A methodology to obtain accurate potential energy Functions for diatomic systems: mathematical point of view

Uma metodologia para obter funções de energia potencial precisas para sistemas diatômicos: ponto de vista matemático

Judith de P. Araújo [a,*], **Maikel Y. Ballester** [b], **Mariana P. Martins** [a], **Rafael P. Silva** [a], **Isadora G. Lugão** [a], **Ituen B. Okon** [c], **and Clement A. Onate** [d]

[a] Instituto Federal Sudeste de Minas Gerais, Juiz de Fora - MG, Brasil; [b] Universidade Federal de Juiz de Fora, Juiz de Fora - MG, Brasil; [c] University of Uyo, Uyo, Nigéria; [d] Kogi State University, Anyigba, Nigéria

* Correspondence: judith.araujo@ifsudestemg.edu.br

Abstract: The mathematics used in physical chemistry has changed greatly in the past forty years and it will certainly continue to change more quickly. Theoretical chemists and physicists must have an acquaintance with abstract mathematics if they are to keep up with their field, as the mathematical language in which it is expressed changes. Thinking about it, in this article, we want to show some of the most important concepts of Mathematical Analysis involved in obtaining analytical functions to represent the potential energy interaction for diatomic systems. A basic guide for the construction of a potential based on Dunham's coefficients and an example of a new potential obtained from this methodology is also presented.

keywords: Mathematical Analysis; Analytical potential energy functions; Born-Oppenheimer Approximation; Dunham coefficients; Morse-type potential.

Resumo: A matemática usada na físico-química mudou muito nos últimos quarenta anos e certamente continuará a mudar mais rapidamente. Químicos e físicos teóricos devem ter um conhecimento da matemática abstrata se quiserem manter-se atualizados em seu campo à medida que a linguagem matemática na qual ela é expressa muda. Pensando nisso, neste artigo, queremos mostrar alguns dos conceitos mais importantes da Análise Matemática envolvidos na obtenção de funções analíticas para representar a interação de energia potencial para sistemas diatômicos. Também é apresentado um guia básico para a construção de um potencial baseado nos coeficientes de Dunham e um exemplo de um novo potencial obtido a partir desta metodologia.

Palavras-chave: Análise Matemática; Funções de energia potencial analíticas; Aproximação de Born-Oppenheimer; coeficientes de Dunham; potenciais tipo-Morse.

Classification MSC: 70-11; 81Q05

1 Introduction

The Born-Oppenheimer approximation is a cornerstone for molecular systems in the study of quantum mechanics. It introduces the concept of the molecular potential energy surface (PES). The molecular potential energy surface is the potential energy

that determines the motion of nuclei. In the Born-Oppenheimer Approximation (BOA) the electrons adjust their positions instantaneously to follow any movement of the nuclei so that the potential energy surface can be equally thought of as the potential for the movements of atoms within a molecule or atoms in collision with each other. The motion with this characteristic is called adiabatic, where the dynamic of the system is associated with a single potential energy surface [1].

Considering an isolated molecular system composed of electrons and atomic nuclei, the time-dependent Schrödinger equation is given by:

$$i\hbar \frac{\partial}{\partial t} \Phi(\{r_i\}, \{R_I\}, t) = \mathscr{H} \Phi(\{r_i\}, \{R_I\}, t) \tag{1}$$

where $\mathscr{H}$ is the Hamiltonian:

$$\mathscr{H} = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{e^2}{|r_i - r_j|} + -\frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|R_I - r_i|}$$
$$+ \frac{1}{4\pi\epsilon_0} \sum_{I<J} \frac{e^2 Z_I Z_J}{|R_I - R_J|} \tag{2}$$

for the electronic $\{r_i\}$ and nuclear $\{R_I\}$ degrees of freedom. In Eq. (2), M_I and Z_I are mass and atomic number the Ith nucleus; m_e and $-e$ are electron mass and charge; and ϵ_0 is the vacuum permittivity. Naming:

$$V_{n-e}(\{r_i\}, \{R_I\}) = \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{e^2}{|r_i - r_j|} + -\frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|R_I - r_i|} + \frac{1}{4\pi\epsilon_0} \sum_{I<J} \frac{e^2 Z_I Z_J}{|R_I - R_J|} \tag{3}$$

and replacing in Eq. (2), we then have:

$$\mathscr{H} = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_I^2 + V_{n-e}(\{r_i\}, \{R_I\}). \tag{4}$$

Calling

$$\mathscr{H}_e(\{r_i\}, \{R_I\}) = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}(\{r_i\}, \{R_I\}) \tag{5}$$

we get

$$\mathscr{H} = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \mathscr{H}_e(\{r_i\}, \{R_I\}). \tag{6}$$

Since for each nuclei configuration $\{R_I(t)\}$, the time-independent Schrödinger equation for a given k electronic state

$$\mathscr{H}_e(\{r_i\}, \{R_I\})\Psi_k = E_k(\{R_I\})\Psi_k(\{r_i\}, \{R_I\}) \tag{7}$$

is solving for fixed nuclei in all configurations $\{R_I\}$, and the adiabatic eigenfunctions are knowing at all possible nuclear configurations, the total wave function can be expanded as:

$$\Phi(\{r_i\}, \{R_I\}, t) = \sum_{l=0}^{\infty} \Psi_l(\{r_i\}, \{R_I\})\chi_l(\{R_I\}, t) \tag{8}$$

in terms of the complete set of eigenfunctions $\{\psi_l\}$ of $\mathscr{H}_e$ and time dependent nuclear wave functions $\{\chi_l\}$.

From adiabatic approximation, the wave function $\Phi(\{r_i\}, \{R_I\}; t)$: can be decoupled as a single product of an electron and a nuclear wave equation:

$$\Phi(\{r_i\}, \{R_I\}; t) \approx \Psi_k(\{r_i\}, \{R_I\}) \cdot \chi_k(\{R_I\}; t). \tag{9}$$

and from Born-Oppenheimer approximation, the Schödinger equation Eq. (1) becomes

$$\left(-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{R_I\}) \right) \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \tag{10}$$

that is what will lead to the decoupling of the nuclear and electronic movements, allowing to calculate them separately.

Now, it is easy to see that nuclei can be approximated to classical point particles. For this, it is necessary to extract the semi-classical mechanic from the quantum mechanic (for more details see Ref. [2]) to obtain the differential equation involving the effective potential V_k^{BO}

$$M_I \ddot{R}_I(t) = -\nabla_I V_k^{BO}(\{R_I(t)\}). \tag{11}$$

Thus, within the Born-Oppenheimer approximation, the nuclei move according to the classical mechanics on an effective potential V_k^{BO}, given by the PES E_k obtained from solving, for each nuclei configuration $\{R_I(t)\}$, the time-independent Schrödinger equation for a given k electronic state.

This potential for time-local interaction of many bodies due to quantum electrons is a function of the set of all classical nuclear positions at a time t.

We are interested in the case of two bodies, where the potential will depend only on the internuclear distance R. The construction of an accurate analytical potential energy function satisfying the Born-Oppenheimer Approximation for diatomic systems from experimental data is still an important problem in chemistry and molecular physics.

In recent work[3], we have reviewed and compared fifty analytical representations of potential energy interaction for diatomic systems, proposed from 1920 to 2020. They can be gathered into two groups: those directly obtained from the spectroscopic constants, and those depending upon parameters fine-tuned to reproduce ab initio energies. Functions containing a product of an exponential by a polynomial (with its variations) are, in general, the best representation of the potential energy functions. The studied cases have shown that a function that escapes this configuration hardly provides accurate results [3].

Thus, this work aims to show that functions composed of a product of an exponential and a polynomial are the main candidates for describing accurate diatomic potentials. For such, concepts of Mathematical Analysis Theory have been followed.

The conditions of differentiability, continuity, and convergence of the functions were the first to be verified, since these are necessary to obtain the spectroscopic parameters and to evaluate the system dissociation process, respectively. Then, we have shown some examples of well-known potentials that satisfy these conditions, and others, such as Dunham and Morse, that produce inaccuracies in some required ranges. Next, a

step-by-step to build a potential based on the exponential-polynomial model is suggested. A methodological pathway for obtaining coefficients from experimental data is also provided.

We expect readers will also be able to build their analytical functions depending only on experimental data and considering all the necessary physical criteria. Perhaps it is not a generalized potential, but one that meets the researcher's needs. In addition, our proposal may assist in obtaining surfaces for certain diatomic systems that have accurate data described in the literature, yet without accurate theoretical calculations. For these cases, a function that depends uniquely on experimental data becomes indispensable.

The manuscript is categories into different subsections. Section 2 covers the basic criteria that every potential energy function satisfying the BOA must satisfy. Section 3 presents definitions and important results of Mathematical Analysis that will be useful to support the construction of functions. Section 4 some of the most used potentials in the literature for their accuracy are presented, highlighting the mathematical characteristics that they have in common. Section 5, a method to construct correct potential energy functions is described. Finally, in Section 6 a potential that was obtained using the described methodology can be seen, followed by the conclusions in Section 7.

2 The choice of functions

To our knowledge, there is not an analytical representation of potential energy capable to accurately describing all diatomic systems so far studied. Some models describe satisfactorily the energy of interaction for a reasonable number of systems, mainly in their ground electronic state. However, for excited states, there are few precise analytical models and, in general, these can be applied to a minimal number of diatomics (see our Review [3] where we discussed in detail).

In general, the more accurate and physically well-behaved potentials have some mathematical characteristics in common: they are sums and/or products of exponential functions and polynomials (or functional rational) involving spectroscopic constants and the distance R.

An appropriate non-repulsive potential of Born Oppenheimer $V(R)$ satisfies three criteria:

(i) $\left.\frac{dV}{dR}\right|_{R=R_e} = 0$, *i. e.*, $V(R)$ has a minimum at $R = R_e$;

(ii) V(R) come asymptotically to finite value as $R \to \infty$, in general 0 or $-D_e$, where D_e is the depth of the well ;

(iii) If $R \to 0$, then V(R)$\to \infty$.

How do choose such functions? Although we are talking about a function that describes a physical problem, we will find the answer first in mathematics. Let us begin our discussion with the primordial Dunham potential.

3 Mathematical theory

This section includes mathematical aspects considered as fundamentals for the topics covered in this paper.

Dunham obtained relationships to calculate the most important spectroscopic parameters, and these depend on derivatives of potential. Then, the "ideal" potential energy function must satisfy some mathematical properties related to differentiability and continuity. Although derivatives of an order greater than 4 are hardly necessary, the ideal is to guarantee that the potential energy functions are of class $\mathscr{C}^n$ (at least in some points), as defined below.

While it is chronologically more obvious to define continuity before differentiability, we are going to reverse the order here. Soon it will be clear why this.

The most significant spectroscopic parameters k_e, α_e, $\omega_e x_e$ and ω_e are obtained from derivatives of the potential at R_e, the equilibrium distance (for more details see Ref. [3]).

Definition Consider $V : X \to \mathbb{R}$ and $a \in X \cap X'$, where X' is the set of accumulation points of x (for more details see Ref. [4], p.52). The derivative of function V at point a is given by

$$V'(a) = \lim_{x \to a} \frac{V(x) - V(a)}{x - a} = \lim_{h \to 0} \frac{V(a + h) - V(a)}{h}. \tag{12}$$

Theorem *For the function $V : X \to \mathbb{R}$ to be differentiable at point a, it is necessary and sufficient that there is $c \in \mathbb{R}$ so that $a + h \in X \Rightarrow V(a + h) = f(a) + c \cdot h + R(h)$, where $\lim_{h \to 0} R(h)/h = 0$. In this case, $c = V'(a)$.*

Corollary *A function is continuous at points at which it is differentiable.*

This is a relevant result of the Theory of Mathematical Analysis. It is important to highlight that, the reciprocal is not true, *i.e.*, not all continuous functions are differentiable (*e.g.* the function $f(x) = |x|$).

Definition Consider an open range I on $\mathbb{R}$ and a function $V : I \to \mathbb{R}$. Let n be a non-negative integer. The function V is said to be of class $\mathscr{C}^n$ if it is n times differentiable on I, and if all its derivatives are continuous [4].

Then, the first mathematical requirement to start building a potential candidate: the function must be differentiable n times at $R_e \in I$. We could demand that the potential function is of class $\mathscr{C}^n$ for all points in I, ensuring that the function (and its derivatives) are also continuous at all these points. Although this (the continuity) to be necessary for every interatomic distance R, the condition of being differentiable for all of them is strong.

Thus, the second fundamental characteristic is the continuity of the potential function, defined below.

Definition A function $V : X \to \mathbb{R}$, defined in set $X \subset \mathbb{R}$, is called continuous at point $a \in X$, if for all $\epsilon > 0$ given arbitrary, it is possible to obtain $\delta > 0$ so that $x \in X$ and $|x - a| < \delta \Rightarrow |V(x) - V(a)| < \epsilon$ [4].

Theorem *For the function $V : X \to \mathbb{R}$ to be continuous at point a, it is necessary and sufficient that, for all sequence of points $x_n \in X$ with $\lim x_n = a$, implies in $V(x_n) = V(a)$* [4].

Corollary *If V, $U : X \to \mathbb{R}$ are continuous at point $a \in X$, then the functions $V + U$, $V \cdot U : X \to \mathbb{R}$ are continuous at same point. Furthermore, if $U(a) \neq 0$, the function $V/U : X \to \mathbb{R}$ is continuous at a* [4].

This corollary is essential to support the possible combinations with the exponential functions and polynomial expansions that we will suggest next for the construction of the potential energy function.

From the results above, we can state:

Statement All polynomial $p : \mathbb{R} \to \mathbb{R}$ is a continuous function. All rational function $p(x)/q(x)$ (quotient of two polynomials) is continuous in its domain, which is the set of points x such that $q(x) \neq 0$.

Statement All exponential function $e : \mathbb{R} \to \mathbb{R}^*$, where $\mathbb{R}^*$ denotes $\mathbb{R} - \{0\}$, is continuous and differentiable for all $x \in \mathbb{R}$.

Now, a third (and perhaps one of the most important) characteristic that the potential function must satisfy is related to convergence. We knew that one of the characteristics of the BO potential energy function is that $V(R)$ should assume a finite value as $R \to \infty$, in general, 0. In contrast, the potential must also satisfy $V(R) \to \infty$, as $R \to 0$.

It is important to note that, if one does not impose correct asymptotic behavior at infinity the potential will be useless for studying atomic collisions, or even for high-energy rotation-vibration states of the system [1].

This can be a problem when dealing with infinite expansions in the power series of some types. However, there are many results of Analysis to ensure the convergence of such functions, so that it will guide us in choosing the terms of the expansion.

Definition A power series is a function given by [4]

$$V(x) = \sum_{n=0}^{\infty} a_n(x - x_0)^n = a_0 + a_1(x - x_0) + \cdots + a_n(x - x_0)^n + \cdots . \tag{13}$$

These functions are considered the most important functions of Analysis and are a natural generalization of polynomials [4]. The set of values to which this series converges is a range centered at x_0.

Definition A series $\sum a_n$ is absolutely convergent if $\sum |a_n|$ converges.

Theorem *A power series $\sum_{n=0}^{\infty} a_n(x - x_0)^n$, or converges only to $x = 0$, or there is r, with $0 < r < \infty$, such that the series converges absolutely in the open range $(-r, r)$, and diverges outside the closed range $[-r, r]$. At the extremes, $-r$ and r, the series can converge or diverge. The number r is called convergence radius.*

Theorem *Suppose that r is the convergence radius of power series $\sum\limits_{n=0}^{\infty} a_n(x-x_0)^n$. The function $V : (-r, r) \to \mathbb{R}$, defined by $V(x) = \sum\limits_{n=0}^{\infty} a_n(x-x_0)^n$, is differentiable, with $V'(x) = \sum\limits_{n=0}^{\infty} n\, a_n(x-x_0)^{n-1}$, and the power series of $V'(x)$ still has a convergence radius equal to r.*

This theorem ensures that if the candidate function has a convergence radius r, it will then be automatically differentiable of class $\mathscr{C}^{\infty}$. Therefore, the choice of a function that has a good convergence radius is fundamental, because, consequently, this will ensure that the other required properties are also satisfied.

The following theorem presents a necessary condition, but not enough to investigate the convergence of a power series.

Theorem *The general term of a convergent series has a limit equal to zero.*

Note that this theorem ensures that if the general term of a power series is not zero, then it diverges. However, if the general term is zero, we can´t ensure the convergence of the power series.

Statement The power series

$$\sum_{n=0}^{\infty} \frac{x^n}{n!}, \tag{14}$$

converges for all $x \in \mathbb{R}$, then the function $V : \mathbb{R} \to \mathbb{R}$, defined by $V(x) = \sum\limits_{n=0}^{\infty} \frac{x^n}{n!}$ is of class $\mathscr{C}^{\infty}$. Deriving term by term, we have $V'(x) = V(x)$. Now, as $V(0) = 1$, it follows that $V(x) = e^x$ for all $x \in \mathbb{R}$, and then

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots . \tag{15}$$

Therefore, the choice of polynomial and exponential functions is not arbitrary, since in most cases both are expansions in series of powers.

4 Discussion

The Dunham [5] potential given by

$$V_D = a_0[(R - R_e)/R_e]^2 \left\{ 1 + \sum_{i=1}^{\infty} a_n[(R - R_e)/R_e]^n \right\}, \tag{16}$$

is a power series expansion, and we can easily verify that this is differentiable and therefore continuous for all $R \in \mathbb{R}$. Although the Dunham potential has correct behavior in the spectroscopic region ($R \leq R_e$), the potential does not converge for very large values of R.

Thus, in general, a series of powers alone is not enough to provide the appropriate potential energy for interaction for diatomic systems.

The same occurs with potentials that involve only exponentials. The well known Morse [6] potential

$$V_{MOR}(R) = D_e e^{-2a(R-R_e)} - 2D_e e^{-a(R-R_e)}$$ (17)

is an example of this.

The functional form to describe diatomic potentials is quite adequate to represent atoms forming a chemical bond, providing greater precision in the region of the minimum potential. Besides, this function is differentiable and continuous for all R. However, note that when $R \to 0$, $V_{MOR}(R)$ assumes the finite value $D_e(e^{2aR_e} - 2e^{aR_e})$, and then does not satisfy the criterion (iii). Furthermore, the Morse potential does not have a correct asymptotic behavior for many systems, where his function is too negative at large R.

We chose the potential of Dunham and Morse as a reference because they are the most widely known diatomic potentials. Furthermore, they have the characteristics of potentials that we want to unite: one is composed only by exponential and the other by a series of powers.

The history [3] and recent comparative studies [7] have shown that, in general, accurate analytical potential energy functions are obtained by joining both functions. We can list the following functions as good examples of accurate analytical potentials:

() Extended Rydberg [8, 9]

$$V_{ER}(R) = D_e(1 + a_1(R - R_e) + a_2(R - R_e)^2 + a_3(R - R_e)^3)e^{-\gamma(R-R_e)}.$$ (18)

() Varshni III [10]

$$V_{VAR_{III}}(R) = D_e \left\{ 1 - \frac{R_e}{R} \exp\left[-\beta(R^2 - R_e^2)\right] \right\}^2$$ (19)

() Levine [11]

$$V_{LEV}(R) = D_e \left\{ 1 - \frac{R_e}{R} \exp\left[-a(R^p - R_e^p)\right] \right\}^2.$$ (20)

The Extended Rydberg is still considered one of the most accurate analytical potentials [3]. The Levine function can be considered a modified version of $V_{VAR_{III}}$.

The Hulburt-Hirschfelder [12] potential

$$V_{HH}(R) = D_e[(1 - e^{-x})^2 + (1 + bx)cx^3 e^{-2x}]$$ (21)

does not appear in this list, in turn, it corresponds to the type of function we are searching for. This potential is considered a Morse modified function, being the repulsive branch of the potential multiplying by a polynomial in $(R - R_e)$. However, the attractive branch is not modified and therefore does not produce significant improvements over the Morse potential.

Now, we can also list some functions that are sums and/or product of exponential by polynomials, and in this case, they have adjustable parameters:

(i) EHFACE2U [13]

$$V_{EHFACE2U} = V_{EHF} + V_{dc} \tag{22}$$

where

$$V_{EHF}(R) = -DR^{\alpha}\left(1 + \sum_{i=1}^{3} a_i r^i\right)\exp(-\gamma r), \tag{23}$$

and

$$V_{dc} = -\sum_{n=6,8,10,\cdots} C_n^{AB}\chi_n(R)R^{-n} \tag{24}$$

(ii) Aguado and Paniagua [14]

$$V_{AP}^{(2)}(R_{AB}) = V_{short}^{(2)} + V_{long}^{(2)} \tag{25}$$

where

$$V_{short}^{(2)} = \frac{c_0 e^{-\alpha_{AB}R_{AB}}}{R_{AB}} \tag{26}$$

and

$$V_{long}^{(2)} = \sum_{i=1}^{N} c_i \rho_{AB}^{i} \tag{27}$$

with

$$\rho_{AB} = R_{AB}e^{-\beta_{AB}^{(2)}R_{AB}}, \quad \beta_{AB}^{(2)} > 0. \tag{28}$$

Both potentials satisfy all the criteria described in Section 3. These are two of the most well-known and used functions for fitting potential energy curves to ab initio points. Very flexible, these functions can be used for many different diatomic systems in their fundamental and excited electronic states (see more details in Ref [3]).

5 Proposed Methodology

In this section, we will describe a methodology for building potential, based on Dunham's function.

1. First, two functions that satisfy all the criteria described in Section 3 must be chosen, one being a polynomial expansion and the other an exponential one;

2. Make the product of the chosen functions. Remember that one must satisfy the short-range while the other satisfies R large. To verify this, do the test with $R \to 0$ and $R \to \infty$ using the complete function;

3. The function can be given, for example, by:

$$V(R) = b_0 G^2(R)F^2(R)\left(1 + \sum_{i=1}^{N} b_n G^n(R)\right) \tag{29}$$

or even by

$$V(R) = b_0 G^2(R)\left(1 + \sum_{i=1}^{N} b_n G^n(R)F^n(R)\right). \tag{30}$$

where $F(R)$ is a exponential-type function involving powers of R and R_e, such as those presented in Section 4, $G(R)$ is a polynomial term (in general $(R - R_e)$ and its variations) and N must be truncated in some satisfactory value;

4. In the region of its convergence, the Dunham potential converges to the RKR [15–17] potential derived from the energy levels (see Ref. [18]). Then, for the corresponding property to hold for the new expansion $V(R)$, it must be equal to the Dunham expansion in the region where both series converge:

$$b_0 G^2(R) F^2(R) \left(1 + \sum_{i=1}^{N} b_n G^n(R) \right)$$

$$= a_0 [(R - R_e)/R_e]^2 \left\{ 1 + \sum_{i=1}^{\infty} a_n [(R - R_e)/R_e]^n \right\} \tag{31}$$

or

$$b_0 G^2(R) \left(1 + \sum_{i=1}^{N} b_n G^n(R) F^n(R) \right)$$

$$= a_0 [(R - R_e)/R_e]^2 \left\{ 1 + \sum_{i=1}^{\infty} a_n [(R - R_e)/R_e]^n \right\} \tag{32}$$

by considering Eq. Eq. (30).

5. The coefficients b_n can be straightforwardly obtained, taking the derivatives of both sides of Eqn. 32 regarding to R and equated them at $R = Re$;

6. Then, a series of expressions relating the new potential coefficients b_n and the Dunham coefficients a_n is obtained, providing the full potential.

This method, although simple and illustrative, can be used to obtain potential energy surfaces. One of the difficulties that may arise concerns the Dunham's coefficients a_i. These are not widely available in the literature and in general, for $i > 6$, they are quite inaccurate and difficult to obtain (some of them can be obtained from Refs. [19, 20]). Thus, to use this method, the function must not have a degree greater than 8.

6 Results

The following function was obtained from the methodology described in the previous section, and this new potential is published in Ref. [21], and is given by:

$$V(R) = \begin{cases} \sum_{n=2}^{8} c_n \left[\left(1 + e^{-2\beta \left(\frac{R - R_e}{R_e} \right)} \right) \left(\frac{R - R_e}{R} \right) \right]^n, & R \le R_e \\ \\ D_e \left[\frac{(1 - e^{-2\alpha(R - R_e)})}{(1 + e^{-\gamma\alpha(R - R_e)})} \right]^2, & R > R_e \end{cases} \tag{33}$$

where $\beta = \frac{1}{3}\alpha$ with α the Morse [6] parameter, γ is a fine-tuning parameter $1 \le \gamma \le 3$, to be fixed by direct comparison with RKR data. The c_n, $n = 2, \cdots, 8$ are coefficients related with the Dunham [5] coefficients, as can be seen below.

The potential Eq. (33) presents accuracy in the spectroscopic region and the correct asymptotic behavior, being given by two distinct functions. The function chosen to represent the short-range is Dunham type. Although the Dunham potential [5] is accurate around the minimum, it does not have adequate asymptotic behavior.

Thus, the Morse-type function $D_e \left[\frac{(1-e^{-2\alpha(R-R_e)})}{(1+e^{-\gamma\alpha(R-R_e)})} \right]^2$, at $R > R_e$ was introduced, ensuring by construction, that the potential has an asymptotically correct form.

Note that as we commented in Section 4, Dunham-type functions describe the spectroscopic region well, but in general, do not describe the asymptotic region well. On the other hand, Morse-type functions describe the asymptotic region well, but fail in the short range. Thus, to obtain the "ideal" potential, it was necessary to join the two potentials to guarantee convergence, without forgetting also to verify the continuity in the coupling of the two functions in R_e.

The coefficients c_n have been obtained using items 4 and 5 described in Section 5, from the following procedure:

a) Calculating the second derivative of $V(R)$ (at $R \leq R_e$) and of Dunham's potential Eq. (16) at $R = R_e$, we obtain:

$$\frac{d^2}{dR^2} \left[\sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e} \right)} \right) \left(\frac{R - R_e}{R} \right) \right]^n \right]_{R=Re} = \frac{8 \cdot c_2}{R_e^2} \tag{34}$$

$$\frac{d^2}{dR^2} \left[a_0[(R - R_e)/R_e]^2 \left\{ 1 + \sum_{i=1}^{\infty} a_n[(R - R_e)/R_e]^n \right\} \right]_{R=Re} = \frac{2 \cdot a_0}{R_e^2} \tag{35}$$

Then,

$$\frac{8 \cdot c_2}{R_e^2} = \frac{2 \cdot a_0}{R_e^2} \tag{36}$$

$$\Rightarrow c_2 = \frac{1}{4} a_0.$$

b) Calculating the third derivative of $V(R)$ (at $R \leq R_e$) and of Dunham's potential Eq. (16) at $R = R_e$, we obtain:

$$\frac{d^3}{dR^3} \left[\sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e} \right)} \right) \left(\frac{R - R_e}{R} \right) \right]^n \right]_{R=Re} = \frac{48[c_3 - c_2(1+\beta)]}{R_e^3} \tag{37}$$

$$\frac{d^3}{dR^3} \left[a_0[(R - R_e)/R_e]^2 \left\{ 1 + \sum_{i=1}^{\infty} a_n[(R - R_e)/R_e]^n \right\} \right]_{R=Re} = \frac{6 \cdot a_0 \cdot a_1}{R_e^3} \tag{38}$$

Then,

$$\frac{48[c_3 - c_2(1+\beta)]}{R_e^3} = \frac{6 \cdot a_0 \cdot a_1}{R_e^3} \tag{39}$$

$$\Rightarrow c_3 = \frac{1}{8} \left[a_0 a_1 + 8(1+\beta) c_2 \right].$$

c) Calculating the fourth derivative of $V(R)$ (at $R \leq R_e$) and of Dunham's potential Eq. (16) at $R = R_e$, we obtain:

$$\frac{d^4}{dR^4}\left[\sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right)\left(\frac{R-R_e}{R}\right)\right]^n\right]_{R=Re} =$$

(40)

$$= \frac{96[4c_4 - 6c_3(1+\beta) + c_2(3\beta^2 + 4\beta + 3)]}{R_e^4}$$

$$\frac{d^4}{dR^4}\left[a_0[(R-R_e)/R_e]^2\left\{1 + \sum_{i=1}^{\infty} a_n[(R-R_e)/R_e]^n\right\}\right]_{R=Re} = \frac{24 \cdot a_0 \cdot a_2}{R_e^4} \quad (41)$$

Then,

$$\frac{96[4c_4 - 6c_3(1+\beta) + c_2(3\beta^2 + 4\beta + 3)]}{R_e^4} = \frac{24 \cdot a_0 \cdot a_2}{R_e^4} \quad (42)$$

$$\Rightarrow c_4 = \frac{1}{16}\left[a_0 a_2 + 24(1+\beta)c_3 - 4(3\beta^2 + 4\beta + 3)c_2\right].$$

Continuing with this procedure until the eighth derivative, we obtained the relations for the function's coefficients $c_2, \cdots c_8$, in terms of the Dunham coefficients $a_0, \cdots, a_6$:

$$c_2 = \frac{1}{4}a_0; \quad (43)$$

$$c_3 = \frac{1}{8}\left[a_0 a_1 + 8(1+\beta)c_2\right] \quad (44)$$

$$c_4 = \frac{1}{16}\left[a_0 a_2 + 24(1+\beta)c_3 - 4(3\beta^2 + 4\beta + 3)c_2\right]; \quad (45)$$

$$c_5 = \frac{1}{32}\left[a_0 a_3 + 64(1+\beta)c_4 - 4(12\beta^2 + 18\beta + 12)c_3\right.$$

$$\left. + 4\left(\frac{10}{3}\beta^3 + 6\beta^2 + 6\beta + 4\right)c_2\right]; \quad (46)$$

$$c_6 = \frac{1}{64}\left[a_0 a_4 + 160(1+\beta)c_5 - 4(40\beta^2 + 64\beta + 40)c_4\right.$$

$$+ 4\left(18\beta^3 + 36\beta^2 + 36\beta + 20\right)c_3 \quad (47)$$

$$\left. - 4\left(3\beta^4 + \frac{20}{3}\beta^3 + 9\beta^2 + 8\beta + 5\right)c_2\right];$$

$$c_7 = \frac{1}{128}\left[a_0 a_5 + 384(1+\beta)c_6 - 4(120\beta^2 + 200\beta + 120)c_5\right.$$

$$+ 4\left(\frac{224}{3}\beta^3 + 160\beta^2 + 160\beta + 80\right)c_4$$

$$- 4(22\beta^4 + 54\beta^3 + 72\beta^2 + 60\beta + 30)c_3 \quad (48)$$

$$\left. + 4\left(\frac{34}{15}\beta^5 + 6\beta^4 + 10\beta^3 + 12\beta^2 + 10\beta + 6\right)c_2\right];$$

$$c_8 = \frac{1}{256} \left[a_0 a_6 + 896(1 + \beta)c_7 - 4(336\beta^2 + 576\beta + 336)c_6 \right.$$

$$+ 4 \left(\frac{800}{3}\beta^3 + 600\beta^2 + 600\beta + 280 \right) c_5$$

$$- 4 \left(\frac{340}{3}\beta^4 + \frac{896}{3}\beta^3 + 400\beta^2 + 320\beta + 140 \right) c_4 \tag{49}$$

$$+ 4 \left(\frac{114}{5}\beta^5 + 66\beta^4 + 108\beta^3 + 120\beta^2 + 90\beta + 42 \right) c_3$$

$$\left. - 4 \left(\frac{22}{15}\beta^6 + \frac{68}{15}\beta^5 + 9\beta^4 + \frac{40}{3}\beta^3 + 15\beta^2 + 12\beta + 7 \right) c_2 \right].$$

The potential Eq. (33) fulfill the necessary continuity conditions in $R = R_e$:

(a) Note that

$$\lim_{R \to R_e^-} \sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e}\right)} \right) \left(\frac{R - R_e}{R} \right) \right]^n = 0$$

$$\lim_{R \to R_e^+} D_e \left[\frac{(1 - e^{-2\alpha(R-R_e)})}{(1 + e^{-\gamma\alpha(R-R_e)})} \right]^2 = 0. \tag{50}$$

(b) The same occurred with the first order derivatives,

$$\lim_{R \to R_e^-} \frac{d}{dR} \left[\sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e}\right)} \right) \left(\frac{R - R_e}{R} \right) \right]^n \right] = 0$$

$$\lim_{R \to R_e^+} \frac{d}{dR} \left[D_e \left[\frac{(1 - e^{-2\alpha(R-R_e)})}{(1 + e^{-\gamma\alpha(R-R_e)})} \right]^2 \right] = 0. \tag{51}$$

Furthermore, the new potential Eq. (33) satisfies the following necessary criteria [10]:

(i) $\left. \frac{dV}{dR} \right|_{R=R_e} = 0$, *i. e.*, V(R) has a minimum at $R = R_e$;

(ii) V(R) come asymptotically to finite value as $R \to \infty$, and in this case $V(\infty) = D_e$;

(iii) If $R \to 0$, then V(R)$\to \infty$.

We have also added the condition, $V(R_e) = 0$, which simply shifts the zero of potential, without physically affecting its properties.

This potential function, obtained within the methodology here introduced, proved to be accurate for 22 diatomic systems. Among them, for the ground electronic state of the ion CO^+, for CN and Na_2 in their excited electronic states ($A^2\Pi$) and ($B^1\Pi$) respectively. Furthermore, diatomic systems formed by heavier atoms and/or with many electrons, such as I_2, BiI, Cs_2, Mg_2, Na_2 were also well described by this function (For more details see Ref. [21]).

7 Conclusions

We have described all the mathematical details to obtain good potentials. The search for a correct functional form is not so simple, it also requires a lot of physical knowledge to define the parameters that will compose the functional form and in which positions. These difficulties were confirmed when we built our potential from the methodology described here.

The five listed functions, with adjustable or not adjustable parameters, besides involving exponential and polynomials, have another characteristic in common: the correct asymptotic behavior of the potential for dissociation into atoms. This is a necessary condition to obtain a potential that is satisfactory overall accessible values of R [1].

Significants points were also observed to obtain a correct potential energy curve. Firstly, we proposed only the function defined at $R \leq R_e$ as being a function for all R. However, we found that the behavior of this function at $R \to \infty$ was not correct. It providing non-zero values for such R. Then, we searched for functions that could correct this asymptotic limit. Again, we obtained a function in terms of the exponential function, as Morse-type potential.

Thus, to obtain correct potential energy functions, it is necessary to ensure convergence and all other requirements described in Section 3 of this paper. In general, functions not satisfying the aforementioned conditions will hardly represent the inter atomic potentials accurately.

ORCID

Judith de Paula Araújo ● https://orcid.org/0000-0002-4608-492X
Maikel Y. Ballester ● https://orcid.org/0000-0002-5475-8808
Mariana P. Martins ● https://orcid.org/0009-0004-5340-0689
Rafael P. Silva ● https://orcid.org/0009-0000-9506-3159
Isadora G. Lugão ● https://orcid.org/0009-0003-4430-7055
Ituen B. Okon ● https://orcid.org/0000-0002-8172-7249
Clement A. Onate ● https://orcid.org/0000-0002-9909-4718

Disclosure statement. No potential conflict of interest was reported by the author(s).

Referências

1. J. N. Murrell and S. Carter and S. C. Farantos and P. Huxley and A. J. C. Varandas, *Molecular Potential Energy Functions*. New York: Wiley, 1977.

2. D. Marx and J. Hutter. *Ab Initio Molecular Dynamics*. New York,: Cambridge University Press, 2009.

3. J. P. Araújo and M. Y. Ballester, "A comparative review of 50 analytical representation of potential energy interaction for diatomic systems: 100 years of history", *International Journal of Quantum Chemistry*, vol. 121, pp.e26808 1–102, 2021. https://doi.org/10.1002/qua.26808

4. E. L. Lima, *Análise Real: Funções de uma variável*, Rio de Janeiro: IMPA, 2008.

5. J. L. Dunham, "The Energy Levels of a Rotating Vibrator ", *Physical Review*, vol. 41, pp.721–731, 1932. https://doi.org/10.1103/PhysRev.41.721

6. P. M. Morse, "Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels", *Physical Review*, vol. 34, pp.57–64, 1929. https://doi.org/10.1103/PhysRev.34.57

7. J. P. Araújo and M. D. Alves and R. S. da Silva and M. Y. Ballester, "A comparative study of analytic representations of potential energy curves for O_2, N_2, and SO in their ground electronic states", *Journal of Molecular Modeling*, vol. 25, pp.1–17,2019. https://doi.org/10.1007/s00894-019-4079-3

8. J. N. Murrell and K. S. Sorbie, "New Analytic Form for the Potential Energy Curves of Stable Diatomic States", *Journal of the Chemical Society, Faraday Transactions 2*, vol.70, pp.1552–1556, 1974. https://doi.org/10.1039/F29747001552

9. P. Huxley and J. N. Murrell, "Ground-state Diatomic Potentials", *Journal of the Chemical Society, Faraday Transactions 2*, vol. 79, pp.323–328, 1983. DOI https://doi.org/10.1039/F29837900323

10. Y. P. Varshni, "Comparative Study of Potential Energy Functions for Diatomic Systems", *Reviews of Modern Physics*, vol. 29, pp.664–682, 1957. https://doi.org/10.1103/RevModPhys.29.664

11. I. N. Levine, "Accurate Potential Energy Function for Diatomic Molecules", *The Journal of Chemical Physics*, vol.45, pp.827–828, 1966. https://doi.org/10.1063/1.1727689

12. H. M. Hulburt and J. O. Hirschfelder, "Potential Energy Functions for Diatomic Molecules "textitThe Journal of Chemical Physics, vol. 9, pp. 61–69, 1941. https://doi.org/10.1063/1.1750827

13. A. J. C. Varandas and J. D. da Silva, "Potential model for diatomic molecules including the united-atom limit and its use in a multiproperty fit for argon", *Journal of the Chemical Society, Faraday Transactions*, vol. 88, pp. 941–954, 1992. https://doi.org/10.1039/FT9928800941

14. A. Aguado and M. Paniagua, "A new functional form to obtain analytical potentials of triatomic molecules", *The Journal of Chemical Physics*, vol. 96, pp. 1265–1275, 1992. https://doi.org/10.1063/1.462163

15. R. Rydberg, "Graphische Darstellung einiger bandenspektroskopischer Ergebnisse", *Zeitschrift für Physik*, vol. 73, pp. 376–385, 1932. https://doi.org/10.1007/BF01341146

16. O. Z. Klein, "Zur Berechnung von Potentialkurven für zweiatomige Moleküle mit Hilfe von Spektraltermen", *Zeitschrift für Physik*, vol. 76, pp. 226–2355, 1932. https://doi.org/10.1007/BF01341814

17. A. L. G. Rees, "The calculation of potential-energy curves from band-spectroscopic data", *Proceedings of the Physical Society of London A*, vol. 59, pp. 998–1008,1947. https://doi.org/10.1088/0959-5309/59/6/310

18. A. C. Hurley, "Equivalence of RydbergKleinRees and Simplified Dunham Potentials", *The Journal of Chemical Physics*, vol.36, pp.1117–1118, 1962. http://dx.doi.org/10.1063/1.1732678

19. J. F. Ogilvie and D. Koo, "Dunham potential energy coefficients of the hydrogen halides

and carbon monoxide", *Journal of Molecular Spectroscopy*, vol. 61, pp. 332–336, 1976. https://doi.org/10.1016/0022-2852(76)90323-4

20. J. F. Ogilvie, "Dunham energy parameters of isotopic carbon monoxide, hydrogen halide, and hydroxyl radical molecules", *Journal of Molecular Spectroscopy*, vol. 69, pp.169–172, 1978. https://doi.org/10.1016/0022-2852(78)90056-5

21. J. P. Araújo and M. Y. Ballester, "New generalized potential energy function for diatomic systems", *Physica Scripta*, vol. 96, pp.125407 1-10, 2021. https://doi.org/10.1088/1402-4896/ac3150

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of Edições UESB and/or the editor(s). Edições UESB and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.