The Pascal Triangle connection between Dunham and Simons-Parr-Finlan diatomic potential energy functions

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Abstract

The polynomial forms of the Dunham and Simons-Parr-Finlan (SPF) interatomic potential energy functions are commonly used for quantifying the bond-stretching and bond compression potential energy. Due to the limitations of the Dunham and SPF potential functions for $r > 2R$ and $r < 0.5R$ respectively, where $r =$ internuclear distance and $R =$ equilibrium bond length, two sets of converting functions are proposed. Each set of converting function enables the coefficients of one potential function to be converted to those of the other potential function so that when the limitations of one potential function is encountered, one may continue the theoretical model using the other potential function. The converting functions were obtained by imposing Maclaurin series expansion on both potential functions, followed by comparison of terms. It is herein shown that the converting functions take on the form of binomial coefficients – thereby allowing the converting functions to be schematically represented using the Pascal Triangle. The use of Pascal Triangle is convenient and is therefore advantageous especially for generating the converting functions up to very high orders. Illustrations on the conversion of Dunham to SPF coefficients and vice versa reveal good agreement.

1. Introduction

In spite of its long and illustrious history, the binomial coefficients have continued to be applicable even outside the realms of mathematics. For example, the application of binomial coefficients can be found within the context of physics [1-14] and chemistry [13-21]. In this paper, we apply the Maclaurin series expansion on the interatomic potential energy functions of Dunham [22] and Simons-Parr-Finlan (SPF) [23] such that both potentials can be related through binomial coefficients. Although Ogilvie [24] proposed a "central" potential of these two potential functions to address the former's deficiencies, the latter nevertheless encounters some limitations. Hence a relationship is developed herein that converts the Dunham coefficients into those of SPF upon encountering realms that are not suited for the Dunham function, and vice versa.

2. Analysis

In spite of its ease of execution, the harmonic potential energy function

$$U_H = \frac{1}{2}k_H(r-R)^2 \tag{1}$$

where k_H = force constant, r = internuclear distance and R = equilibrium bond length, gives an unrealistically symmetric energy distribution about $r = R$. The Dunham potential function [22]

$$U_a = a_0\xi_a^{2}\left(1 + \sum_{i=1} a_i\xi_a^{i}\right) \quad ; \quad i = 1,2,3,\cdots \tag{2}$$

where

$$\xi_a = \frac{r-R}{R} \tag{3}$$

allows better fit through its power series. It can be easily seen that the Dunham function reduces to the harmonic function when $a_i = 0$; $i = 1,2,3,\cdots$. However, the Dunham function does not converge for $r > 2R$. As a result of this deficiency, Simons et al. [23] proposed an alternative potential function (SPF)

$$U_b = b_0 \xi_b{}^2 \left(1 + \sum_{i=1} b_i \xi_b{}^i \right) \quad ; \quad i = 1,2,3,\cdots \tag{4}$$

where

$$\xi_b = \frac{r - R}{r}. \tag{5}$$

It can be seen that when $b_i = 0$; $i = 1,2,3,\cdots$ the SPF potential function reduces to the Kratzer [25] potential function

$$U_{Kra} = D\left(\frac{r - R}{r}\right)^2 \tag{6}$$

where D is the dissociation energy. Although the SPF potential function overcomes the deficiency encountered by the Dunham potential function, the former does not converge for $r < 0.5R$. Arising from these shortcomings, Ogilvie [24] proposed a function

$$U_c = c_0 \xi_c{}^2 \left(1 + \sum_{i=1} c_i \xi_c{}^i \right) \quad ; \quad i = 1,2,3,\cdots, \tag{7}$$

which is "central" to the earlier two potential functions whereby

$$\frac{1}{\xi_c} = \frac{1}{2}\left(\frac{1}{\xi_a} + \frac{1}{\xi_b}\right). \tag{8}$$

This function, however, does not converge for $r < 0.3333$ and $r > 3$. Figure 1 shows a schematic for the convergence range of ξ with reference to r/R.
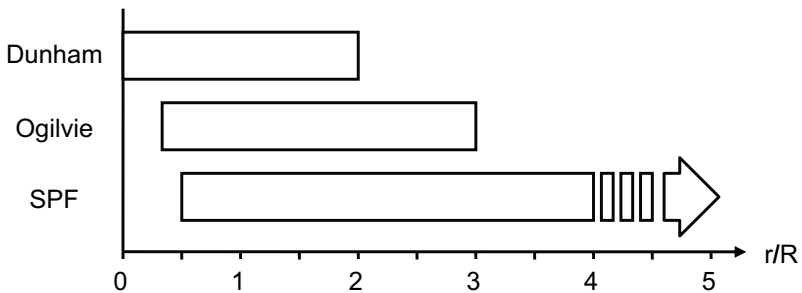

Fig. 1. Convergence range of the parameter ξ for all three potential functions.

It is clear that either the Dunham or the SPF potential function would be sufficient for all values of r so long as there exists a set of functions that convert Dunham coefficients into those of SPF and vice versa. Introducing the change in bond length as

$$\delta r = r - R,\tag{9}$$

then the Dunham and SPF parameters raised to any positive integer powers can be written as

$$(\xi_a)^n = \left(\frac{\delta r}{R}\right)^n\tag{10}$$

and

$$(\xi_b)^n = \sum_{n=1}\left[\sum_{m=1}(-1)^{m+1}\binom{m+n-2}{n-1}\left(\frac{\delta r}{R}\right)^{m+n-1}\right]\tag{11}$$

respectively, where m and n are positive integers. Substituting Eqs.(10) and (11) into Eqs.(2) and (4) respectively, we arrive at

$$\frac{U_a}{a_0} = \left(\frac{\delta r}{R}\right)^2 + \sum_{j=3}a_{j-2}\left(\frac{\delta r}{R}\right)^j\tag{12}$$

and

$$\frac{U_b}{b_0} = \left(\frac{\delta r}{R}\right)^2 + \sum_{j=3}\left[(-1)^j(j-1) + \sum_{i=1}^{j-2}(-1)^{i+j}\binom{j-1}{i+1}b_i\right]\left(\frac{\delta r}{R}\right)^j.\tag{13}$$

Comparing the LHS of Eqs.(12) and (13) gives

$$a_0 = b_0\tag{14}$$

while comparison of terms on the RHS of these equations leads to

$$a_j = (-1)^j(j+1) + \sum_{i=1}^{j}(-1)^{i+j}\binom{j+1}{i+1}b_i,\tag{15}$$

which converts SPF coefficients onto those of Dunham potential function. Equation (15) can be solved to express the SPF coefficients in terms of Dunham coefficients as

$$b_j = (j+1) + \sum_{i=1}^{j}\binom{j+1}{i+1}a_i.\tag{16}$$

The appearance of binomial coefficients in the conversion function established in Eqs.(15) and (16) implies that they can be conveniently generated by reference to the

Pascal Triangle, as shown in Fig. 2. The trapezium encloses all the coefficients described in Eqs.(15) and (16), while the triangle encompasses only the coefficients that are multiplied with b_j or a_j for obtaining a_j and b_j respectively. The bold numbers refer to those that are negative when computing a_j from b_j, as described in Eq.(15).
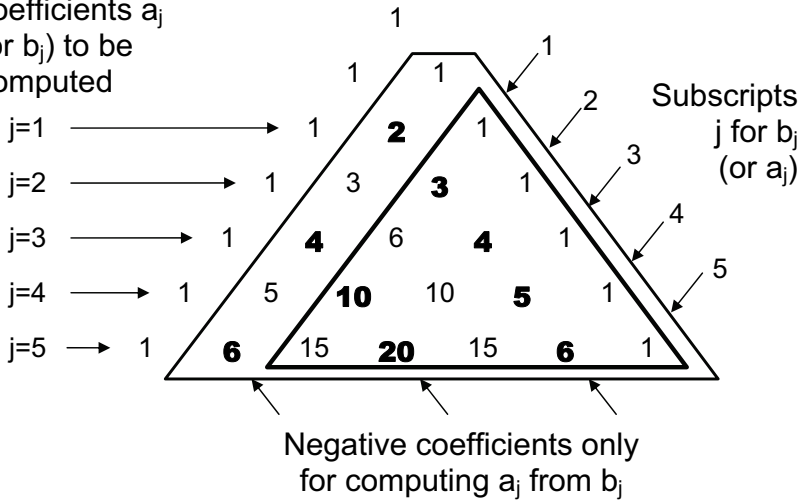

Fig. 2. The Pascal Triangle that can be used for convenient extraction of Eqs.(15) and (16), shown here up to $j = 5$.

3. Results and Discussion

For the purposes of illustration, we select a set of Dunham coefficients for conversion into SPF coefficients and vice versa for another set. In Table 1 the Dunham coefficients, a_j, refer to those of LiH diatomic molecules [26]. Based on Eq.(16) or Fig.2, the equivalent SPF coefficients are

$$b_1 = 2 + a_1 \tag{17a}$$

$$b_2 = 3 + 3a_1 + a_2 \tag{17b}$$

$$b_3 = 4 + 6a_1 + 4a_2 + a_3 \qquad (17c)$$

$$b_4 = 5 + 10a_1 + 10a_2 + 5a_3 + a_4 \qquad (17d)$$

up to $j = 4$.

Table 1. Extraction of SPF coefficients (b_j) from Dunham coefficients (a_j) for LiH [26].

j	a_j	b_j
0	$153796\,cm^{-1}$	$153796\,cm^{-1}$
1	-2.70062	-0.70062
2	5.101	-0.00086
3	-7.86	0.34028
4	10.03	-0.2662

Substituting the values of a_j from Table 1 into Eq.(17), the calculated SPF coefficients b_j are listed on the right-most column of Table 1. The SPF coefficients b_j in Table 2 are taken from GeS diatoms [27]. Using Eq.(15), the Dunham coefficients can be calculated as

$$a_1 = -2 + b_1 \qquad (18a)$$

$$a_2 = 3 - 3b_1 + b_2 \qquad (18b)$$

$$a_3 = -4 + 6b_1 - 4b_2 + b_3 \qquad (18c)$$

$$a_4 = 5 - 10b_1 + 10b_2 - 5b_3 + b_4 \qquad (18d)$$

up to $j = 4$. Alternatively, Eq.(18) can be obtained by referring to the Pascal Triangle in Fig.2, with the bolded numbers assigned negative values. Upon substituting the values of b_j in Table 2 into Eq.(18), the Dunham coefficients were computed and furnished in the middle column of Table 2.

Table 2. Extraction of Dunham coefficients (a_j)from SPF coefficients (b_j) for GeS [27].

j	a_j	b_j
0	$441896.64\,cm^{-1}$	$441896.64\,cm^{-1}$
1	-3.059895	-1.059895
2	5.777875	-0.40181
3	-8.50683	0.2453
4	10.03735	-0.317

Plots of dimensionless interatomic energy, $U_x / x_0 \; ; (x = a, b)$, versus the non-dimensionalized bond length, r / R, are shown in Figs.3 and 4 for LiH and GeS diatomic molecules respectively.
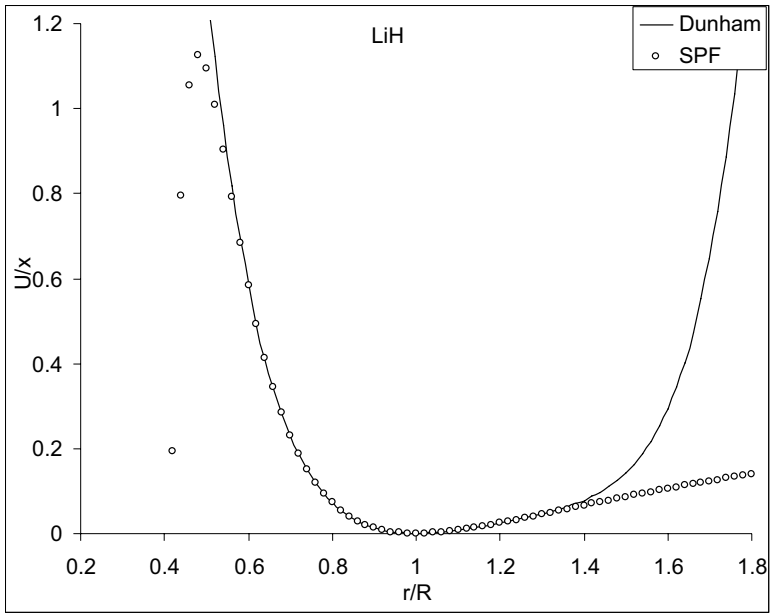

Fig. 3. Plot of SPF potential energy curve based on the Dunham coefficients for LiH [26].

The good agreement between the Dunham and SPF potential energy curves in both diatomic molecules for $r < 1.4R$ illustrates the validity of the developed converting functions. Needless to say, the extent of correlation can be extended to longer bond length if more terms are taken into consideration.
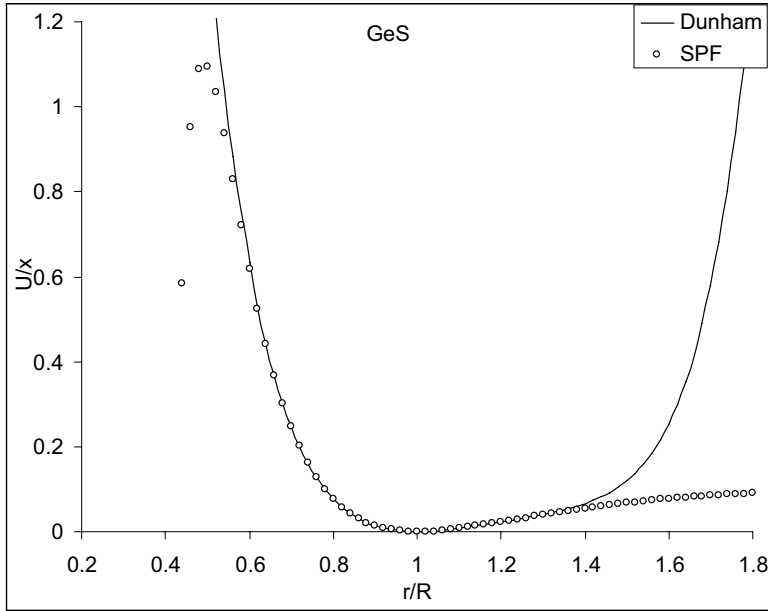

Fig. 4. Plot of Dunham potential energy curve based on the SPF coefficients for GeS [27].

4. Conclusions

Two sets of converting functions have been developed herein to relate the coefficients of the Dunham and the SPF potential energy functions. Instead of proposing new potential functions or refining these two potential functions for overcoming their limitations, two sets of converting functions were developed so that when one of the potential functions falls into the range of non-convergence, its coefficients can be converted into those of the other potential function for continued computation. The

validity of the converting functions has been illustrated through two examples. It is worth noting that the converting functions rely heavily on binomial coefficients, thereby enabling these converting functions to be easily generated up to very high orders by mere reference to the Pascal Triangle. On the other hand, the binomial coefficient form is useful for computing purposes. In view of the very good agreement at $r = R$, it is herein suggested that future computation of potential energy curve using either of these two potential functions to incorporate the developed converting function. This will allow the Dunham potential function to be automatically converted into SPF function for $r > 2R$, and the SPF function to be automatically converted to Dunham potential function for $r < 0.5R$.

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