Relationship and discrepancies between the Extended-Rydberg and the Generalized Buckingham potential energy functions

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Abstract: This paper relates the interatomic energy according to the Exdended-Rydberg and the Generalized Buckingham potential functions by applying a Maclaurin series expansion on the latter and thereafter comparing it with the former. In so doing, the plotted curves of these two functions not only show equal curvature at the equilibrium state, but also reveal a discrepancy for the finite distortion. It is shown that, when equated at equilibrium, the Generalized Buckingham gives a lower energy in comparison to the Extended-Rydberg at finite bond compression and stretching. However, the energy difference diminishes when the interatomic distance exceeds twice that at equilibrium. Due to such discrepancies upon comparative normalization, it would be beneficial for computational chemists to select the appropriate potential function for the purpose of conservative molecular modeling.

Keywords: Extended-Rydberg, Generalized Buckingham, interatomic energy, Maclaurin series, potential functions

INTRODUCTION

Several contemporary empirical potential energy functions of 2-body portion can be traced to pioneering classical works. For example, the 2-body portion of the Pearson–Takai–Halicioglu–Tiller,[1] the Biswas–Hamann,[2] the Murrell-Mottram[3] and the Bauer–Maysenholder–Seeger[4] potential functions were either adopted or adapted from the Lennard-Jones,[5] the Morse,[6] the Rydberg[7] and the Buckingham[8] potentials, respectively. The importance of the interatomic potential function is indeed extensive.[9] However, with the plethora of empirical interatomic potential energy functions introduced,[10] there is a need to understand how these potentials are related, the extent of their relatedness and the discrepancies when parametrically related. Based on preliminary work on potential functions used in computational

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chemistry softwares, a prototype molecular potential function converter has been shown to be technically feasible.[11,12] In regard to relationships among potential energy functions applicable in many-body condensed matter systems, most of the approaches have hitherto been based primarily on equating derivatives at the minimum well-depth and/or equating the corresponding indices of the repulsive and atractive tems.[13–23] An alternate approach would be to take advantage of series expansions – which can be useful when relating interatomic potential functions consists of polynomial series. The latter approach has been implemented for relating potentials that are commonly used in computational chemistry softwares.[24–28] In this paper, advantage of the Maclaurin series is taken to relate the Generalized Buckingham potential and the Extended-Rydberg potential *via* their parameters. These potential functions are commonly used in simulations of various lattice systems (including copper, silver, gold, silicon and carbon among others).[4, 29–32] The availability of parametric relationship across these two parameters would serve to:

(*i*) enable preferred parameters from one potential to be used in softwares which adopt another potential,

(*ii*) allow the influence of each potential function in modeling finite distortion to be known.

Whilst the first objective attempts to find the similarities, the second – and more important – objective reveals the discrepancies of the equated potentials.

ANALYSIS

The Generalized Buckingham potential:

$$U_{GB} = A \exp(-Br) - \frac{C}{r^n} \tag{1}$$

is the 2-body portion of the Bauer–Maysenholder–Seeger potential,[4] where A and C are the coefficients of the repulsive and attractive terms, respectively, whilst B and n are the repulsive and attractive indices, respectively. The interatomic distance is denoted by r. The attractive index has been stated to be usually $n = 6$,[4] which, upon substituting into Eq. (1), reduces the Generalized Buckingham into the original Buckingham potential.[8]

The Extended-Rydberg potential was given by Huxley and Murrell as:[33]

$$U_{ER} = -D \left[1 + \sum_{m=1}^{3} a_m \rho^m \right] \exp(-a_1 \rho) \tag{2}$$

where $\rho = r - R$, with R being the equilibrium interatomic distance. Although Yang *et al.*[34] added the term $a_4 \rho^4$ into the square parenthesis for their analysis of the hydrogen molecule, they appreciated the fact that satisfactory results can, in general, be obtained when $m = 3$.[35]

Let:

$$(U_{\mathrm{GB}})_{r=R} = -D \tag{3}$$

and

$$\left(\frac{\partial U_{\mathrm{GB}}}{\partial r}\right)_{r=R} = 0, \tag{4}$$

then Eq. (1) can be rewritten in an alternate form:

$$U_{\mathrm{GB}} = D\left[\frac{n}{BR-n} - \frac{BR}{BR-n}\left(1+\frac{\rho}{R}\right)^{-n} \exp(B\rho)\right]\exp(-B\rho) \tag{5}$$

in preparation for comparison with the Extended-Rydberg potential shown in Eq. (2). There is therefore a need at this point to express the terms in the square parenthesis of Eq. (5) in polynomial form. To do so, the following terms are expanded up to the third power using the Maclaurin series

$$\left(1+\frac{\rho}{R}\right)^{-n} = \frac{1}{(n-1)!}\sum_{m=0}^{3}\frac{(n+m-1)!}{m!}\left(-\frac{\rho}{R}\right)^{m} \tag{6}$$

$$\exp(B\rho) = \sum_{m=0}^{3}\frac{(B\rho)^{m}}{m!} \tag{7}$$

Hence, substituting Eqs. (6) and (7) into the square parenthesis of Eq.(5) and neglecting the terms with powers greater than 3, one obtains:

$$U_{\mathrm{GB}} = -D\left[\sum_{m=0}^{3}a_{m}\rho^{m}\right]\exp(-a_{1}\rho) \tag{8a}$$

where

$$a_{0} = 1 \tag{8b}$$

$$a_{1} = B \tag{8c}$$

$$a_{2} = \frac{B}{2R}\left((BR-n)+\frac{n}{(BR-n)}\right) \tag{8d}$$

$$a_{3} = \frac{B}{6R^{2}}\left((BR-n)^{2}+3n-\frac{2n}{(BR-n)}\right) \tag{8e}$$

Equation (8a) shows the Generalized Buckingham potential function in a form similar to the Extended-Rydberg potential function, whilst the RHS of Eqs. (8c) to (8e) give the Extended-Rydberg parameters in terms of the Generalized Buckingham parameters. Needless to say, Eq.(8b) is reflected in the square parenthesis of Eq.(2) as 1.

RESULTS AND DISCUSSION

To verify the validity of the parametric relationships between both potential functions considered herein, the non-dimensionalized potential energy (U/D) is plotted against the non-dimensionalized interatomic distance (r/R) using the common case where $n = 6$.[4,8] One select $BR = 12$ in order to coincide with other commonly used potential functions, such as the Lennard-Jones (12–6) and the Morse potentials. Hence, substituting

$$BR = 2n = 12 \qquad (9)$$

into Eq.(5) and substituting Eqs. (8b) to (8e) into Eq. (2) gives:

$$\frac{U_{GB}}{D} = \exp\left(12\left(1 - \frac{r}{R}\right)\right) - 2\left(\frac{R}{r}\right)^6 \qquad (10)$$

and

$$\frac{U_{ER}}{D} = -\left[1 + 12\left(\frac{r}{R} - 1\right) + 42\left(\frac{r}{R} - 1\right)^2 + 140\left(\frac{r}{R} - 1\right)^3\right]\exp\left(12\left(1 - \frac{r}{R}\right)\right) \quad (11)$$

which enable the ready computation of (U/D) *versus* (r/R), as shown in Fig. 1. Although Fig. 1 shows that the Generalized Buckingham potential function gives lower energies compared with the Extended-Rydberg potential function for finite changes in the interatomic distance, the discrepancy is minor for bond stretching. The parametric relations developed herein exhibit excellent agreement near the equilibrium, ($0.9 \leq (r/R) \leq 1.2$), and at large separations, ($r/R \geq 2$).
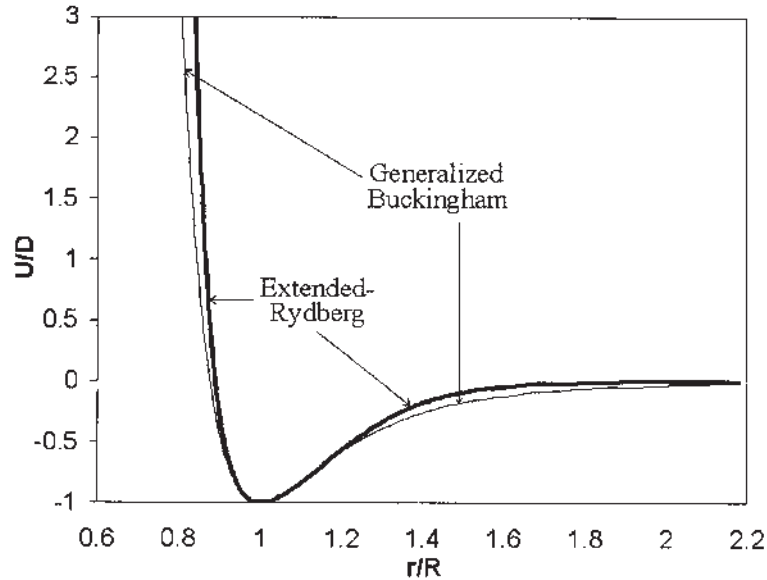

Fig. 1. Comparison between the Extended-Rydberg and the Generalized Buckingham potentials after equating their parameters using Maclaurin series expansions.

In should be pointed here that a "hard" or ("soft") bond is independent from a "strong" (or "weak") bond, in that the former is exhibited by the shape of the potential energy curve whilst the latter is a measure of the magnitude of the minimum well-depths D. The more abrupt change in (U/D) with respect to (r/R) for the Extended-Rydberg potential suggests its suitability in modeling hard bonds. Conversely the more gradual rise in (U/D) with respect to (r/R) for the Generalized Buckingham potential suggests its suitability in modeling soft bonds. In addition, the plotted discrepancies do not exclude the cases whereby (a) the Extended-Rydberg potential overstimates and/or (b) the Generalized Buckingham potential understimates the bond "hardness".

CONCLUSIONS

The relationship between the parameters of the Extended-Rydberg and the Generalized Buckingham interatomic potential energy functions were developed in this study by utilizing Maclaurin series expansion on the latter and rearranging for comparison of the terms with the former. The plotted results reveal very good correlation between the two potentials upon relating their parameters. The illustration demonstrates the comparative discrepancies, which will enable practitioners of molecular modeling to select the appropriate potential function for their computational objectives.

И З В О Д

РЕЛАЦИЈА И РАЗЛИКЕ ИЗМЕЂУ EXTENDED-RYDBERG И GENERALIZED BUCKINGHAM ФУНКЦИЈЕ ПОТЕНЦИЈАЛНЕ ЕНЕРГИЈЕ

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Рад повезује међуатомску енергију са Проширеном Ридберговом (Extended-Rydberg) и Генерализованом Бекингамовом (Generalized Buckingham) функцијом потенцијалне енергије применом развијеног Маклореновог (Maclaurin) реда на другу и упоређује са првом. Графици ове две функције показују једнаку закривљеност у равнотежном стању, али и разлику у крајњим областима кривих. Показано је да иако су у равнотежи исте, Генерализована Бекингамова функција даје мању вредност енергије него Проширена Ридбергова за сабијање и истезање веза. Међутим, разлика вредности енергија се смањује када се међуатомско растојање удвостручи у односу на равнотежно. Због такве разлике при компаративној нормализацији, упутно у рачунарској хемији одабрати одговарајућу функцију код конзервативног молекуларног моделовања.

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