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Approximate Relationships Between the Generalized Morse and the Extended-Rydberg Potential Energy Functions

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Abstract

Parameters of the Generalized Morse and the Extended-Rydberg potential functions are connected herein. Due to the existence of a polynomial portion in the latter, we apply the Maclaurin series expansion to the former to allow comparison of terms that lead to the parametric relationships. Two schemes for the parametric connections were developed in order to cater to two broad categories of the Extended-Rydberg parameters on the basis of the sign of a_2. In either case, it was shown that the curvatures at the minimum well-depth are equal, thereby indicating validity of the parametric connections for small distortion. Theoretical plots also reveal that, in the case of large interatomic distortion, the Generalized Morse approximation gives slight over-estimation and under-estimation to the Extended-Rydberg potential for $a_2<0$ and $a_2>0$ respectively.

Keywords: interatomic potentials, Maclaurin series, parametric connections

Introduction

Mathematical functions have been exploited in recent years to relate interatomic potential functions, as well as to observe any discrepancies upon equating them.[1–4] A result of these works led to the development of a prototype interatomic potential function converter,[5,6] which relates various potential functions within the categories of bond-stretching, bond-bending, bond-torsion and van der Waals interaction. Although connections of potential functions have been extensively established for various combinations of pair potentials, these have been largely confined to simple potentials such as the harmonic,[7] Lennard-Jones,[8] Morse,[9] Rydberg[10] and Buckingham[11] potential functions (see ref. 12, 13). Potential functions with greater flexibility – which consist of more parameters such as the Generalized Morse potential (adopted as the 2-body portion of the Biswas-Hamann potential)[14] and the difference of two Gaussians (adopted as the 2-body portion of Kaxiras-Pandey)[15] – were also related to simple potential functions by equating derivatives of these potentials at the equilibrium bond length and by introducing scaling functions.[16–23] This paper takes advantage of the Maclaurin series[24,25] to relate the parameters of the Generalized Morse and the Extended-Rydberg potential functions. The reason for so doing is discussed with reference to the mathematical forms of these two potentials.

It should be stated herein that interatomic potential energy functions – like intramolecular and intermolecular functions – have no exact analytical expressions. Given that the results of the quantum chemical calculations and the potentials derived from experimental data are furnished in tabular form, the approximate functionals discussed in this paper are nonetheless of great practical importance. It has been appreciated that "the simple functions such as Morse, Rydberg, Born-Mayer, etc., give a qualitatively correct description of the potential and only modest extensions are needed to obtain functions which stand up to the most stringent experimental test".[26]

Analysis

The Generalized Morse potential[14]

$$U_{GM} = \sum_{i=1}^{2} A_i \exp(-\lambda_i r) \tag{1}$$

where subscripts 1 and 2 refer to the repulsive and attractive terms respectively, and the Extended-Rydberg potential[27]

$$U_{ER} = -D\left[\sum_{n=0}^{3} a_n \rho^n\right]\exp(-a_1\rho) \tag{2}$$

in which

$$\rho = r - R, \tag{3}$$

are the more generalized forms of the Morse potential[9]

$$U_M = D[\exp(-2\alpha\rho) - 2\exp(-\alpha\rho)] \tag{4}$$

and that of the Rydberg potential[10]

$$U_{Ryd} = -D[1 + a_1\rho]\exp(-a_1\rho) \tag{5}$$

respectively. Here, we refer to the Generalized Morse potential as that applicable for the diatom molecule. For the case of multiatom molecules, the generalization of Morse potentials can be expressed by the Empirical Valence Bond (EVB) approach.[28]

Reduction of the generalized forms to the original forms of these potential functions can be made by the following substitution

$$\left(\frac{\lambda_i - \lambda_j}{\lambda_j}\right) A_i \exp(-\lambda_i R) = D\,;\,(i, j = 1,2) \tag{6}$$

and

$$\lambda_1 = 2\lambda_2 = 2\alpha \tag{7}$$

for the case of Generalized Morse to original Morse, and

$$a_2 = a_3 = 0 \tag{8}$$

for the case of Extended-Rydberg to original Rydberg function. A brief examination of the Extended-Rydberg's parameters (Table 1 of reference 27) reveals that D, R, a_1 and a_3 are positive while the parameter a_2 is negative for some ground-states, although most are positive. As such, we develop two sets of relationship between the Generalized Morse and the Extended-Rydberg parameters: (i) for the case where $a_2<0$, and (ii) for the case where $a_2>0$. For both cases, we begin with the Generalized Morse potential written in another, but equivalent, form as

$$U_{GM} = D\left[\frac{\lambda_2}{\lambda_1 - \lambda_2}\exp(-\lambda_1\rho) - \frac{\lambda_1}{\lambda_1 - \lambda_2}\exp(-\lambda_2\rho)\right] \tag{9}$$

where D is defined from Equation (6). We next proceed with the analysis, bearing in mind the following bounds for the Morse indices:

$$\lambda_1 > 0 \tag{10}$$

$$\lambda_2 > 0 \tag{11}$$

$$(\lambda_1 - \lambda_2) > 0 \tag{12}$$

For $a_2<0$

Here we express Equation (9) as

$$U_{GM} = D\left[\frac{\lambda_2}{\lambda_1 - \lambda_2}\exp[-(\lambda_1 - \lambda_2)\rho] - \frac{\lambda_1}{\lambda_1 - \lambda_2}\right]\exp(-\lambda_2\rho) \tag{13}$$

whereupon substituting the first four terms of the Maclaurin series,

$$\exp[-(\lambda_1 - \lambda_2)\rho] \approx \sum_{n=0}^{3}\frac{[-(\lambda_1 - \lambda_2)]^n}{n!}\rho^n, \tag{14}$$

Equation (13) becomes

$$U_{GM} = -D\left[1 + \lambda_2\rho - \frac{1}{2}\lambda_2(\lambda_1 - \lambda_2)\rho^2 + \frac{1}{6}\lambda_2(\lambda_1 - \lambda_2)^2\rho^3\right]\exp(-\lambda_2\rho) \tag{15}$$

Comparing the terms of the Extended-Rydberg potential, Equation (2), with those of Equation (15) gives the following relationships

$$a_1 = \lambda_2 \tag{16}$$

$$a_2 = -\frac{1}{2}\lambda_2(\lambda_1 - \lambda_2) \tag{17}$$

$$a_3 = \frac{1}{6}\lambda_2(\lambda_1 - \lambda_2)^2 \tag{18}$$

With reference to equations (11) and (12), Equation (17) implies that a_2 is negative, hence indicating that equations (16) to (18) apply for the following five ground-states: Al-O, Be-S, F-Mg, Mg-O and Mg-S, as specified by the negative values of their a_2 parameters (in Table 1 of reference 27).

For $a_2>0$

For this case, we express Equation (9) as

$$U_{GM} = D\left[\frac{\lambda_2}{\lambda_1 - \lambda_2} - \frac{\lambda_1}{\lambda_1 - \lambda_2}\exp[(\lambda_1 - \lambda_2)\rho]\right]\exp(-\lambda_1\rho) \tag{19}$$

which, upon substituting the following first four terms of the Maclaurin series

$$\exp[(\lambda_1 - \lambda_2)\rho] \approx \sum_{n=0}^{3}\frac{(\lambda_1 - \lambda_2)^n}{n!}\rho^n, \tag{20}$$

gives

$$U_{GM} = -D\left[1 + \lambda_1\rho + \frac{1}{2}\lambda_1(\lambda_1 - \lambda_2)\rho^2 + \frac{1}{6}(\lambda_1 - \lambda_2)^2\rho^3\right]\exp(-\lambda_1\rho)\,. \tag{21}$$

Comparison of terms in this equation with those of Equation (2) leads to the following connections

$$a_1 = \lambda_1 \tag{22}$$

$$a_2 = \frac{1}{2}\lambda_1(\lambda_1 - \lambda_2) \tag{23}$$

$$a_3 = \frac{1}{6}\lambda_1(\lambda_1 - \lambda_2)^2 \tag{24}$$

By virtue of Equations (10) and (12), Equations (22) to (24) are applicable for 66 other ground-states with positive a_2 (as listed in Table 1 of reference 27).

Discussion

The reason for using the Maclaurin Series for relating the two generalized forms of interatomic potentials can be seen in the polynomial portion of the Extended-Rydberg potential function. This polynomial portion can be easily reproduced from Equations (13) and (19), thereby allowing comparison of terms to be made. Since it is well known that both potential functions adhere to sharp rise, minimum well-depth and zero at bond compression, at equilibrium and at bond dissociation respectively, then the only theoretical verification required for small distortion about equilibrium is equal curvature at the equilibrium interatomic distance, $r=R$. Taking double derivatives for the Generalized Morse and the Extended-Rydberg potential functions, we have

$$\left(\frac{\partial^2 U_{GM}}{\partial \rho^2}\right)_{\rho=0} = \lambda_1 \lambda_2 D \tag{25}$$

and

$$\left(\frac{\partial^2 U_{ER}}{\partial \rho^2}\right)_{\rho=0} = \left(a_1^{\,2} - 2a_2\right) D \tag{26}$$

respectively at equilibrium. Substituting either equations (16) and (17), or equations (22) and (23), into Equation (26), we recover the result shown in Equation (25). Equal minimum well-depth and curvature at equilibrium therefore proves the validity of the parametric connections establish herein at and near the minimum well-depth. Further to this, plots of Be-S and H-Na potentials, as examples of $a_2<0$ and $a_2>0$ respectively, were plotted using the Extended-Rydberg parameters given by Huxley and Murrell.[27] Using equations (16) and (17), the Generalized Morse parameters were obtained for Be-S potential (with $a_2<0$) as

$$\lambda_1 = a_1 - 2\frac{a_2}{a_1} \tag{27}$$

and

$$\lambda_2 = a_1 . \tag{28}$$

From Equations (22) and (23), the Generalized Morse parameters of H-Na (i.e. $a_2>0$) were obtained as

$$\lambda_1 = a_1 \tag{29}$$

and

$$\lambda_2 = a_1 - 2\frac{a_2}{a_1} . \tag{30}$$

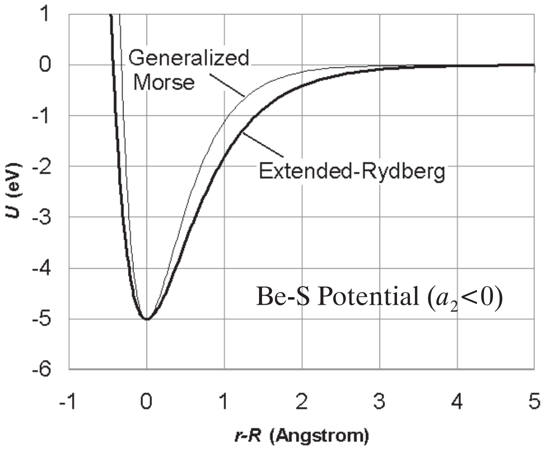

Figure 1. Generalized Morse approximation to Extended-Rydberg curve for Be-S potential.

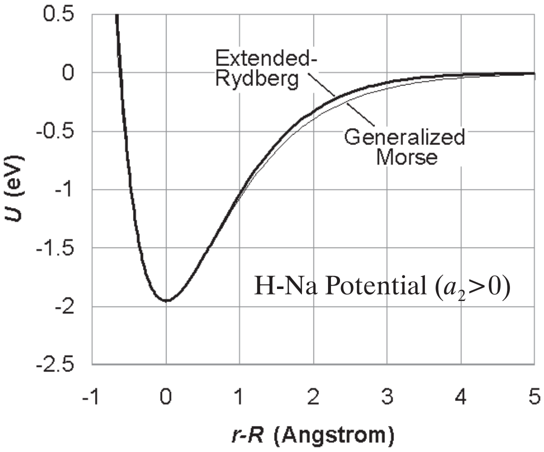

Figure 2. Generalized Morse approximation to Extended-Rydberg curve for H-Na potential.

Figures 1 and 2 depict the potentials of Be-S and H-Na respectively, using the Extended-Rydberg and Generalized Morse potential functions, whereby the latter was plotted on the basis of the former's parameters. See Table 1 for the potential functions' parameters. The plotted potential curves reveal that: Good correlation is seen at and near equilibrium, as the theoretical analysis indicates.

Table 1. Potential function parameters for Be-S and H-Na based on Extended-Rydberg parameters[27] and Generalized Morse parameters calculated in this paper.

Ground-State	D(eV)	$R\left(\mathrm{\AA}\right)$	$a_1\left(\mathrm{\AA}^{-1}\right)$	$a_2\left(\mathrm{\AA}^{-2}\right)$	$a_3\left(\mathrm{\AA}^{-3}\right)$	λ_1	λ_2
Be-S	1.7415	5.007	2.128	–0.308	0.220	4.27086	2.128
H-Na	1.8874	1.952	2.154	1.071	0.365	2.154	1.13159

Generalized Morse function over-estimates the Extended-Rydberg potential at long range for $a_2<0$.

Generalized Morse function under-estimates the Extended-Rydberg potential at long range for $a_2>0$.

For completeness' sake, we extend the present parametric connection to those of the original Morse potential. Substituting Equation (7) into Equations (16) to (18) gives

Table 2. Parametric conversion between Generalized Morse (GM) and Extended-Rydberg (ER) potential function.

From GM to ER	From ER to GM	Remarks
$a_n = \dfrac{\lambda_i(\lambda_i - \lambda_j)^{n-1}}{n!}$; $(n = 1,2,3)$	$\begin{Bmatrix}\lambda_i \\ \lambda_j\end{Bmatrix} = a_1\begin{Bmatrix}1 \\ 1\end{Bmatrix} - 2\dfrac{a_2}{a_1}\begin{Bmatrix}0 \\ 1\end{Bmatrix}$	For $a_2 < 0$, $\Rightarrow i = 2, j = 1$. For $a_2 > 0$, $\Rightarrow i = 1, j = 2$.

$$a_n = (-1)^{n+1}\left[\frac{\alpha^n}{n!}\right] \quad ; \quad (n = 1,2,3) \qquad (31)$$

for $a_2<0$, whilst substitution into equations (22) to (24) yields

$$a_n = 2\left[\frac{\alpha^n}{n!}\right] \quad ; \quad (n = 1,2,3) \qquad (32)$$

for $a_2>0$. In any case, substituting Equation (7) into Equation (25) gives the same curvature as substituting either equations (31) or (32) into Equation (26), thereby not violating the equality of potential curve at and near the minimum well-depth.

Conclusion and Recommendation

By relating the parameters of the Generalized Morse and the Extended-Rydberg potential functions, we have included as well the parameters of the original Morse and Rydberg potential functions. Parametric connections between Generalized Morse and the Extended-Rydberg potential functions have been attained by taking advantage of the Maclaurin series that elegantly fits into the polynomial portion of the Extended-Rydberg potential. A summary of parametric conversion is furnished in Table 2. Since the number of parameters for Extended-Rydberg exceeds those of Generalized Morse by 1, therefore only a_1 and a_2 (a_3 being redundant) are required for converting the Extended-Rydberg Parameters into Generalized Morse parameters but both the Morse indices are needed to obtain a_1, a_2 and a_3.

Without doubt, vibrational analysis is extremely sensitive to the details of the potential. It would hence be a challenge for the future to solve vibrational 1-D Schrödinger equation for both functional forms (see also ref. 29 and 30).

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Povzetek

Raziskovali smo povezavo med posplošeno Morsejevo in razširjeno Rydbergovo potencialno funkcijo. Ker Rydbergov zapis vsebuje razvoj v potenčno vrsto, smo v Morsejevi funkciji uporabili Mac Laurinov razvoj, kar nam je omogočilo primerjavo med parametri obeh funkcijskih zapisov. Razvili smo dve shemi povezav med parametri z namenom dobiti dve kategoriji parametrov razširjene Rydbergove funkcije glede na predznak parametra a_2. V obeh primerih se je pokazalo, da sta ukrivljenosti krivulj v bližini minimuma enaki, kar kaže na uspešnost opisa potenciala pri majhnih odmikih. Za velike odmike pa se je pokazalo, da posplošeni Morsejev približek da nekoliko večje vrednosti od Rydbergovega pri negativnih a_2, medtem ko je pri pozitivnih vrednostih za a_2 učinek obraten.