqs. 16 and 17, respectively. From the three sets of coefficients, all three non-dimensionalized potential energy U_c/c_0 curves were plotted against non-dimensionalized bond length r/R for HCl diatom. To aid comparison, the potential energy curves for all four diatoms were plotted within a common range of non-dimensionalized energy and bond length axes, i.e. $0 \leq U_c/c_0 \leq 0.2$ and $0.5 \leq r/R \leq 2.5$, as shown in Fig. 2. It can be seen that very good agreement is exhibited for $(r/R) \leq 1.5$, thereby validating the derived potential functions' coefficient relationships.

Lest it be said that the "central" Ogilvie function being bounded by the Dunham and SPF functions, plotted results in Fig. 2 do not support this notion. Of the four potential energy curves plotted in Fig. 2, only the example of HI in Fig. 2d shows the Ogilvie curve being caught between the other two curves. The Ogilvie curve exhibits the lowest energy in HGa and the highest energy in HCl, as evident from Fig. 2b, c, respectively. No conclusive trend appears in Fig. 2a for HH due to the imposed axes range, but numerical comparison shows that the Ogilvie curve is lower than the SPF curve by 0.02–2.37% within $r/R = 1.5$ and $r/R = 2.5$—again showing that the Ogilvie is non-central compared to the other two curves. Similarly the opposing definitions of Dunham and SPF, as shown in Eqs. 3 and 4, do not indicate either of these as the upper or lower estimate in a consistent manner. For example, the Dunham curves take the highest energy in HH and HGa systems but the lowest in HCl and HI in comparison to the other two potential function curves. The SPF curves appear to be clearly "central" among the three potential functions in HGa and HCl, but exhibits the highest

Table 5 Calculated Dunham and SPF coefficients based on Ogilvie coefficients for HH [37], HGa [38], HCl [39] and HI [40]

Diatoms	i	α_i	β_i	γ_i
HH	0	$7970836.8\,\text{m}^{-1}$	$7970836.8\,\text{m}^{-1}$	$7970836.8\,\text{m}^{-1}$
	1	-1.604167	0.395833	-0.604167
	2	1.8665505	0.0540495	0.2103
	3	-1.9712605	-0.1300605	-0.14441
	4	1.9672438	-0.2652238	0.01276
	5	-1.9998741	-0.4968141	-0.1404
	6	2.3533746	-0.6859821	0.1973
	7	-3.2403618	-0.6222718	-0.0524
	8	4.5621963	-0.3348763	-0.0737
HGa	0	$10463044\,\text{m}^{-1}$	$10463044\,\text{m}^{-1}$	$10463044\,\text{m}^{-1}$
	1	-2.3475121	-0.3475121	-1.3475121
	2	3.8098742	-0.2326622	1.038606
	3	-5.1208192	0.0336048	-0.522339
	4	5.9445847	-0.0358907	0.045332
	5	-6.2605049	-0.4204829	-0.11843
	6	6.4596116	-0.7084743	0.25625
	7	-6.9723642	-0.5275952	-0.0462
	8	6.3166787	-1.4575465	-1.632
HCl	0	$21113930\,\text{m}^{-1}$	$21113930\,\text{m}^{-1}$	$21113930\,\text{m}^{-1}$
	1	-2.3633725	-0.3633725	-1.3633725
	2	3.66057575	-0.4295418	0.865517
	3	-4.7492108	-0.2871428	-0.473118
	4	5.45289713	-0.3211241	0.089594
	5	-5.5159807	-0.2758317	0.156448
	6	4.28399839	-0.5500745	-0.6061
	7	-1.7261935	-2.166368	-0.37505
	8	-0.0267283	-4.6094716	1.2601
HI	0	$20469900\,\text{m}^{-1}$	$20469900\,\text{m}^{-1}$	$20469900\,\text{m}^{-1}$
	1	-2.547358	-0.547358	-1.547358
	2	4.056433	-0.585641	0.985396
	3	-5.372729	-0.431145	-0.5809
	4	6.1255375	-0.6473575	-0.0369
	5	-6.6153131	-1.5347331	-0.446
	6	10.269095	0.0333126	3.08
	7	-20.30905	7.3882364	-0.12
	8	-5.8966108	-21.787587	-42.6

energy in HI diatom. Hence the difference in the Dunham, SPF and Ogilvie potentials, as denoted in Eqs. 3–5, does not translate into any consistent trend in the estimated energy comparison.
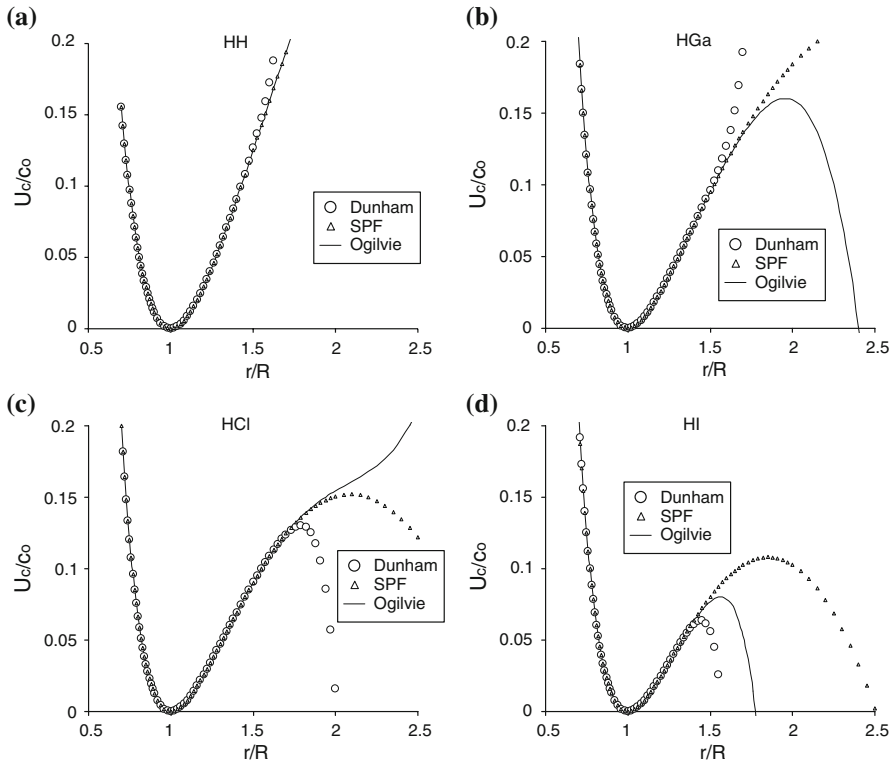
Fig. 2 Potential energy curves for (**a**) HH, (**b**) HGa, (**c**) HCl and (**d**) HI, according to Dunham and SPF potential functions based on Ogilvie coefficients [37–40]

4 Conclusions

The conversion of parameters from one potential to another is useful if the type of potential function adopted in purchased software is not the function preferred by the user. It has been shown herein that the polynomial potential functions of Dunham, SPF and Ogilvie for diatomic molecules can be related not only through the definition of ξ, but also by relationships among coefficients of these functions for attaining equivalent energy behavior near the ground state. The connections obtained among the potential energy functions further reveal a cyclic-like relation, which resembles portion of the Pascal Triangle. An illustration shown for the case of Dunham and SPF functions plotted based upon Ogilvie coefficients for HX (X = H, Ga, Cl, I) reveal very good agreement for $r/R \leq 1.5$. In addition to providing the coefficient interrelatedness and for enabling the potential functions to be conveniently converted from one form into another, the related potential functions pave a way for observations to be made on the normalized potential functions. The observations made herein suggest that although the Ogilvie function is central to the other potentials by definition, i.e., $\xi_\alpha > \xi_\gamma > \xi_\beta$ for $r > R$, the plots of normalized functions do not show any consistent trend in the energy estimates.

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