Extraction of Dunham Coefficients from Murrell-Sorbie Parameters

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Z. Naturforsch. **63a,** 1 – 6 (2008); received May 21, 2007

A set of relationships between parameters of the Dunham and Murrell-Sorbie potential energy function is developed. By employing Taylor series expansion and comparison of terms arranged in increasing order of bond length, a set of Dunham coefficients is obtained as functions of Murrell-Sorbie parameters. The conversion functions reveal the importance of factorials in extracting Dunham coefficients from Murrell-Sorbie parameters. Plots of both functions, based on parameters of the latter, reveal good correlation near the equilibrium bond length for a group of diatomic molecules. Potential function relations, such as that shown in this paper, are useful when the preferred/reliable data is based on a potential function different from that adopted in available computational software.

Key words: Dunham Coefficients; Extended-Rydberg; Murrell-Sorbie Parameters; Potential Functions.
PACS numbers: 02.30.Lt, 02.30.Mv, 33.15.Dj, 33.15.Fm, 34.20.Cf

1. Introduction

It is common knowledge that interatomic and intermolecular potential energy functions are essential to aid the understanding of physical properties of molecules (e. g. [1 – 4]). The fact that the number and types of potential energy functions are numerous calls for efforts to understand and appreciate the discrepancies among them. Indeed an understanding of the potential energy function discrepancy is helpful for molecular physicists to interpret discrepancies in simulated molecular behaviour, and to select specific potential energy functions based on intended applications. There are two broad categories of molecular potential function relationships.

In the first type a generic potential function has one or two additional parameters, which reduce the generic function into specific ones when a numerical value is assigned to the additional parameter(s). For example, Thakkar's parameter p [5] in

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

reduces the potential function

$$U = A\xi\left(1+\sum_{i=1}\alpha_i\xi^{i}\right) \tag{2}$$

into the Dunham [6] or the Simons-Parr-Finlan (SPF) [7] potential functions by substituting $p=-1$ and $p=+1$, respectively. Here, r and R are the internuclear distance and the equilibrium bond length, respectively. In order to incorporate the Ogilvie potential function [8], Molski proposed an alternative parameter a [9, 10] in

$$\xi = \frac{r-R}{ar+(1-a)R}, \tag{3}$$

such that substituting $a = 0, 0.5, 1$ into (3) reduces (2) to the Dunham, Ogilvie and SPF potential functions, respectively. In order to connect potential energy functions consisting of repulsive and attractive terms that exhibit a minimum with a well depth $U_{r=R} = -D$ and $U_{r\to\infty} = 0$, Lim [11] proposed

$$\frac{U}{D} = \frac{n^x S_2^{1-x}}{m^y S_1^{1-y} - n^x S_2^{1-x}}\left(\frac{R}{r}\right)^{my}\exp\left[S_1\left(1-\frac{r}{R}\right)(1-y)\right] - \frac{m^y S_1^{1-y}}{m^y S_1^{1-y} - n^x S_2^{1-x}}\left(\frac{R}{r}\right)^{nx}\exp\left[S_2\left(1-\frac{r}{R}\right)(1-x)\right], \tag{4}$$

where m and n are the repulsive and attractive indices, respectively, and S_1 and S_2 refer to the scaling factors corresponding to the repulsive and attractive terms, respectively. Substituting $(x,y) = (1,1)$, $(0,0)$, $(1,0)$ and $(0,1)$ into (4) reduces it to generalized Lennard-Jones [12 – 14], Morse [15], Buckingham [16, 17] and Linnett [18, 19] potential energy functions, respectively.

0932–0784 / 08 / 0100–0001 $ 06.00

In the second type of molecular potential function relationship the parameters of one potential function is expressed in terms of parameters of another potential function (e. g. [20–22]). Whilst the first category of potential function relationship is useful for gaining insight in the difference between the considered potential functions, the second type allows to convert parameters from literature into another set of parameters, whose potential function is adopted in computational software. In this paper we extract the Dunham coefficients from the Murrell-Sorbie parameters within the context of the second category of potential function relations.

2. Analysis

To pave a way for obtaining a set of relations between parameters of the Dunham (DUN) and Murrell-Sorbie (MS) potential function, we rewrite the former's potential function as

$$U_{\text{DUN}} = A\left(\frac{\rho}{R}\right)^2\left(1+\sum_{i=1}^{\infty}\alpha_i\left(\frac{\rho}{R}\right)^2\right), \tag{5}$$

where $\rho = r - R$, while the Murrell-Sorbie potential function [23]

$$U_{\text{MS}} = -D\left(1+\sum_{n=1}^{3}a_n\rho^n\right)\exp(-a_1\rho) \tag{6}$$

is written in a shifted form:

$$U_{\text{SMS}} = U_{\text{MS}} + D. \tag{7}$$

This shift is crucial, because

$$(U_{\text{DUN}})_{r=R} = 0 \tag{8}$$

and

$$(U_{\text{MS}})_{r=R} = -D. \tag{9}$$

For the sake of completeness, (7) can be expressed as

$$U_{\text{SMS}} = D\left(\exp(+a_1\rho)-\sum_{n=1}^{\infty}a_n\rho^n\right)\exp(-a_1\rho), \tag{10}$$

so that the power series is not limited to the third order. Substituting

$$\exp(+a_1\rho) = \sum_{n=0}^{\infty}\frac{(a_1\rho)^n}{n!} \tag{11}$$

into (10), we arrive at

$$U_{\text{SMS}} = D\left[\sum_{n=2}^{\infty}\left(\frac{a_1^n}{n!}-a_n\right)\rho^n\right]\exp(-a_1\rho). \tag{12}$$

Substituting

$$\exp(-a_1\rho) = \sum_{n=0}^{\infty}(-1)^n\frac{(a_1\rho)^n}{n!} \tag{13}$$

into (12) and rearranging terms according to increasing orders of ρ, we have

$$U_{\text{SMS}} = D\sum_{i=0}^{\infty}\sum_{j=0}^{i}\frac{(-1)^j a_1^j}{j!}\left(\frac{a_1^{i-j+2}}{(i-j+2)!}-a_{i-j+2}\right)\rho^{i-j+2}. \tag{14}$$

Suppose (5) and (14) are expressed as

$$\frac{U_{\text{DUN}}}{\left(\frac{A}{R^2}\right)} = \rho^2 + \sum_{i=1}^{\infty}\frac{\alpha_1}{R^i}\rho^{i+2} \tag{15}$$

and

$$\frac{U_{\text{SMS}}}{D\left(\frac{a_1^2}{2}-a_2\right)} = \rho^2 + \frac{\sum_{i=0}^{\infty}\sum_{j=0}^{i}\frac{(-1)^j a_1^j}{j!}\left(\frac{a_1^{i-j+2}}{(i-j+2)!}-a_{i-j+2}\right)\rho^{i-j+2}}{\left(\frac{a_1^2}{2}-a_2\right)}, \tag{16}$$

then comparison of the left-hand sides and right-hand sides of (15) and (16) gives

$$A = \left(\frac{a_1^2}{2}-a_2\right)DR^2 \tag{17}$$

and

$$a_i = R^i\left(\frac{a_1^2}{2}-a_2\right)^{-1} \cdot \sum_{j=0}^{i}\frac{(-1)^j a_1^j}{j!}\left(\frac{a_1^{i-j+2}}{(i-j+2)!}-a_{i-j+2}\right), \tag{18}$$

respectively. Equation (18) can be split into two summation parts:

$$a_i = R^i\left(\frac{a_1^2}{2}-a_2\right)^{-1} \cdot \left[a_1^{i+2}\sum_{j=0}^{i}\frac{(-1)^j}{j!(i-j+2)!}-\sum_{j=0}^{i}\frac{(-1)^j a_1^j a_{i-j+2}}{j!}\right], \tag{19}$$

to make way for simplification. The first summation part can be simplified as

$$\sum_{j=0}^{i} \frac{(-1)^j}{j!(i-j+2)!} = \frac{(-1)^i}{(i+1)!+i!}. \tag{20}$$

For the case of the Murrell-Sorbie potential function whereby parameters of the fourth order and above are zero, i. e. $\alpha_k = 0$ for $k = 4, 5, 6, \ldots$, the second summative part reduces to

$$\sum_{j=0}^{i} \frac{(-1)^j a_1^j a_{i-j+2}}{j!} = (-1)^i \left(\frac{a_1^i a_2}{i!} - \frac{a_1^{i-1} a_3}{(i-1)!} \right). \tag{21}$$

Finally, substituting (20) and (21) into (19) gives

$$\alpha_i = (-R)^i \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \cdot \left(\frac{a_1^{i+2}}{(i+1)!+i!} - \frac{a_1^i a_2}{i!} + \frac{a_1^{i-1} a_3}{(i-1)!} \right). \tag{22}$$

For convenience, the first eight Dunham coefficients are furnished:

$$\alpha_1 = -R^1 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \left(\frac{a_1^3}{3} - \frac{a_1 a_2}{1} + \frac{a_3}{1} \right), \tag{23a}$$

$$\alpha_2 = +R^2 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \left(\frac{a_1^4}{8} - \frac{a_1^2 a_2}{2} + \frac{a_1 a_3}{1} \right), \tag{23b}$$

$$\alpha_3 = -R^3 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \left(\frac{a_1^5}{30} - \frac{a_1^3 a_2}{6} + \frac{a_1^2 a_3}{2} \right), \tag{23c}$$

$$\alpha_4 = +R^4 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \left(\frac{a_1^6}{144} - \frac{a_1^4 a_2}{24} + \frac{a_1^3 a_3}{6} \right), \tag{23d}$$

$$\alpha_5 = -R^5 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \left(\frac{a_1^7}{840} - \frac{a_1^5 a_2}{120} + \frac{a_1^4 a_3}{24} \right), \tag{23e}$$

$$\alpha_6 = +R^6 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \left(\frac{a_1^8}{5760} - \frac{a_1^6 a_2}{720} + \frac{a_1^5 a_3}{120} \right), \tag{23f}$$

$$\alpha_7 = -R^7 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \cdot \left(\frac{a_1^9}{45360} - \frac{a_1^7 a_2}{5040} + \frac{a_1^6 a_3}{720} \right), \tag{23g}$$

$$\alpha_8 = +R^8 \left(\frac{a_1^2}{2} - a_2 \right)^{-1} \cdot \left(\frac{a_1^{10}}{403200} - \frac{a_1^8 a_2}{40320} + \frac{a_1^7 a_3}{5040} \right). \tag{23h}$$

Table 1. Murrell-Sorbie parameters for similar-atom diatomic molecules [24].

Diatomic molecule	D (eV)	R (Å)	a_1 (Å)$^{-1}$	a_2 (Å)$^{-2}$	a_3 (Å)$^{-3}$
AlAl	1.572	2.466	2.634	1.536	0.038
BB	3.085	1.589	3.581	2.787	0.752
CC	6.325	1.243	5.026	6.63	3.787
ClCl	2.514	1.9879	4.478	6.022	3.749
FF	1.658	1.4119	6.538	12.521	11.717
HH	4.747	0.7414	3.961	4.064	3.574
LiLi	1.068	2.6729	1.919	1.077	0.232
MgMg	0.053	3.8905	2.043	1.005	0.526
NaNa	0.73	3.0789	2.067	1.384	0.365
NN	9.905	1.0977	5.396	7.328	4.988
OO	5.213	1.2075	6.08	11.477	11.003
PP	5.081	1.8934	3.92	4.266	2.246
SiSi	3.242	2.246	2.957	2.3	0.962
SS	4.414	1.8892	3.954	4.312	2.332

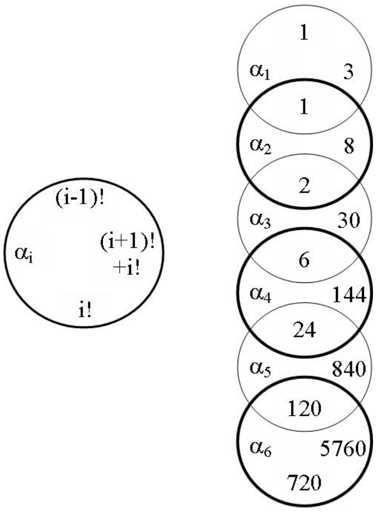

Fig. 1. Schematics for extracting the Dunham coefficients whereby the thin and thick circles represent positive and negative multiplier, whilst the first, second and third denominators are shown by the numbers on the right, bottom and top of each circle.

Figure 1 shows the schematics of obtaining α_1 whereby the alternating thick and thin circles represent negative and positive multipliers, with the numbers referring to the denominators.

3. Results and Discussion

Verification of (17) and (22) was achieved by comparing plots of the shifted Murrell-Sorbie and Dunham potential functions based on the former parameters. Table 1 shows the Murrell-Sorbie parameters (D, R, a_1, a_2, a_3) for similar atom diatomic molecules furnished by Huxley and Murrell [24], i. e. AlAl, BB,

Table 2. Dunham coefficients calculated from Murrell-Sorbie parameters shown in Table 1.

Diatomic molecule	A	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8
AlAl	18.47845	−2.65829	−14.2819	2.484101	−12.354	23.564	−31.4168	33.25499	−29.5483
BB	28.2348	−2.66478	−8.7008	−3.45379	2.292674	−1.30182	0.98755	−1.13995	1.318527
CC	58.63791	−2.64841	−17.6852	−4.62283	6.283525	−9.86041	14.42819	−17.8218	18.45187
ClCl	39.7809	−3.33323	−53.0012	−14.6835	43.70612	−119.664	260.2306	−453.556	654.7353
FF	29.25635	−3.67043	−51.8454	−20.8013	60.55773	−160.666	347.0645	−611.107	899.7176
HH	9.865147	−1.60641	−2.73843	−1.98818	1.770578	−1.29447	0.780169	−0.39496	0.171399
LiLi	5.831623	−1.82155	−17.0669	−0.65335	0.767772	−2.07352	3.597345	−4.32744	4.018142
MgMg	0.867928	−4.72925	−13.1851	−46.5787	110.7441	−214.672	343.5902	−463.456	537.5395
NaNa	5.205627	−1.83371	−36.2541	−0.01434	3.127336	−12.6378	25.70686	−36.4469	40.44843
NN	86.2948	−2.70501	−13.4118	−6.07649	8.670542	−12.2136	15.41233	−16.6914	15.48108
OO	53.25306	−2.78193	−38.823	−12.6645	33.2217	−72.3611	124.225	−172.488	200.0878
PP	62.24498	−3.10398	−28.5699	−10.4925	21.71695	−43.6123	74.23541	−104.615	123.9424
SiSi	33.88492	−3.01294	−18.77	−10.0092	17.94398	−29.9226	42.85413	−51.7868	53.33091
SS	55.21835	−3.17365	−28.1452	−11.5781	24.16255	−48.1276	81.30082	−114.134	135.1123

CC, ClCl, FF, HH, LiLi, MgMg, NaNa, NN, OO, PP, SiSi and SS.

The Dunham coefficients (A, R, α_i, with $i = 1, 2, \ldots, 8$) were calculated using (17) and (23) to give A and α_i, respectively, and are furnished in Table 2. The equilibrium bond length, R, is common for both potential functions. Based on the parameters shown in Tables 1 and 2, potential energy curves, U, in electron volts unit, were plotted against the normalized bond length, r/R, using

$$U_{\mathrm{SMS}} = D - D\left[\sum_{i=0}^{3} a_i R^i \left(\frac{r}{R} - 1\right)^i\right] \exp\left[a_1 R\left(1 - \frac{r}{R}\right)\right] \tag{24}$$

and

$$U_{\mathrm{DUN}} = A\sum_{i=0}^{8} \alpha_i \left(\frac{r}{R} - 1\right)^{i+2} \tag{25}$$

for representing the shifted Murrell-Sorbie and Dunham coefficients, respectively, with $a_0 = \alpha_0 = 1$. The potential energy curves are shown in Fig. 2 with the continuous lines and discrete points referring to the shifted Murrell-Sorbie and Dunham potential function plots, respectively. All the energy curves were furnished within the common energy range of $0.0 < U < 0.2$ eV and the common normalized bond length range of $0.9 < r/R < 1.1$ to allow comparison across all the diatomic molecules considered. These ranges were selected to allow good viewing of all 14 diatomic molecules plotted. It can be seen that, based on the selected diatomic molecules, the Dunham function converted from Murrell-Sorbie parameters appears to underestimate the Murrell-Sorbie function as the normalized bond lengths are compressed or stretched away from the ground state. At and near the equilibrium bond length, however, the conversion functions up to α_8 provide good agreement between both potential functions, as is evident from Figure 2. Needless to say, the extent of correlation is expected to increase when more coefficients are generated from (22) to attain higher-order terms. Reversed conversion can also be performed. Excluding the equilibrium bond length, R, there are four parameters in the Murrell-Sorbie potential function. Hence four independent equations are required to obtain the parameters D, a_1, a_2 and a_3 from A, α_1, α_2 and α_3 in (17) and (23a)–(23c).

4. Conclusions

A set of conversion functions has been established between the parameters of the Murrell-Sorbie and Dunham potential energy functions by expanding both functions by Taylor series expansion, followed by comparison of terms. Analysis revealed that the coefficients are expressed in terms of Murrell-Sorbie parameters and factorials in the numerator and denominator, respectively. Observation of the plotted potential energy curve based on Murrell-Sorbie parameters of AlAl, BB, CC, ClCl, FF, HH, LiLi, MgMg, NaNa, NN, OO, PP, SiSi and SS for both potential functions revealed good agreement, especially near the equilibrium bond length. Far away from the equilibrium state, the Dunham function gave a lower estimation of the Murrell-Sorbie function. The established conversion functions are useful when potential function parameters are available for the Murrell-Sorbie function but the computational software adopts the Dunham function, or vice versa.

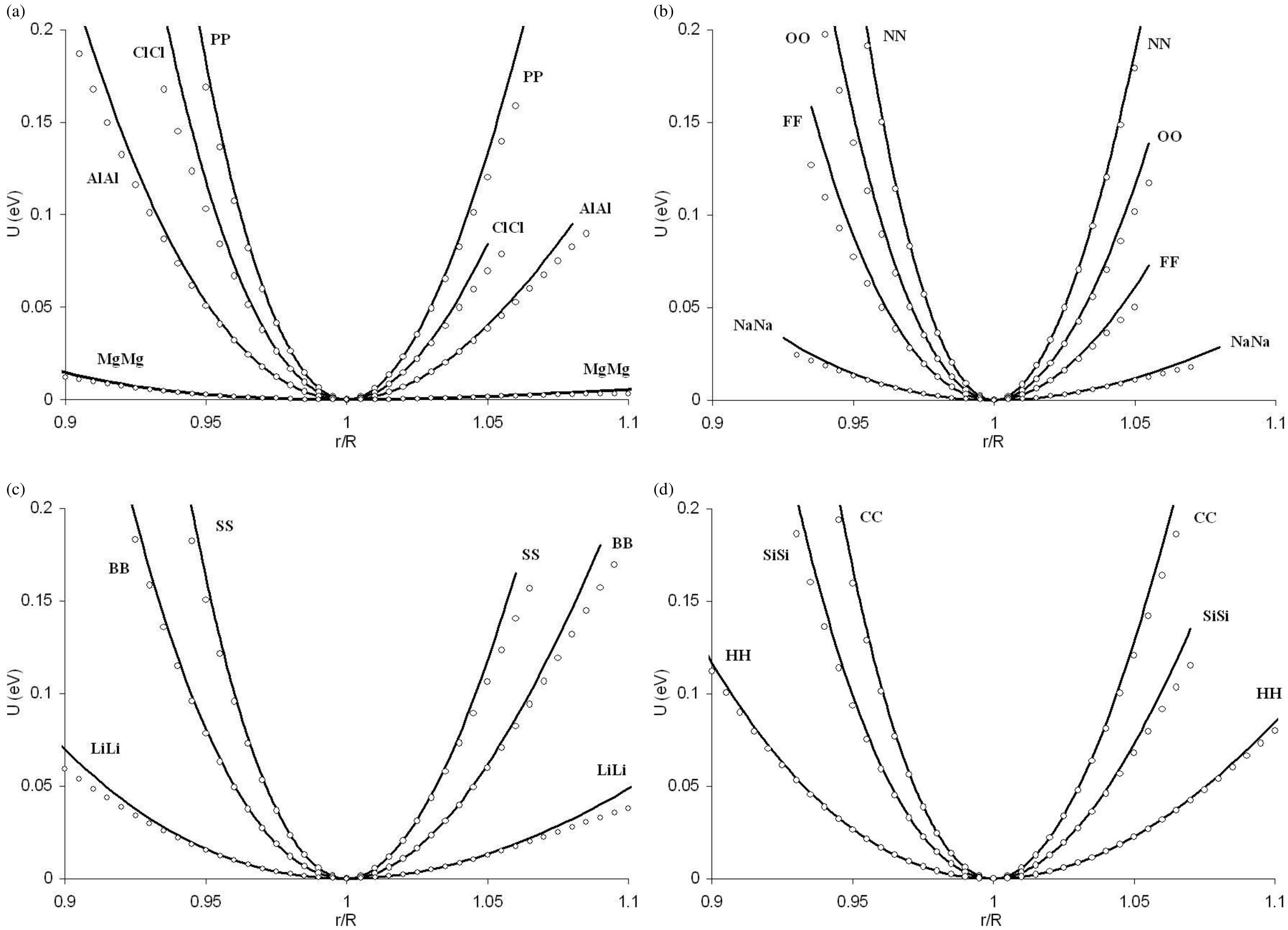

Fig. 2. Comparison of the shifted Murrell-Sorbie potential energy (continuous curves) and the extracted Dunham potential energy (discrete points).

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