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Analytical Representation of Potential Energy Surfaces for Diatomic Systems: A Centenary Historical Review and New Perspectives

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"Analytical Representation of Potential Energy Surfaces for Diatomic Systems: A Centenary Historical Review and New Perspectives"

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To God and Our Lady Aparecida.
To my family.
To my teachers.
To my friends.
I dedicate

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To God and Our Lady, for always watching over me, protecting me and allowing me to get here.

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The mind that opens up to a new idea will never return to its original size.

Albert Einstein

Abstract

Interatomic potentials laid at the heart of the molecular physics. They are a bridge between spectroscopic and structural properties of a molecular systems. In this work, a century-old review, from 1920 to 2020, of functional forms used to analytically represent potential energy as a function of interatomic distance for diatomic systems is presented. With such a purpose fifty functions were selected. For all of them motivation and main mathematical features are discussed. Our goal is to provide a chronological pathway showing how to calculate each parameter that composes the interatomic potentials, as well as the methods to obtain spectroscopic constants from them. A comparative evaluation for the N_2, CO and HeH^+ systems in their ground electronic states is also presented. Some results of a work presented at the Quitel Congress in 2018, are also presented. Moreover, a methodology from a mathematical point of view to obtain correct potential energy functions for diatomic systems is introduced. Finally, a new and flexible function to represent the potential energy interactions of diatomic systems for the whole domain of internuclear separations is proposed. This function is a member of a family of functions containing a product of an exponential and a polynomial. A method for generating the parameters of the new potential as a function of Dunham's parameters is described. Coefficients for 22 selected diatomic systems with elements from the first to the sixth rows, including some ground and excited electronic states, are presented. To quantify the accuracy of the so constructed potential energy functions, the least-squares Z-test method, proposed by Murrell and Sorbie, is used. Furthermore, main spectroscopic parameters are calculated and compared with available data.

Keywords: potential energy curves, diatomic systems, ground electronic state, spectroscopic parameter, analytical representation.

Resumo

Potenciais interatômicos estão no cerne da física molecular. Eles são uma ponte entre as propriedades espectroscópicas e estruturais de um sistema molecular. Neste trabalho, uma revisão centenária, de 1920 a 2020, de formas funcionais usadas para representar analiticamente a energia potencial como uma função da distância interatômica para sistemas diatômicos é apresentada. Com esse propósito, cinquenta funções foram selecionadas. Para todas elas são discutidos a motivação e as principais características matemáticas. Nosso objetivo é fornecer ao leitor um caminho cronológico, mesmo com pouco conhecimento sobre o assunto, para entender como calcular cada parâmetro que compõe os potenciais interatômicos, bem como obter constantes espectroscópicas a partir deles. Uma avaliação comparativa para os sistemas N_2, CO e HeH^+ em seus estados eletrônicos básicos também é apresentada. Alguns resultados de um trabalho apresentado no Congresso Quitel em 2018 são também apresentados. Além disso, uma metodologia do ponto de vista matemático para a obtenção de funções corretas de energia potencial para sistemas diatômicos. Por fim, uma nova e flexível função para representar as potenciais interações de energia de sistemas diatômicos para todo o domínio das separações internucleares é proposta. Esta função é membro de uma família de funções contendo um produto de um exponencial e um polinômio. É descrito um método para gerar os parâmetros do novo potencial em função dos parâmetros de Dunham. São apresentados coeficientes para 22 sistemas diatômicos selecionados com elementos da primeira à sexta fileira, incluindo alguns estados eletrônicos de solo e excitados. Para quantificar a acurácia das funções de energia potencial assim construídas, é utilizado o método dos mínimos quadrados Z-teste, proposto por Murrell e Sorbie. Além disso, os principais parâmetros espectroscópicos são calculados e comparados com os dados disponíveis.

Palavras-chave: curvas de energia potencial, sistemas diatômicos, estado eletrônico fundamental, parâmetros espectroscópicos, representação analítica.

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Nomenclature

ACP Aguado-Camacho-Paniagua

AP Aguado-Paniagua

BM Born-Mayer

BOA Born-Oppenheimer Approximation

CASPT2 Second-Order Multiconfigurational Perturbation Theory

CASSCF Complete Active Space Self-Consistent

CJV Coolidge-James-Vernon

DAV Davidson

DELR Double-Exponential/Long-Range

DF Deng-Fan

DMBE Double-Many-body Expansion

DPF Direct Potential Fit

DUN Dunham

DZ Dmitrieva-Zenevich

EHFACE2U Extended Hartree-Fock Approximate Correlation Energy to Diatomic Systems

ELJ Extended Lennard-Jones

EM Extended Morse

EMO Expanded Morse Oscillator

ER Extended Rydberg

FAY Fayyazudin

FM Frost-Musulin

FWJ Fu-Wang-Jia

GENKRA Generalized Kratzer

GPEF Generalized Potential Energy Function

HEL Heller

HF Hartree-Fock

HFACE Hartree-Fock Approximate Correlation Energy

HH Hulburt-Hirschfelder

HUF Huffaker

HUG Huggins

HYL Hylleraas

icMRCI Internally Contracted Multireference Configuration Interaction

IMPETP Improved Multiparameter Exponential-type

IMPT Improved Pöschl-Teller

KRA Kratzer

LEV Levine

LIN Linnett

LIP Lippincott

LJ Lennard Jones

LS Lippincott-Schroeder

MAT Mattera

MBE Many-body Expansion

MER Modified Extended Rydberg

MLR Morse/Long-Range

MOR Morse

MR Manning-Rosen

MRCI Multireference Configuration Interaction

MRM Modified Rosen-Morse

MS Mecke-Sutherland

MXR Mixed Dunham

NDE Near-Dissociation Expansionn

NDS New Deformed Schiöberg-type

NEW Newing

NMM New Modified Morse

NOF-MP2 Natural-Orbital-Functional Second-Order-Moller-Plesset

NP Noorizadeh-Pourshams

OGI Ogilvie

PEF Potential Energy Function

PES Potential Energy Surface

PG Pseudogaussian

PMO Perturbed-Morse-Oscillator

PT Pöschl-Teller

RAFI Rafi

RKR Rydberg-Klein-Rees

RM Rosen-Morse

RMSD Root-Mean-Square Deviation

RPC Reduced Potential Curves

RYD Rydberg

SCH Schiöberg

SPF Simons-Parr-Filan

SUR Surkus

TDA Tamm-Dancoff Approximation

TDDFT	Time-Dependent Density Functional Theory
TH	Tietz-Hua
THA	Thakkar
UDD	Uddin
VAR	Varshni
WKB	Wentzel-Kramers-Brillouin
WP	Williams-Poulios
WY	Wu-Yang

Summary

1 Introduction

The relationship upon the potential energy and the internuclear distance between two atoms is of the greatest importance in physical-chemical processes. Recent work (see for example Ref. [1]) show the oldie idea of representing potential energy as a function of internuclear distance, is still extremely valuable. The potential energy surface of a specific electronic state is associated with the electronic energy of the potential energy surface for that state for all configurations of the nuclei. Thus to calculate the potential energy surface from the Schrödinger equation one must solve the equation many times, for each of the nuclear configurations that are thought necessary for a correct representation of the surface. However, due to practical limitations in the solution of this equation for molecules, physically supported approximations are required. In 1927 Born and Oppenheimer, also with the contribution of Huang, presented a pathway to circumvent this problem [2].

The Born-Oppenheimer approximation (BOA) consists in the separation of the nuclear and electron motions: once nuclei have a much larger mass than electrons, they can be considered as stationary compared to the moving electrons. The mathematical formalism for such an approach can be followed elsewhere [2] and are fundamental in understanding the key concept of potential energy surface (PES). Since BOA several research works have been attempting to obtain analytical representations of energy as a function of the interatomic distances. Such a representation is usually required to be mathematically simple while accurately reproducing theoretical and experimental data.

Accurate potential energy curves for diatomic molecules are required to evaluate the Franck-Condon factors for transitions between different various electronic states, applied in the calculation of radiative lifetimes, vibrational temperatures, predissociations, the kinetics of energy transfer, and intensities of vibrational band spectra(see for example Ref. [3]). Potential energy curves are also important for the interpretation of molecular spectra and chemiluminescent atom recombination processes (see for example Ref. [4]).

The potential energy curve provides a broad insight into the structure of a molecular system. The minimum in this curve defines the equilibrium length of the diatomic molecule. The second derivative of such function provides the force constants, which are fundamental for obtaining the vibrational and rotational energy levels of the molecule. Higher-order derivatives are required for the calculation of the anharmonicity constants. Thus, finding a simple and easy way to obtain the derivatives of the functional form is also desired.

One of the first observations of the vibrational structure in potential energy curves dates back to 1874, by Roscoe and Schuster [5], for the diatomic systems Na_2 and K_2. However, such work was not clearly explained until the mid-twenties of the XX century. To our knowledge, the most recent analytical way to describe PES of diatomic systems has proposed in 2020 by Desai, Mesquita, and Fernandes [6]. The authors presented a New Modified Morse potential, with four parameters for a high-precision representation of the diatomic potential. In that work, the authors claim such a proposal to be more accurate than the Hulburt-Hirschfelder [7] and the standard Morse [8] potentials, both widely used in atomic and molecular physics. The New Modified Morse potential shown also high accuracy compared to curves Rydberg-Klein-Rees (RKR) [9–11].

Many efforts and advances have also been observed in the computational area to fit spectroscopic parameters and obtain vibrational energy levels. In 2016, intending to obtain accurate potential energy functions for diatomic systems, Le Roy presented the package dPotFit [12]. Such a tool performs the least-squares fitting of spectroscopic data to determine analytic potential energy functions reproducing the observed levels and other known properties of each electronic state. Four families of functions are there available for fitting: the Expanded Morse Oscillator (EMO) function, the Morse/Long-Range (MLR) function, the Double-Exponential/Long-Range (DELR) function, and the Generalized Potential Energy Function (GPEF) of Šurkus, which incorporates a variety of polynomial functional forms. When the experimental information for a particular electronic state is not sufficiently extensive or systematic to define a full potential energy function (PEF) for it, dPotFit allows its energy levels to be represented by (often quite large) sets of independent term values $T_{\nu,J}$ or by a set of band constants $\{G_\nu, B_\nu, D_\nu, H_\nu\}$ for each vibrational level ν of each isotopologue. These last capabilities can be particularly important in the early stage of a multi-state analysis, as it allows one to perform a "direct potential fit" (DPF) analysis to determine an initial PEF for one state at a time.

Interested especially in long-range intramolecular interactions, Stawalley describes the behavior of certain potential regions for diatomic systems H_2, LiH, Li_2, Na_2, K_2, KRb, Rb_2, Cs_2, HgH and Mg_2 [1]. He analyzed the following potential regions: Short Range Chemically Bound Levels, Long Range Weakly Bound Levels, Long Range Purely Repulsive Continuum Levels, Rydberg Levels Based on Short Range Chemically Bound Ions, Rydberg Levels Based on Long-Range Weakly Bound Ions, Long Range "Heavy" Rydberg Levels Based on Atomic Ion Pairs and Long Range Rydberg Levels Based on an Atom @ Rydberg Atom [1], showing the relevance of still studying PES of diatomic systems.

Another recent work to represent potential energy surfaces for diatomic systems is also by Le Roy and dates from 2017 [13]. There, the author describes a computer package RKR1, which implements the first-order semi-classical Rydberg-Klein-Rees procedure for determining the potential energy function for a diatomic molecule from a knowledge of the dependence of the molecular vibrational energies G_ν and inertial rotation constants B_ν on the vibrational quantum number ν. RKR1 allows the vibrational energies and rotational constants to be defined in terms of (i) conventional Dunham polynomial expansions, (ii) near-dissociation expansions (NDE's), or (iii) the mixed Dunham/NDE "MXR" functions [13]. For cases in which only vibrational data are available, RKR1 also allows an overall potential to be constructed by combining directly calculated well widths with inner and the outer turning points generated from a Morse function.

The RKR1 method can be currently seen as an important complement to the more modern and commonly used techniques like DPF. The sophistication of the potential function forms used in such DPF analyses requires an auxiliary tool. Their analytic complexity makes it difficult to generate the sets of realistic initial-trial-parameter values that are required to initiate those non-linear least-squares fits. As a result, the most common approach is to start with a classical analysis involving fits of assigned data to some variant of Dunham's equation, *i. e.*, a power series expansion for the potential energy function to the coefficients of the conventional expansion for vibrational–rotational energies as a double power series in $\left(\nu + \frac{1}{2}\right)$ and $[J(J+1)]$, with G_ν and B_ν represented by one of the expansions Dunham, NDE or MXR. This is then followed by an RKR calculation using a code such as the one described in Ref. [13]. Fits the resulting potential function points using a specialized code, then yields the set of trial parameter values required to initiate the DPF analysis. Thus, an analysis of the performance of RKR calculations is also a crucial part of a modern DPF analysis [13].

Many comparative studies and historical reviews on diatomic potentials have been presented over the years, such as those presented by Varshni [14] and Steele and Lippincott [15]. However, we miss an updated review, covering from the oldest analytical forms such as Kratzer [16], Morse [8], and Rydberg [9] to the most recent ones, such as Jia-Zhang-Peng [17] and Fu-Wang-Jia [18].

Although our aim in this work is to provide a broad view of the most relevant analytical ways to represent diatomic potentials, we will present some with applications for particular systems, as is the case with the potentials of Born-Mayer [19], Huggins [20] and Heller [21], dedicated in the majority of cases to alkali halide crystals (Born-Mayer and Huggins) and van der Waals diatomic molecules (Born-Mayer and Heller).

Preliminary, in the next chapter, we will start considering two methods that supported the development of the diatomic potential theory: the Dunham expansion and the Rydberg-Klein-Rees method, better known as RKR.

The Dunham method motivated the construction of important power functions, such as that of Thakkar[22], which will be presented below, among others, which were based on an expansion in power series of $R - R_e$. Besides, Dunham showed that energy levels were given by a double series in terms of the vibrational and rotational quantum numbers ν and J, and their coefficients Y_{lj}. He demonstrated explicitly how potential relates to the spectroscopic constants of Bohr's theory, which defines the Y_{lj}'s.

The method is known as RKR, in honor of Rydberg [9], Klein [10] and Rees [11], is a procedure to obtain potential energy curves from experimental data for the vibrational term values $E(\nu)$ and rotational constants $B(\nu)$. The great advantage of this method consists precisely in making use of experimental energy levels without reference to any empirical function to represent the PECs. It may seem a little contradictory that we approach this method in this work since our objective is to deal with analytical functions to represent potentials. However, the RKR method that had its construction begun in 1931 by Rydberg, improved by Klein in 1932 and completed (as we know today) by Rees in 1947, is still the most widely used as a parameter of good precision for comparing curves of potential.

In the third chapter, we will present a historical review of about fifty potential energy functions for diatomic systems, which have been proposed from 1920 to 2020. A chronological line is presented at the end of this chapter for a better visualization of the evolutionary process of diatomic potentials. We know that in these 100 years of research other functions have been proposed, however, we have chosen the fifty analytical potentials that we consider most relevant. To choose which potentials should be included in this work, we consider the number of different species to which they can be applied and the simplicity in the calculations, prioritizing those that can be obtained directly from experimental data in the literature. Then, for most potentials, it is not necessary to know how to make complex computational calculations to obtain potential energy curves. This review and its results (presented in chapter four) were accepted to publish at International Journal of Quantum Chemistry in November 2020.

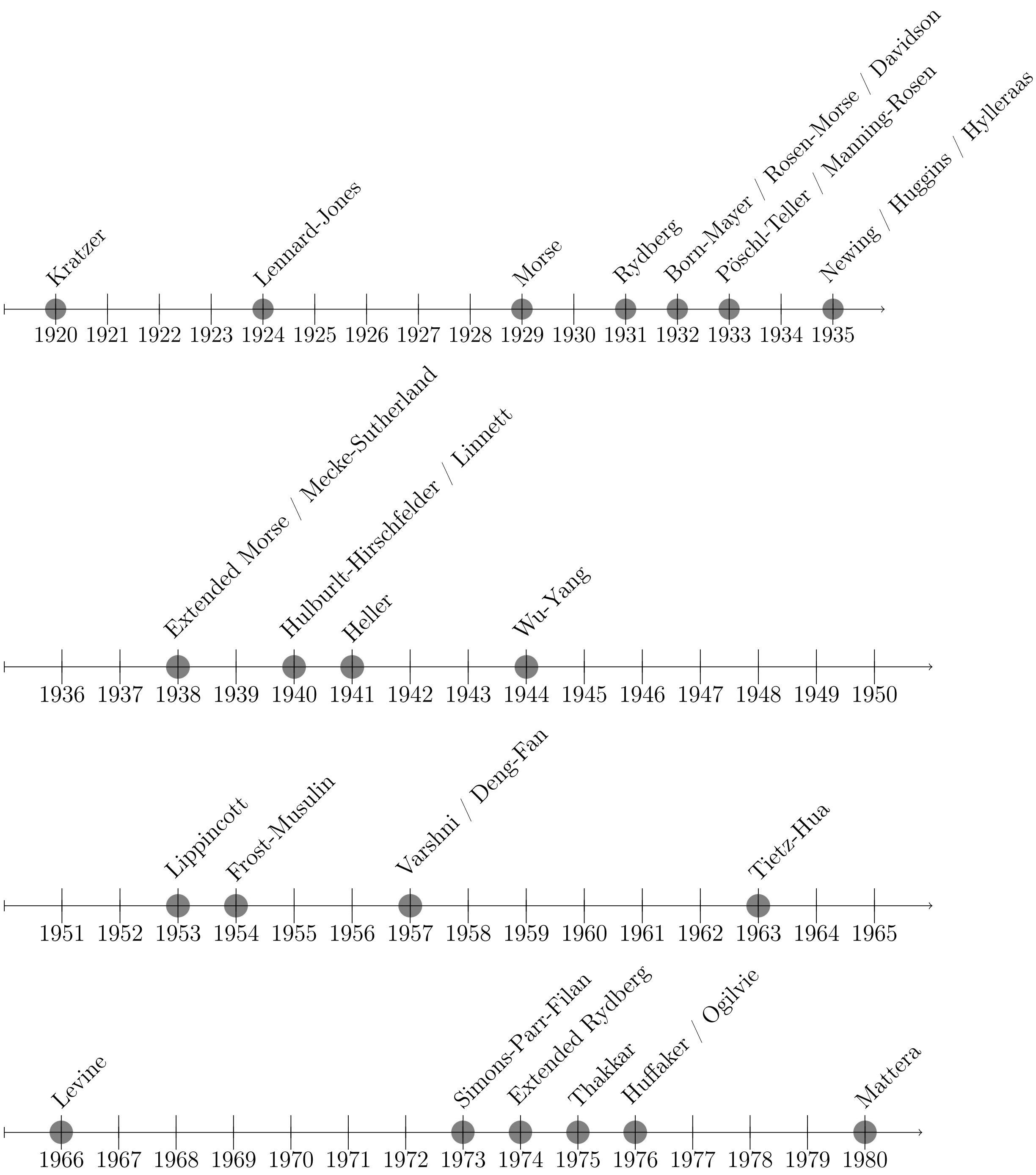
In the fourth chapter, a comparative analyses about all potentials for three diatomic systems, being one homonuclear, one heteronuclear, and one cation in their ground electronic states, they are N_2, CO and HeH^+ will be given. The performance of each potential by comparing them with experimental RKR data will be also presented.

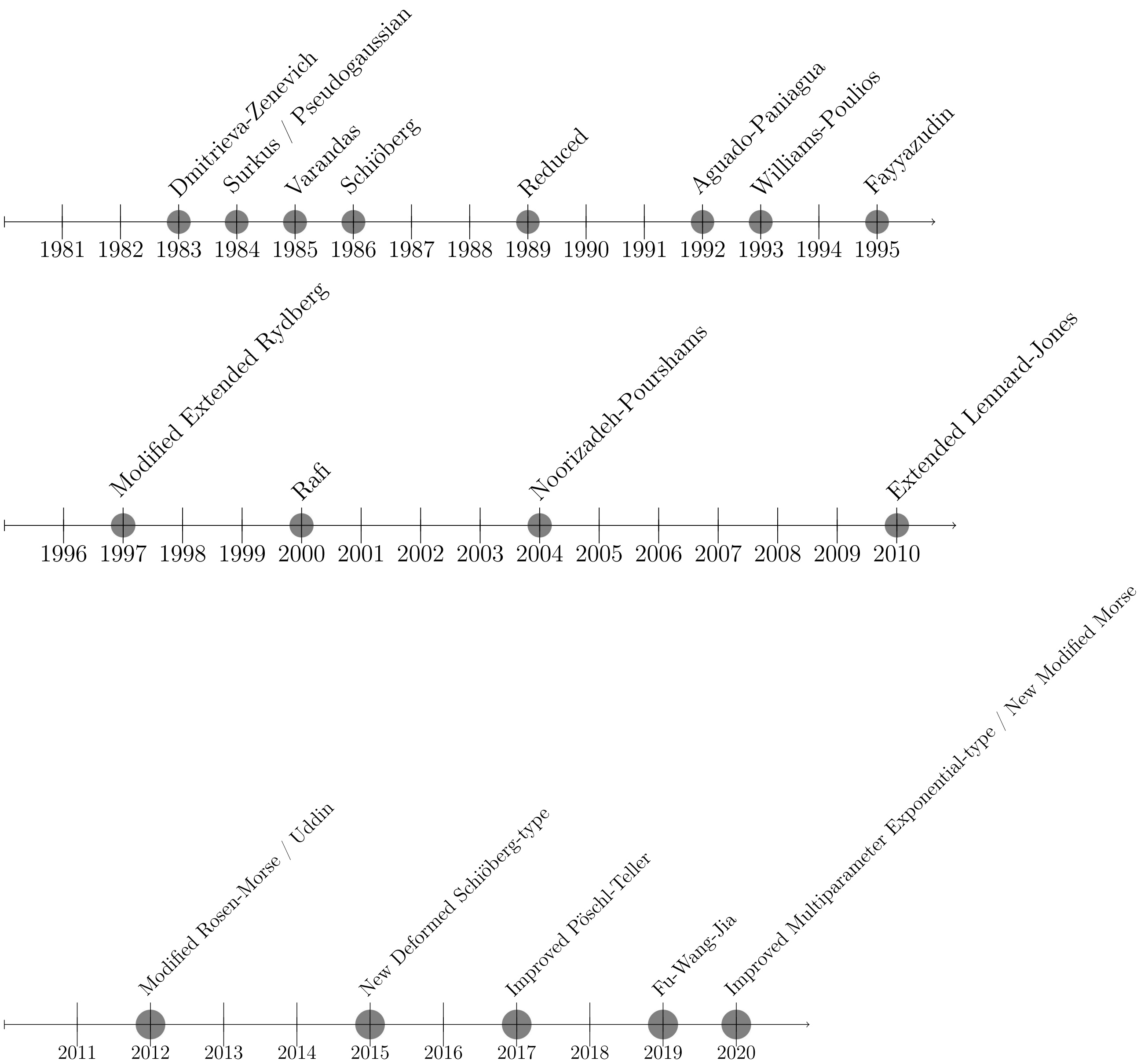
In the fifth chapter, we will present a comparative study between the potential energy functions: Rydberg, Hulburt-Hirschfelder, Murrell-Sorbie, Aguado and Paniagua for O_2, N_2 and SO in their respective ground electronic states. In this case, all potentials were fitted to ab initio points. These results were presented at the 44ª Congreso Internacional de Químicos Teóricos de Expresión Latina (QUITEL 2018), and they are published at Journal of Molecular Modeling [23].

In the sixth chapter, we have described the mathematical way to construct accurate functions to describe the interaction potential energy for diatomic systems. For this, concepts of Mathematical Analysis Theory will be introduced.

Finally, in the seventh chapter we have introduced a new generalized potential energy function for representing the inter-atomic interaction of diatomic systems. The parameters of the function are directly obtained from relations with Dunham's coefficients. The model was tested in 22 cases, comprising both ground and excited states.

Chronology




Dmitrieva-Zenevich
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Varandas
Schiöberg
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Aguado-Paniagua
Williams-Poulios
Fayyazudin
1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995
Modified Extended Rydberg
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Noorizadeh-Pourshams
Extended Lennard-Jones
1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010
Modified Rosen-Morse / Uddin
New Deformed Schiöberg-type
Improved Pöschl-Teller
Fu-Wang-Jia
Improved Multiparameter Exponential-type / New Modified Morse
2011 2012 2013 2014 2015 2016 2017 2018 2019 2020

2 Preliminary

2.1 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is corner stone for quantum mechanically study molecular systems. It introduces the concept of the molecular potential energy surface (PES). The calculations presented in this section follows the formalism from Ref. [2], yet with more mathematical details.

First, let's consider an isolated molecular system composed by electrons and atomic nuclei, the time-dependent Schrödinger equation is written as:

$$i\hbar\frac{\partial}{\partial t}\Phi(\{r_i\},\{R_{\mathrm{I}}\},t) = \mathscr{H}\Phi(\{r_i\},\{R_{\mathrm{I}}\},t) \tag{2.1}$$

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

$$\mathscr{H} = -\textstyle\sum_{\mathrm{I}}\dfrac{\hbar^2}{2M_{\mathrm{I}}}\nabla_{\mathrm{I}}^2 - \textstyle\sum_i\dfrac{\hbar^2}{2m_e}\nabla_{\mathrm{i}}^2 + \dfrac{1}{4\pi\epsilon_0}\textstyle\sum_{i<j}\dfrac{e^2}{|r_i - r_j|} + -\dfrac{1}{4\pi\epsilon_0}\textstyle\sum_{\mathrm{I},i}\dfrac{e^2 Z_{\mathrm{I}}}{|R_{\mathrm{I}} - r_i|}$$
$$+\dfrac{1}{4\pi\epsilon_0}\textstyle\sum_{\mathrm{I}<J}\dfrac{e^2 Z_{\mathrm{I}} Z_J}{|R_{\mathrm{I}} - R_J|} \tag{2.2}$$

for the electronic $\{r_i\}$ and nuclear $\{R_I\}$ degree of freedom. In (2.2), 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:

$$V_{n-e}(\{r_i\},\{R_{\mathrm{I}}\}) = \frac{1}{4\pi\epsilon_0}\sum_{i<j}\frac{e^2}{|r_i - r_j|} + -\frac{1}{4\pi\epsilon_0}\sum_{\mathrm{I},i}\frac{e^2 Z_{\mathrm{I}}}{|R_{\mathrm{I}} - r_i|} + \frac{1}{4\pi\epsilon_0}\sum_{\mathrm{I}<J}\frac{e^2 Z_{\mathrm{I}} Z_J}{|R_{\mathrm{I}} - R_J|} \tag{2.3}$$

and replacing in (2.2), we then have:

$$\mathscr{H} = -\sum_{\mathrm{I}}\frac{\hbar^2}{2M_{\mathrm{I}}}\nabla_{\mathrm{I}}^2 - \sum_i\frac{\hbar^2}{2m_e}\nabla_{\mathrm{I}}^2 + V_{n-e}(\{r_i\},\{R_{\mathrm{I}}\}). \tag{2.4}$$

Calling

$$\mathscr{H}_e(\{r_i\},\{R_{\mathrm{I}}\}) = -\sum_i\frac{\hbar^2}{2m_e}\nabla_{\mathrm{i}}^2 + V_{n-e}(\{r_i\},\{R_{\mathrm{I}}\}) \tag{2.5}$$

we get

$$\mathscr{H} = -\sum_{\mathrm{I}} \frac{\hbar^2}{2M_{\mathrm{I}}}\nabla_{\mathrm{I}}^2 + \mathscr{H}_e(\{r_i\}, \{R_{\mathrm{I}}\}). \tag{2.6}$$

Suppose the exact solution of the corresponding time-independent, *i. e.*, stationary electronic Schrödinger equation:

$$\mathscr{H}_e(\{r_i\}, \{R_{\mathrm{I}}\})\Psi_k = E_k(\{R_{\mathrm{I}}\})\Psi_k(\{r_i\}, \{R_{\mathrm{I}}\}) \tag{2.7}$$

is known for fixed nuclei in all configurations $\{R_I\}$. Assuming the orthonormalization relationship of bound states:

$$\int \Psi_k^*(\{r_i\}, \{R_{\mathrm{I}}\})\Psi_l(\{r_i\}, \{R_{\mathrm{I}}\})dr = \delta_{kl} \tag{2.8}$$

in all possible positions of the nuclei, being the integration performed on all variables $r = r_i$.

Knowing all theses adiabatic eigenfunctions at all possible nuclear configurations, the total wave function can be expanded as:

$$\Phi(\{r_i\}, \{R_{\mathrm{I}}\}, t) = \sum_{l=0}^{\infty} \Psi_l(\{r_i\}, \{R_{\mathrm{I}}\})\chi_l(\{R_{\mathrm{I}}\}, t) \tag{2.9}$$

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

Such expansion is an *ansatz* of the total wave function, introduced by Born in 1951, for the time-independent problem, in order to separate the light electrons from the heavy nuclei [2].

Replacing (2.9) in (2.1):

$$\underbrace{i\hbar\frac{\partial}{\partial t}\sum_{l=0}^{\infty} \Psi_l(\{r_i\}, \{R_{\mathrm{I}}\})\chi_l(\{R_{\mathrm{I}}\}, t)}_{(i)} = \underbrace{\mathscr{H}\sum_{l=0}^{\infty} \Psi_l(\{r_i\}, \{R_{\mathrm{I}}\})\chi_l(\{R_{\mathrm{I}}\}, t)}_{(ii)}. \tag{2.10}$$

Multiplying both sides of the equation by $\Psi_k^*(\{r_i\}, \{R_{\mathrm{I}}\})$ and integrating over r, will have for (i):

$$\begin{aligned} i\hbar\sum_{l=0}^{\infty}\left\{\int \Psi_k^*(\{r_i\}, \{R_{\mathrm{I}}\})\Psi_l(\{r_i\}, \{R_{\mathrm{I}}\})dr\right\}\frac{\partial}{\partial t}\chi_l(\{R_{\mathrm{I}}\}, t) &= i\hbar\delta_{kl}\frac{\partial}{\partial t}\chi_l(\{R_{\mathrm{I}}\}, t) \\ &= i\hbar\frac{\partial}{\partial t}\chi_l(\{R_{\mathrm{I}}\}, t). \end{aligned} \tag{2.11}$$

For (ii), replacing (2.6) in $\mathcal{H}$, multiplying by $\Psi_k^*(\{r_i\},\{R_\mathrm{I}\})$ and integrating over r:

$$\int \Psi_k^* \left(-\sum_\mathrm{I} \frac{\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2 + \mathcal{H}_e\right) \sum_{l=0}^{\infty} \Psi_l \chi_l(\{R_\mathrm{I}\},t)dr =$$
$$= \int \Psi_k^* \left(-\sum_\mathrm{I} \frac{\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2\right) \sum_{l=0}^{\infty} \Psi_l \chi_l(\{R_\mathrm{I}\},t)dr + \int \Psi_k^* \mathcal{H}_e \sum_{l=0}^{\infty} \Psi_l \chi_l(\{R_\mathrm{I}\},t)dr. \tag{2.12}$$

Now whereas $l = k$ and $l \neq k$ and add both possibilities:

$$(ii) = -\sum_\mathrm{I} \frac{\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2 \chi_k(\{R_\mathrm{I}\},t) + E_k(\{R_\mathrm{I}\})\chi_k(\{R_\mathrm{I}\},t) +$$
$$\underbrace{\sum_{l=0}^{\infty} \int \Psi_k^* \left[-\sum_\mathrm{I} \frac{\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2\right] (\Psi_l \chi_l(\{R_\mathrm{I}\},t))dr}_{(*)} + \sum_{l=0}^{\infty} \int \Psi_k^* E_l(\{R_\mathrm{I}\})\Psi_l \chi_l(\{R_\mathrm{I}\},t)dr. \tag{2.13}$$

Calculating $(*)$ will have:

$$\sum_{l=0}^{\infty} \int \Psi_k^* \sum_\mathrm{I} \frac{-\hbar^2}{2M_\mathrm{I}} \left[\nabla_\mathrm{I}^2 \Psi_l \cdot \chi_l + 2\nabla_\mathrm{I}\Psi_l \nabla_\mathrm{I}\chi_l + \Psi_l \nabla_\mathrm{I}^2 \chi_l\right] dr =$$
$$= \sum_{l=0}^{\infty} \int \Psi_k^* \left(\sum_\mathrm{I} \frac{-\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2 \Psi_l\right) \chi_l dr + \sum_{l=0}^{\infty} \int \Psi_k^* \sum_\mathrm{I} \frac{-\hbar^2}{M_\mathrm{I}} (\nabla_\mathrm{I}\Psi_l)(\nabla_\mathrm{I}\chi_l)dr + \tag{2.14}$$
$$+ \sum_{l=0}^{\infty} \int \Psi_k^* \sum_\mathrm{I} \frac{-\hbar^2}{M_\mathrm{I}} \Psi_l \nabla_\mathrm{I}^2 \chi_l dr.$$

Returning to (ii):

$$(ii) = \left(-\sum_\mathrm{I} \frac{\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2 + E_k(\{R_\mathrm{I}\})\right) \chi_k(\{R_\mathrm{I}\},t) + \sum_{l=0}^{\infty} \int \Psi_k^* \left(\sum_I \frac{-\hbar^2}{2M_I}\nabla_I^2 \Psi_l\right) \chi_l dr +$$
$$+ \sum_{l=0}^{\infty} \int \Psi_k^* \sum_\mathrm{I} \frac{-\hbar^2}{M_\mathrm{I}} (\nabla_\mathrm{I}\Psi_l)(\nabla_\mathrm{I}\chi_l)dr, \tag{2.15}$$

and calling in (ii):

$$c_{kl} = \int \Psi_k^* \left(\sum_\mathrm{I} \frac{-\hbar^2}{2M_\mathrm{I}}\nabla_\mathrm{I}^2 \Psi_l\right) dr + \frac{1}{M_\mathrm{I}} \sum_\mathrm{I} \left[\int \Psi_k^* (-i\hbar\nabla_\mathrm{I})\Psi_l dr\right] (-i\hbar\nabla_\mathrm{I}) \tag{2.16}$$

which is the exact non-adiabatic operator coupled.

Equation (2.1) then becomes:

$$\left(-\sum_{\mathrm{I}} \frac{\hbar^2}{2M_{\mathrm{I}}}\nabla_{\mathrm{I}}^2 + E_k(\{R_{\mathrm{I}}\})\right)\chi_k + \sum_{l=0}^{\infty} c_{kl}\chi_l = i\hbar\frac{\partial}{\partial t}\chi_k \tag{2.17}$$

The first approximation for this problem is the so-called "adiabatic approximation", which consists of considering only the diagonal terms c_{kk} of the matrix, which represents a correction of the eigenvalues E_k of the electronic equation of Schrödinger (2.7) in the Kth state

$$c_{kk} = -\sum_{\mathrm{I}} \frac{-\hbar^2}{2M_{\mathrm{I}}} \int \Psi_k^* \nabla_{\mathrm{I}}^2 \Psi_k dr, \tag{2.18}$$

where the second term of (2.16) is zero when the electronic wave functions is real.

From there, we will have:

$$\left(-\sum_{\mathrm{I}} \frac{\hbar^2}{2M_{\mathrm{I}}}\nabla_{\mathrm{I}}^2 + E_k(\{R_{\mathrm{I}}\}) + c_{kk}(\{R_{\mathrm{I}}\})\right)\chi_k = i\hbar\frac{\partial}{\partial t}\chi_k, \tag{2.19}$$

and this set of decoupled differential equations leads to the fact that the motion of the nuclei occurs without changing the quantum state k during the time evolution.

Thus, the wave function $\Phi(\{r_i\},\{R_{\mathrm{I}}\};t)$: can be decoupled as a single product of an electron and a nuclear wave equation:

$$\Phi(\{r_i\},\{R_{\mathrm{I}}\};t) \approx \Psi_k(\{r_i\},\{R_{\mathrm{I}}\}) \cdot \chi_k(\{R_{\mathrm{I}}\};t). \tag{2.20}$$

The last and most famous simplification to be made known as the Born-Oppenheimer approximation is to neglect the terms of the coupled diagonal, so that equation (2.1) becomes

$$\left(-\sum_{\mathrm{I}} \frac{\hbar^2}{2M_{\mathrm{I}}}\nabla_{\mathrm{I}}^2 + E_k(\{R_{\mathrm{I}}\})\right)\chi_k = i\hbar\frac{\partial}{\partial t}\chi_k. \tag{2.21}$$

Both, the adiabatic and the Born-Oppenheimer approximation are only possible due to the *ansatz* proposed by Born, which is what will lead to the decoupling of the nuclear and electronic movements, allowing to calculate them separately.

The next step is to show that nuclei can be approximated to classical point particles. For this, we will make the traditional way to extract the semi-classical mechanic from the quantum mechanic. To do this, consider the corresponding wave function:

$$\chi_k(\{R_{\mathrm{I}}\};t) = A_k(\{R_{\mathrm{I}}\};t) \cdot \exp\{[iS_k(\{R_{\mathrm{I}}\};t)/\hbar)]\} \tag{2.22}$$

where the amplitude factor $A_k > 0$ and the phase S_k are real.

Substituting (2.22) into (2.21) we will have the real and imaginary parts for the nuclei given by:

$$\mathrm{Re}\{\chi_k\} : \frac{\partial S_k}{\partial t} + \sum_{\mathrm{I}} \frac{1}{2M_{\mathrm{I}}}(\nabla_{\mathrm{I}} S_k)^2 + E_k = \hbar^2 \sum_{\mathrm{I}} \frac{1}{2M_{\mathrm{I}}} \frac{{\nabla_{\mathrm{I}}}^2 A_k}{A_k} \tag{2.23}$$

$$\mathrm{Im}\{\chi_k\} : \frac{\partial A_k}{\partial t} + \sum_{\mathrm{I}} \frac{1}{M_{\mathrm{I}}}(\nabla_{\mathrm{I}} A_k)(\nabla_{\mathrm{I}} S_k) + \sum_{\mathrm{I}} \frac{1}{2M_{\mathrm{I}}} A_k({\nabla_{\mathrm{I}}}^2 S_k) = 0. \tag{2.24}$$

Multiplying $\mathrm{Im}\{\chi_k\}$by $2A_k$:

$$2A_k \frac{\partial A_k}{\partial t} + \sum_{\mathrm{I}} \frac{1}{M_{\mathrm{I}}} 2A_k(\nabla_{\mathrm{I}} A_k)(\nabla_{\mathrm{I}} S_k) + \sum_{\mathrm{I}} \frac{1}{M_{\mathrm{I}}} {A_k}^2({\nabla_{\mathrm{I}}}^2 S_k) = 0 \tag{2.25}$$

which can be rewritten as a continuity equation:

$$\frac{\partial {A_k}^2}{\partial t} + \sum_{\mathrm{I}} \frac{1}{M_{\mathrm{I}}} \nabla_{\mathrm{I}}({A_k}^2 \nabla_{\mathrm{I}} S_k) = 0 \tag{2.26}$$

Identifying the nuclear probability density ρ_k which derives directly from equation (2.22), and with the associated current density $J_{k,\mathrm{I}}$, given by

$$\rho_k = |\chi_k|^2 \equiv {A_k}^2 \tag{2.27}$$

and

$$J_{k,\mathrm{I}} = {A_k}^2(\nabla_{\mathrm{I}} S_k)/M_{\mathrm{I}}. \tag{2.28}$$

Thus, the equation (2.26) can be written as

$$\frac{\partial \rho_k}{\partial t} + \sum_{\mathrm{I}} \nabla_{\mathrm{I}} J_{k,\mathrm{I}} = 0. \tag{2.29}$$

In the $\mathrm{Re}\{\chi_k\}$ part, there is the dependency with $\hbar$, but in the classic limit $\hbar \to 0$, then

$$\mathrm{Re}\{\chi_k\} : \frac{\partial S_k}{\partial t} + \sum_{\mathrm{I}} \frac{1}{2M_{\mathrm{I}}}(\nabla_{\mathrm{I}} S_k)^2 + E_k = 0. \tag{2.30}$$

This equation is isomorphic to the equation of motion in the formulation in the Hamilton-Jacobi of classical mechanics,

$$\frac{\partial S_k}{\partial t} + H_k(\{R_{\mathrm{I}}\}, \{\nabla_{\mathrm{I}} S_k\}) = 0. \tag{2.31}$$

In the classic Hamilton function

$$H_k(\{R_\text{I}\}, \{\nabla_\text{I} S_k\}) = T(\{P_\text{I}\}) + V_K(\{R_\text{I}\}) \tag{2.32}$$

we associate

$$\sum_\text{I} \frac{1}{2M_\text{I}}(\nabla_\text{I} S_k)^2 \leftrightarrow T(\{P_\text{I}\}) \quad \text{and} \quad E_k \leftrightarrow V_K(\{R_\text{I}\}). \tag{2.33}$$

For a given conservative energy $dE_k^{tot}/dt = 0$, defined in terms of the coordinates $\{R_\text{I}\}$ and its conjugated canonical moments $\{P_\text{I}\}$, then we will have

$$\frac{\partial S_k}{\partial t} = -(T + E_k) = -E_k{}^{tot} = \text{cte}. \tag{2.34}$$

Now, with the help of connection transformation

$$P_\text{I} \equiv \nabla_\text{I} S_k \quad \left[= \frac{M_\text{I} J_{k,\text{I}}}{\rho_k}\right] \tag{2.35}$$

the Newton equations of motion corresponding to the Hamilton-Jacobi equation form,

$$\dot{P}_\text{I} = -\nabla_\text{I} V_k(\{R_\text{I}\}) \tag{2.36}$$

can be rewritten as

$$\dot{P}_\text{I} = -\nabla_\text{I} E_k. \tag{2.37}$$

Now, using that

$$\dot{R}_\text{I} = \frac{\partial H}{\partial P_\text{I}} = \frac{\partial\left[T(\{P_\text{I}\}) + V_K(\{R_\text{I}\})\right]}{\partial P_\text{I}} = \frac{dT(\{P_\text{I}\})}{dP_\text{I}} \tag{2.38}$$

then

$$\begin{aligned}\ddot{R}_\text{I} = \frac{d}{dt}\frac{dT(\{P_\text{I}\})}{dP_\text{I}} &= \frac{d}{dt}\left[\frac{d\left(\sum_\text{I} \frac{1}{2M_\text{I}}(\nabla_\text{I} S_k)^2\right)}{d\nabla_\text{I} S_k}\right] \\ &= \sum_\text{I} \frac{1}{M_\text{I}}\frac{d}{dt}\nabla_\text{I} S_k \\ &= \sum_\text{I} \frac{1}{M_\text{I}}\frac{dP_\text{I}}{dt}.\end{aligned} \tag{2.39}$$

Then, as

$$\dot{P}_\text{I} = \frac{dP_\text{I}}{dt} = -\nabla_\text{I} E_k \tag{2.40}$$

for a configuration I, we will have:

$$\ddot{R}_{\mathrm{I}} = \frac{1}{M_{\mathrm{I}}}\frac{dP_{\mathrm{I}}}{dt} = -\frac{1}{M_{\mathrm{I}}}\nabla_{\mathrm{I}}E_k \\ \Rightarrow M_{\mathrm{I}}\ddot{R}_{\mathrm{I}} = -\nabla_{\mathrm{I}}E_k \tag{2.41}$$

i.e.,

$$M_{\mathrm{I}}\ddot{R}_{\mathrm{I}}(t) = -\nabla_{\mathrm{I}}V_k^{BO}(\{R_{\mathrm{I}}(t)\}). \tag{2.42}$$

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 $\{R_{\mathrm{I}}(t)\}$, 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.

2.2 The Dunham Expansion

In 1932, thinking of providing a method for the direct quantitative study of molecular structure from the spectra of bands of diatomic molecules, Dunham [24] vastly explored the theory of the rotanting vibrator. He calculated the energy levels of this system in considerable detail by means of the method Wentzel-Kramers-Brillouin (WKB) [25–27]. For such, firstly Dunham obtained the characteristics values of Schrödinger's equation for this system, which is:

$$\frac{d^2\psi}{d\xi^2} + \frac{8\pi^2\mu R_e^2}{\hbar^2}\left[E(I,\kappa) - V - \frac{\kappa}{{R_e}^2(1-\xi)^2}\right]\psi = 0, \tag{2.43}$$

where $\xi = (R - R_e)/R_e$, being R_e the equilibrium nuclear separation; μ is reduced nuclear mass; V the potential function with minimum at R_e. Here $\kappa = \frac{\hbar^2 J(J+1)}{8\pi^2\mu}$ and the last term in (2.43) will be call by $V_r = \frac{\kappa}{{R_e}^2(1-\xi)^2}$, being V_r the potential centrifugal. The term $E(I,\kappa)$ is the vibrational and rotational energy expressed as a function of the action I and the square of the angular momentum κ.

The Morse [8] potential at this time, 1932, was the most used to obtain energy levels since it was the only potential that solved exactly the Schrodinger equation, which provided very good precision for such levels. However, to include the rotational effect on its potential was not easy.

Dunham [24] (DUN) then proposes to expand the potential V in a power series around the point $\xi = 0$, since the rotational term V_r has a simple expansion about this point, first neglecting the rotation, *i. e.* for $J = 0$:

$$V_{DUN} = \hbar c a_0 \xi^2(1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots) \tag{2.44}$$

where $a_0 = \omega_e^2/4B_e$, being ω_e the classical frequency of small oscillations and $B_e = \hbar/(8\pi^2\mu R_e^2 c)$, with μ the reduced mass of the diatomic molecule, c the speed of light and $\hbar$ the Planck constant.

Now, taking into account the rotation, and in order to express all the quantities involving energy in terms of wave numbers, Dunham considered $E(I,\kappa) = \hbar c F(\nu, J)$ and $V = \hbar c U$, so that the effective potential function become $U + U_r = U_J$,

$$U_J = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots) + B_e J(J+1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots). \quad (2.45)$$

where

$$U = a_0\xi^2(1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots) \quad (2.46)$$

and

$$U_r = B_e J(J+1)(1 - 2\xi + 3\xi^2 - 4\xi^3 + \cdots). \quad (2.47)$$

Dunham then proceeds to solve equation (2.43) by the WBK method, and obtains an expression for the energy as a doubly infinite power series in the quantum numbers vibrational ν and rotational J:

$$F_{\nu J} = \sum_{lj} Y_{lj} \left(\nu + \frac{1}{2}\right)^l J^j (J+1)^j. \quad (2.48)$$

Dunham calculated the first fifteen Y_{lj} and showed that the coefficients of the various powers of $(\nu + \frac{1}{2})$ e $J(J+1)$ in the energy level formula are a series in powers of the ratio ${B_e}^2/{\omega_e}^2$. By relating the Y_{lj} to the coefficients of Bohr's theory he noticed that these are not exactly equal, differing by for ${B_e}^2/{\omega_e}^2$ in the case of the coefficient Y_{10} of $(\nu + \frac{1}{2})$ that is not equal to ω_e, the same happens with the others Y_lj. Thus:

$$\begin{array}{ccc} Y_{10} \sim \omega_e & Y_{20} \sim -\omega_e x_e & Y_{30} \sim \omega_e y_e \\ Y_{01} \sim B_e & Y_{11} \sim -\alpha_e & Y_{21} \sim \gamma_e \\ Y_{02} \sim D_e & Y_{12} \sim \beta_e & Y_{40} \sim \omega_e z_e \\ Y_{03} \sim F_e & Y_{04} \sim H_e & \end{array} \quad (2.49)$$

With the possible exception of hydrides, the Y_{lj}'s in (2.48) are equal to the related spectroscopic constants. Thus, since the Y_{lj}'s are determined from the experimental data, the potential function based on this data can be determined from Eq. (2.45).

Thus, the experimentally determined molecular levels are given for:

$$\begin{aligned} \tfrac{E(\nu,J)}{\hbar c} &= \omega_e\left(\nu + \tfrac{1}{2}\right) - \omega_e x_e \left(\nu + \tfrac{1}{2}\right)^2 + \omega_e y_e \left(\nu + \tfrac{1}{2}\right)^3 \\ &- \omega_e z_e \left(\nu + \tfrac{1}{2}\right)^4 + \cdots + B_\nu J(J+1) - D_\nu J^2(J+1)^2 + \cdots \end{aligned} \quad (2.50)$$

with $B_\nu = B_e - \alpha_e\left(\nu + \frac{1}{2}\right) + \gamma_e\left(\nu + \frac{1}{2}\right)^2$ and $D_\nu = D_e + \beta_e\left(\nu + \frac{1}{2}\right)$.

Dunham related the coefficients Y_{lj} with the a_i's coefficients of potential U_J. Some these spectroscopic parameters are:

$$
\begin{aligned}
Y_{10} &= \omega_e \left[1 + \tfrac{B_e^2}{4\omega_e^2}\left(25a_4 - \tfrac{95a_1a_3}{2} - \tfrac{67a_2^2}{4} + \tfrac{459a_1^2a_2}{8} - \tfrac{1155a_1^4}{64}\right)\right] \\
Y_{20} &= \left(\tfrac{B_e}{2}\right)\left[3\left(a_2 - \tfrac{5a_1^2}{4}\right) + \tfrac{B_e^2}{2\omega_e^2}\left(245a_6 - \tfrac{1465a_1a_5}{2} - \tfrac{885a_2a_4}{2} - \tfrac{1085a_3^2}{4} + \tfrac{8535a_1^2a_4}{8} + \tfrac{1707a_2^3}{8}\right.\right. \\
&\quad \left.\left. + \tfrac{7335a_1a_2a_3}{4} - \tfrac{23865a_1^3a_3}{16} - \tfrac{62013a_1^2a_2^2}{32} + \tfrac{239985a_1^4a_2}{128} - \tfrac{209055a_1^6}{512}\right)\right] \\
Y_{30} &= \left(\tfrac{B_e^2}{2\omega_e}\right)\left[10a_4 - 35a_1a_3 - \tfrac{17a_2^2}{2} + \tfrac{225a_1^2a_2}{4} - \tfrac{705a_1^4}{32}\right] \\
Y_{11} &= \left(\tfrac{B_e^2}{\omega_e}\right)\left[6(1+a_1) + \left(\tfrac{B_e^2}{\omega_e^2}\right)\left(175 + 285a_1 - \tfrac{335a_2}{2} + 190a_3 - \tfrac{225a_4}{2} + 175a_5 + \tfrac{2295a_1^2}{8}\right.\right. \\
&\quad -459a_1a_2 + \tfrac{1425a_1a_3}{4} - \tfrac{795a_1a_4}{2} + \tfrac{1005a_2^2}{8} - \tfrac{715a_2a_3}{2} + \tfrac{1155a_1^3}{4} - \tfrac{9639a_1^2a_2}{16} + \tfrac{5145a_1^2a_3}{8} \\
&\quad \left.\left. + \tfrac{4677a_1a_2^2}{8} - \tfrac{14259a_1^3a_2}{16} + 31185\tfrac{(a_1^4+a_1^5)}{128}\right)\right] \\
Y_{21} &= \left(\tfrac{6B_e^2}{\omega_e^2}\right)\left[5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 + 15\tfrac{(a_1^2+a_1^3)}{2}\right].
\end{aligned} \tag{2.51}
$$

Since in this work we are interested in potential functions dependent on R and not ν, let suppose that any function can be expanded in the Taylor series, around the equilibrium position R_e, so that the potential for diatomic systems is written as:

$$
V = V(R_e) + \left(\frac{dV}{d_R}\right)_{R=R_e}(R-R_e) + \frac{1}{2!}\left(\frac{d^2V}{d_R^2}\right)_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{d_R^3}\right)_{R=R_e}(R-R_e)^3 + \frac{1}{4!}\left(\frac{d^4V}{d_R^4}\right)_{R=R_e}(R-R_e)^4 + \cdots \tag{2.52}
$$

where,

$$
\left(\frac{dV}{d_R}\right)_{R=R_e}(R-R_e) = 0 \tag{2.53}
$$

since R_e is the minimum of the potential.

Now, doing $\rho = R - R_e$ and $f_n = \left(\frac{d^nV}{dR^n}\right)_{R=R_e}$, we have:

$$
V = V(0) + \frac{1}{2}f_2\rho^2 + \frac{1}{6}f_3\rho^3 + \frac{1}{24}f_4\rho^4 + \cdots . \tag{2.54}
$$

Then, we can explicit the coefficients a_n in terms of derivatives of potential V, by relating (2.44) and (2.54):

$$\begin{aligned} a_0 &= \tfrac{f_2 R_e^2}{2\hbar c} \qquad a_1 = \tfrac{R_e f_3}{12\pi^2 c^2 \omega_e^2 \mu} \qquad a_2 = \tfrac{R_e^2 f_4}{48\pi^2 c^2 \omega_e^2 \mu} \\ a_3 &= \tfrac{R_e^3 f_5}{240\pi^2 c^2 \omega_e^2 \mu} \quad a_4 = \tfrac{R_e^4 f_6}{240\pi^2 c^2 \omega_e^2 \mu} \quad a_5 = \tfrac{R_e^5 f_7}{10080\pi^2 c^2 \omega_e^2 \mu} \cdots . \end{aligned} \tag{2.55}$$

Substituting $a_0 = \omega_e^2/4B_e$ and $B_e = \hbar/(8\pi^2 \mu R_e^2 c)$ for f_2, we have

$$f_2 = \left(\frac{d^2V}{d_R^2}\right)_{R=R_e} = 4\pi^2 \mu c^2 \omega_e^2 = k_e \tag{2.56}$$

where k_e is the force constant.

Two other parameters that will be displayed for all potentials described in this work can be easily obtained by the following relationships with those derived from the potential:

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{R_e f_3}{3f_2}\right) \tag{2.57}$$

representing the vibrational rotational coupling parameter, and

$$\omega_e x_e = \left[\frac{15}{8}\left(\frac{f_3}{f_2}\right)^2 - \frac{3}{2}\left(\frac{f_4}{f_2}\right)\right]\frac{\hbar}{8\pi^2 c\mu} = \left[\frac{5}{3}\left(\frac{f_3}{f_2}\right)^2 - \left(\frac{f_4}{f_2}\right)\right]\frac{2.1078 \times 10^{-16}}{\mu} \tag{2.58}$$

representing the anharmonicity parameter.In addiction, the frequency ω_e can be obtained from:

$$\omega_e = \left(\frac{4B_e f_2 R_e^2}{2\hbar c}\right)^{1/2}. \tag{2.59}$$

The theoretical work of Dunham depends on the validity of its expression for the potential (2.44), and it is necessary to evaluate if a molecular model with this form of potential expression can represent a molecular behavior. Two questions arise [28]:

1. Even if V is expressible near $\xi = 0$ by such an expression, it does not necessarily follow that the series will converge over the whole range covered by the vibrational motion;

2. Since V = const., for $R \to \infty$, a model in which V is represented by a power series is not necessarily the most suitable approximation to use.

To justify the method employed by Dunham, Sandeman [28] by expanding into power series of ξ such as in (2.44), two of the most well known and important potentials of the time, Morse [8] and Kratzer [16], he showed that both were convergent to all values which ξ assumes.

In order to establish criteria for which the expansion of Dunham converges, Sandeman [28] applying the Gauss's test, he verified that the maximum value of ξ, which we will call $\overline{\xi}$ during the motion should be given by the approximation:

$$\overline{\xi}^2 = \left(\nu + \frac{1}{2}\right) u_e \tag{2.60}$$

where $u_e = \frac{2B_e}{\omega_e}$.

Since B_e is inversely proportional to the reduced mass μ, for most H_2 states u_e is considered to be large when compared to any other molecule.

This does not prejudice the validity of the Dunham expansion for this type of molecule, however, the convergence of the series will be slower, which is not desirable to obtain good approximation results.

Thus, experimental functions can be developed based on any mathematical functions of ξ, which, when expanded as power series in ξ, do not contain the first power. Since the series converged, this was the most flexible way to represent a potential, taking into account the functions available at the time, which had a maximum of three constants, such as the Rosen-Morse [29] and Pöschl-Teller [30] functions.

The Dunham method is sufficient in the order to demonstrate the relation of the various spectroscopic constants used in describing the observed energy levels of a non-rigid, rotating, anharmonic oscillator to the parameters of any empirical function which may be expanded in a power series in $(R - R_e)$ [15].

The method of expansion of Dunham was highlighted by presenting good accuracy in the region of the minimum in the potential energy curve. However, the method should be used with caution at higher vibrational levels as it diverges as the energy approaches the dissociation limit [24].

2.3 The Rydberg-Klein-Rees (RKR) method

The Rydberg method [9], which will be presented in more detail in section 3.1.4, is a graphic procedure, quite laborious and, although efficient to represent certain diatomic systems at the time, does not present good accuracy for low vibrational levels. Klein [10] proposes modifications in the Rydberg method, introducing a more practical and accurate way of obtaining the PECs. He expressed the two internuclear distances maximum and minimum respectively for R_1 and R_2, corresponding to the given potential energy (effective) of a diatomic molecule vibrating with an energy U as

$$R_{1,2}(U) = (f/g + f^2)^{\frac{1}{2}} \pm f, \tag{2.61}$$

where f and g are the partials derivatives of an integral S,

$$f = \frac{\partial S}{\partial U} \tag{2.62}$$

and

$$g = -\frac{\partial S}{\partial \kappa} \tag{2.63}$$

S is a function of the energy and the angular moment of the molecule, given by:

$$S(U, \kappa) = \frac{1}{\pi\sqrt{2\mu}} \int_0^{I'} \sqrt{U - E(I, \kappa)} dI, \tag{2.64}$$

being $E(I, \kappa)$ the sum of the vibrational and rotational energy of the molecule, with

$$I = \hbar\left(\nu + \frac{1}{2}\right) \tag{2.65}$$

and

$$\kappa = \left(\frac{\hbar^2}{8\pi^2\mu}\right) J(J+1) \tag{2.66}$$

which are the expressions quantum-mechanics equivalents of the classical quantities I and κ.

Here, ν and J are the vibrational and the rotational quantum numbers respectively, μ is the reduced mass of the molecule, and $I = I'$ when $U = E$.

According to Klein [10], the knowledge of the quantities f and g for a value of κ and different values of U gives directly the solution to the problem initially placed because the definition of these quantities follows immediately

$$R_1(U) = \sqrt{\frac{f}{g} + f^2} + f \quad \text{and} \quad R_2(U) = \sqrt{\frac{f}{g} + f^2} - f \tag{2.67}$$

in which the potential curve is determined on both sides of the minimum. As you can see, the minimum of this curve is, as it should, at the point $I = 0$, corresponding to a movement in which the two nuclei rotate in circular motions.

In fact, Klein [10] obtained the expressions for f and g from the period of vibration au_ν and of $\left(\overline{\frac{1}{R^2}}_\nu\right)$, as well as the Rydberg method (see the section 3.1.4) . The integral S was introduced for mathematical convenience and has a relevant graphical interpretation in the Klein method since it represents half the area between the total constant energy U and the effective potential energy curve, as shown by Vanderslice, Mason, Maisch, and Lippincott [31].

Klein [10] then reduced the problem to the solution of two integral equations:

$$f(U) = \frac{1}{2\pi\sqrt{2\mu}} \int_0^{I'} \frac{dI}{\sqrt{U - E(I, \kappa)}} \tag{2.68}$$

and

$$g(U) = \frac{1}{2\pi\sqrt{2\mu}} \int_0^{I'} \frac{(\partial E / \partial \kappa) dI}{\sqrt{U - E(I, \kappa)}} \tag{2.69}$$

whereas

$$f = \frac{1}{2}(R_{\max} - R_{\min}) \tag{2.70}$$

and

$$g = \frac{1}{2}\left(\frac{1}{R_{\min}} - \frac{1}{R_{\max}}\right) \tag{2.71}$$

However, the solution of Klein [10] for S, as well as of f and g, could only be obtained numerically, having a high computational cost for the time [32].

In 1947, Rees [11] suggested that the expression to be integrated (2.64) was known, since the energy $E(I,\kappa)$ can be expressed in terms of quantum numbers ν and J, and the derived spectroscopic constants ω_e, $\omega_e x_e$,$\omega_e y_e$,B_e, α_e and D_e are given by the accuracy of the experimental data. Then f and g could be calculated and $R(U)$ can be obtained in terms of such spectroscopic constants, as was desirable. In this way, he proposed to write $E(I,\kappa)$ as a quadratic in $I = \hbar(\nu + 1/2)$, using the expansion of Dunham for energy (2.50):

$$E(I,\kappa) = E(\nu,J) = \omega_e\left(\nu+\tfrac{1}{2}\right) - \omega_e x_e\left(\nu+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(\nu+\tfrac{1}{2}\right)^3 + B_e J(J+1)$$
$$+D_e J^2(J+1)^2 - \alpha_e J(J+1)\left(\nu+\tfrac{1}{2}\right)\cdots \tag{2.72}$$

which is the total energy of the nuclear motion, assuming the Born-Oppenheimer approximation [33], and can be expressed by $E(\nu,J) = E(\nu) + E(J)$, where

$$E(\nu) = \omega_e\left(\nu+\frac{1}{2}\right) - \omega_e x_e\left(\nu+\frac{1}{2}\right)^2 + \omega_e y_e\left(\nu+\frac{1}{2}\right)^3\cdots \tag{2.73}$$

and

$$E(J) = B_e J(J+1) + D_e J^2(J+1)^2 - \alpha_e J(J+1)\left(\nu+\frac{1}{2}\right)\cdots. \tag{2.74}$$

Substiting (2.72) in (2.64), considering only the three fist terms of $E(I,\kappa)$ already introducing the variable I and κ, we have:

$$\begin{aligned} S(U,\kappa) &= \tfrac{1}{\pi\sqrt{2\mu\hbar}}\int_0^{I'}\{\hbar[U - B_e J(J+1) - D_e J^2(J+1)^2] - [\omega_e - \alpha_e J(J+1)]I \\ &+ \left[\tfrac{\omega_e x_e}{\hbar}\right] I^2\}^{\frac{1}{2}}\,dI, \end{aligned} \tag{2.75}$$

which leads to the following expressions for f and g for the rotationaless state ($J = 0$):

$$f = \left(\frac{\hbar}{8\pi^2 c\mu\omega_e x_e}\right)^{\frac{1}{2}}\log e\left\{\frac{({\omega_e}^2 - 4\omega_e x_e U)^{\frac{1}{2}}}{\omega_e - (4\omega_e x_e U)^{\frac{1}{2}}}\right\} \tag{2.76}$$

and

$$g=\left(\frac{2\pi^2\mu c}{\hbar(\omega_e x_e)^3}\right)^{\frac{1}{2}}\left[\alpha_e(4\omega_e x_e U)^{\frac{1}{2}}+(2\omega_e x_e B_e-\alpha_e\omega_e)\log e\left\{\frac{({\omega_e}^2-4\omega_e x_e U)^{\frac{1}{2}}}{\omega_e-(4\omega_e x_e U)^{\frac{1}{2}}}\right\}\right]. \tag{2.77}$$

being c is the speed of light.

Expressions for the energy of dissociation D and for the distance of equilibrium R_e were also determined by Rees [11]:

$$D=\frac{{\omega_e}^2}{4\omega_e x_e} \tag{2.78}$$

and

$$R_e=\left(\frac{\hbar}{8\pi^2 c B_e\mu}\right)^{\frac{1}{2}}. \tag{2.79}$$

Rees further considered the case where $E(I,\kappa)$ is expressed as a cubic in I, however, we will not cover it here (for more details see Ref. [11]).

Vanderslice, Mason, Lippincott and Maish [31] extended the study of Rees, taking into account that in most cases, energy $E(I,\kappa)$ can not be represented throughout the experimental range by expression (2.72). Thus, they proposed to represent it as a series of quadratics covering the interval in different regions. Thus, the integral S in Eq.(2.75) should be written as:

$$\begin{aligned} S(U,\kappa) &= \tfrac{1}{\sqrt{2\pi^2\mu\hbar}}\textstyle\sum_{i=1}^{n}\int_{I_{i-1}}^{I_i}\{\hbar[U-B_iJ(J+1)-D_iJ^2(J+1)^2]-[\omega_i-\alpha_iJ(J+1)]I \\ &+ \left[\tfrac{(\omega x)_i}{\hbar}\right]I^2\Big\}^{\frac{1}{2}}dI \end{aligned} \tag{2.80}$$

where $I_0=0$ and $I_n=I'$ and the sum extends over the vibrational energy levels.

From (2.80), for $J=0$, the expressions for f and g will now be given by [31]:

$$f=\sqrt{\frac{\hbar}{8\pi^2\mu c}}\sum_{i=1}^{n}\frac{\ln W_i}{\sqrt{(\omega x)_i}} \tag{2.81}$$

and

$$g=\sqrt{\frac{2\pi^2\mu c}{\hbar}}\sum_{i=1}^{n}\left[\frac{\alpha_i\left(\sqrt{U_i}-\sqrt{U_{i-1}}\right)}{4(\omega x)_i}+\frac{\left(2B_i-\alpha_i{(\omega x)_i}^{-1}\omega_i\right)\ln W_i}{\sqrt{(\omega x)_i}}\right] \tag{2.82}$$

being

$$W_i=\sqrt{\frac{{\omega_i}^2-4(\omega x)_iU_i}{{\omega_i}^2-4(\omega x)_iU_{i-1}}}\left[\frac{\omega_i-2\sqrt{(\omega x)_i}\sqrt{U_{i-1}}}{\omega_i-2\sqrt{(\omega x)_i}\sqrt{U_i}}\right] \tag{2.83}$$

Vanderslice *et al.* [31] perform tests and compare the Rydberg-Klein graphical procedure with the Rees analytic, verifying that the Rees method is much faster and more accurate.

Thus the Rydberg-Klein-Rees (RKR) method becomes one of the most accurate and fast methods of obtaining PECs employing experimental data, without an analytical function. It is a method particularly favored compared to the others when a large number of levels are known considering the situation close to the limit of dissociation.

One of the disadvantages of the RKR method is that the PEC can be constructed only in the region for which sufficient spectroscopic data are available. However, this was great difficulty in the past decades, when there were computational and technological barriers, which is no longer the case today. Incidentally, in the 1960s, there was a fair amount of experimental data available [15].

Later work such as Singh and Jain [34], and later by Richards and Barrow [35] proposed even simpler ways to obtain f and g, making it even easier to obtain an accurate PEC.

3 A review of fifty analytical representation of potential energy interaction for diatomic systems: One Hundred Years of History

3.1 Potential energy functions

3.1.1 The Kratzer function

Our starting point is to consider the wave equation [33] for the nuclear motion of a diatomic molecule of nuclear masses M_1 and M_2 and charges Z_1 and Z_2 is:

$$\nabla^2\Psi + \frac{8\pi^2\mu}{\hbar^2}\left[E - (e^2 Z_1 Z_2/R) + V_e(R)\right]\Psi = 0 \tag{3.1}$$

where $\mu = M_1M_2/(M_1 + M_2)$ is the reduced mass, R is the internuclear distance and $V_e(R)$ the electronic energy.

The function of nuclear potential energy will be a combination of the term representing the nucleus-nucleus repulsion energy with the electronic energy V_e:

$$V(R) = e^2 Z_1 Z_2/R - V_e(R). \tag{3.2}$$

Writing the wave function in the well-known approximate form

$$\Psi = \Phi(\phi, R) \cdot \Theta(\theta, \phi) \cdot \mathcal{R}(R)/R \tag{3.3}$$

which differs from the exact molecular equation by small terms treated as perturbations. These effects can be either neglected or they can be calculated (see details in Ref. [36]).

In Eq. (3.3), $\Theta(\theta, \phi)$ is a function of the angular coordinates which fix the direction of the internuclear axis in space. $\Phi(\phi, R)$ is a function of all the electronic coordinates ϕ and also of the internuclear distance R. It is, in fact, the solution of the equation for the molecule with the nuclei fixed at separation R.

Then, $\mathcal{R}$ in Eq. (3.3) satisfies the radial part equation of Schrödinger, given by:

$$\frac{d^2\mathcal{R}}{dR^2} - \frac{J(J+1)\mathcal{R}}{R^2} + \frac{8\pi^2\mu}{\hbar^2}[E - V(R)]\mathcal{R} = 0. \tag{3.4}$$

Among many proposed diatomic potentials few are those that solve exactly the Schrodinger radial equation (3.4). Proposed in 1920, the Kratzer [16] potential was one of the first to have this important characteristic since the wave function contains all the information necessary to describe a quantum system in its entirety. Work such as Bayrak, Boztosun, and Ciftci [37] and Hooydonk [38] emphasize the importance and applicability of obtaining the eigenvalues explicitly in theoretical chemistry problems, especially when they result from the use of the Kratzer potential in the place of $V(R)$ in the Eq. (3.4).

The Kratzer [16] (KRA) potential is given by:

$$V_{KRA}(R) = -2D_e\left(\frac{R_e}{R} - \frac{1}{2}\frac{{R_e}^2}{R^2}\right) \tag{3.5}$$

where D is the depth of the well and R_e is the equilibrium internuclear separation.

The Kratzer potential is composed of a repulsive part and a long-range attraction. This potential presents three characteristics that will be desirable to all the potentials. They are:

(i) $V(R)$ has a minimum at $R = R_e$, and in this case it occurs for $V(R = R_e) = -D_e$;

(ii) $V(R) \to \infty$, when $R \to 0$, due to internuclear repulsion;

(iii) $V(R) \to 0$ when $R \to \infty$, occurring the dissociation of the molecule [1].

In 1922, an approximate form of Kratzer's potential was already considered [39], with the addition of D_e in (3.5), *i. e.*, $V_{KRA}(R) = -2D_e\left(\frac{R_e}{R} - \frac{1}{2}\frac{{R_e}^2}{R^2}\right) + D_e$, resulting in:

$$V_{Modf.KRA}(R) = D_e\left(\frac{R - R_e}{R}\right)^2. \tag{3.6}$$

The spectroscopic constants for the modified Kratzer potential are quite problematic, as shown by Varshni [14]. When the conditions (i), (ii) and (iii) are satisfied, what one has is the relation:

$$\frac{k_e R_e}{2D_e} = 1 \tag{3.7}$$

being $k_e = \left(\frac{d^2V_{KRA}}{dR^2}\right)_{R_e}$. However, this can not be obtained for any of the 23 molecules tested by Varshni [14].

[1] In fact, the requirement is that when $R \to \infty$ the potential curve is asymptotic for a finite value, which in general is very close to zero for systems in the ground state that has a conventional potential curve, *i. e.*, with only a global minimum, maxims.

Besides, C.Berkdemir, A. Berkdemir, and Han pointed in 2005, Kratzer's modified potential did not provide an analytical solution for the Schrödinger equation if the centrifugal part was included in it. However, they provided a method for eigenvalues to be obtained (for more details see Ref. [40]).

The modified Kratzer potential (3.6) is still of the few to have only two adjustable parameters, D_e and R_e. For that reason, when compared to potentials such as Morse [8], Rydberg [9], Deng-Fan [41] and others with 3 or more adjustable parameters, Kratzer will generally have the worst fit of the curve as a whole. This can be observed, for example, in the work of Royappa, Suri, and McDonought [42], where the Kratzer potential was compared to 20 other potentials containing 3, 4, 5, and 8 adjustable parameters for 14 diatomic systems in the ground state. The Z-test proposed by Murrell and Sorbie (can be seen in detail in section 3.1.26) was used, where the curves with the fitted parameters are compared to the curve obtained by the RKR method. The mean of the deviations for the Kratzer function was only surpassed, surprisingly, by Lippincott [43] function (see section 3.1.19 of this work). With 4 parameters fitted, the Lippincott potential does not have the expected behavior when $R \to 0$, since $V(R)$ converges to a finite value. The values of D_e are overestimated in relation to the RKR data in the attractive branch, and these high values lead the potential, when $R \to 0$, becomes smaller than the value of the potential with such R and D_e, which does not happen with the modified Kratzer potential.

Varshni [14] further proposed another way to modify the Kratzer potential so that the spectroscopic constants could be calculated. He called the generalized Kratzer (GENKRA) function:

$$V_{GENKRA}(R) = D_e \left[1 - \left(\frac{R_e}{R}\right)^n\right]^2, \tag{3.8}$$

where

$$n^2 = \Delta \tag{3.9}$$

being Δ the Sutherland parameter [44] given for $\Delta = k_e R_e^2/2D_e$. The spectroscopic constants in this case are given by:

$$\alpha_e = \Delta^{1/2}\frac{6B_e}{\omega_e} \tag{3.10}$$

and

$$\omega_e x_e = [8\Delta + 12\Delta^{1/2} + 4]\frac{2.1078 \times 10^{-16}}{{R_e}^2\mu}. \tag{3.11}$$

3.1.2 The Lennard-Jones function

For a molecule consisting of two atoms, we have known that there is a repulsive force between the atoms at close separation distances which keeps the atoms from overlapping, and an attractive force at large separation distances which provides the binding of the atoms into a molecule. At some intermediate distance, these forces are in balance. A potential form commonly used to describe this situation, first suggested by Mie [45] in 1903, and later applied by Lennard-Jones [46] in 1924.

The Lennard-Jones [46, 47] (LJ) spherical-symmetric potential, whose parameters are derived from the coefficients of second virial or viscosity, was considered one of the most widely studied, especially between 1920 and 1990.

First, he considered the viscosity problem. The interest was to deduce the appropriate law of dependence of the viscosity of a gas on temperature. To this end, Lennard-Jones considered the formula given by Chapman for the coefficient of the viscosity of a gas whose molecules may be regarded as spherically symmetrical [47]:

$$\mu = \frac{5}{\pi}\frac{kT}{\kappa_0}(1+\epsilon), \tag{3.12}$$

where T is temperature, k the usual gas content, ϵ a small number which depends on the molecular model, and κ_0 is given by:

$$\kappa_0 = \frac{16}{15\sqrt{\pi}}\int_0^\infty e^{-y^2}\phi^{(2)}(\tau y)y^6 dy, \tag{3.13}$$

with

$$\phi^{(2)}(\tau y) = 10\tau y\int_0^\infty [(1-P_2(\cos\chi)]pdp, \tag{3.14}$$

being P_2 a zonal harmonic of the second order, p is the perpendicular distance between one molecule and the direction of motion of a second relative to it before an encounter, and χ is the angle turned through by the relative velocity during the encounter.

Further, τ is a function of the temperature and the mass of the colliding molecules given by [47]:]

$$\tau^2 = \frac{2kT}{m_1+m_2} = \frac{1}{j(m_1+m_2)} \tag{3.15}$$

and

$$\tau y = C_{\mathcal{R}} = \frac{V(m_1m_2)^{1/2}}{m_1+m_2}, \tag{3.16}$$

where V is the relative velocity before collision, $C_{\mathcal{R}}$ is a variable used by Chapman. In a simple gas, $m_1 = m_2$ and then $\tau y = V/2$.

Firstly, any model χ has to be found in terms of p and V, and this required an investigation of the dynamics collision. If the potential of the field between two molecules when separated by a distance R is $\phi(R)$, then the motion of one relative to the other during an encounter is the same as that of a particle of unit mass about a fixed center of force, of potential $\frac{m_1+m_2}{m_1m_2}\phi(R)$.

LJ assumed that the molecules repel according to a inverse nth power law, and that they attract according to the inverse third power, *i. e.*:

$$f(R) = \frac{\lambda_n}{R^n} - \frac{\lambda_3}{R^3}. \tag{3.17}$$

so that

$$\phi(R) = \frac{\lambda_n}{(n-1)R^{n-1}} - \frac{\lambda_m}{(m-1)R^{m-1}}. \tag{3.18}$$

The new formula to observed variation of viscosity with temperature is given [47]:

$$\mu = \frac{AT^{\frac{n+3}{2(n-1)}}}{1 + \sum_{R=1}^{\infty} S_R T^{-R\frac{n-3}{n-1}}}, \tag{3.19}$$

The quantity A is independent of temperature and we have:

$$A = \frac{5\sqrt{\pi m k}}{8I_2(n)\Gamma\left(4 - \frac{2}{n-1}\right)} \left(\frac{2k}{\lambda_n}\right)^{\frac{2}{n-1}} \tag{3.20}$$

and the “attractive constants” S_R are given by:

$$S_R = \frac{\pi J_R(n)}{2f(R)I_2(n)} \frac{\lambda_3}{\lambda_n^{2/n-1}} \frac{\Gamma\left(\frac{n-5-2Rn-3}{2n-1} + \frac{7}{2}\right)}{\Gamma\left(4 - \frac{2}{n-1}\right)(2k)^{R\left(\frac{n-3}{n-1}\right)}} \tag{3.21}$$

and so are function only of the force constants λ_3 and λ_n and of the index of the repulsive power law n. For details about the calculations of I_R and J_R see Ref. [47].

When the attractive force is weak compared with the repulsive field, the formula for the coefficient of viscosity reduces to:

$$\mu = \frac{AT^{3/2}}{T^{\frac{n-3}{n-1}} + S} \tag{3.22}$$

where A has the same value as before and S is given by:

$$S = \frac{\pi J_1(n)}{2I_2(n)\Gamma\left(4 - \frac{2}{n-1}\right)(2k)^{\frac{n-3}{n-1}}} \frac{\lambda_3}{\lambda_n^{2/n-1}}. \tag{3.23}$$

Another case considered by Lennard-Jones [47] was the Sutherland model, consisting of a rigid sphere with an attractive field surrounding it. The formula appropriate can be deduced from (3.22), making $n \to \infty$, such that:

$$\mu = \frac{AT^{\frac{1}{2}}}{1 + S/T} \tag{3.24}$$

which is a known Sutherland formula.

Based on the work of Enskog and James, it is possible to give a simple physical interpretation of S, since the value of S for the Sutherland model to be proportional to $\Delta\phi(\sigma)$, where $\phi(\sigma)$ is the work required to separate two molecules from contact to infinity against the attractive field, and Δ is a pure number depending only on the nature of the field. Thus, if $\phi(R)$ is the potential of two molecules separated by a distance R, and σ is the diameter of a molecule, then the value of S is given by:

$$S = \Delta_m \frac{\phi(\sigma)}{k} \tag{3.25}$$

being Δ_m depending only on the index m of the attractive field (R^{-m}) and its value varies from 0.213 to 0.156 as m varies from 4 to 9.

The physical interpretation of S is given supposing that two molecules repelling each other according to a inverse nth power law move towards each other in a direct encounter with a relative velocity of the molecules of a gas at first absolute. At the closets distance of approach:

$$\frac{\lambda_n}{(n-1)\sigma^{n-1}} = \frac{3}{2}k \tag{3.26}$$

and so

$$\sigma = \left(\frac{2\lambda_n}{3(n-1)k}\right)^{\frac{1}{n-1}}. \tag{3.27}$$

The distance σ is defined as the diameter of such molecules. If molecules are considered rigid spheres, the force constant λ_n is infinite, and n is infinite, but $\lambda_n^{1/n-1}$ has definite limiting equal to the diameter.

Thus, expression obtained for S, writing δ for the numerical values is given by [47]:

$$S = \delta \frac{\lambda_3}{\lambda_n^{2/n-1}} \frac{1}{(2k)^{n-3/n-1}}, \tag{3.28}$$

and substituting λ_n in terms of the σ, we have:

$$S = \frac{\delta}{3^{2/n-1}} \frac{\lambda_3}{2k\sigma^2} \left(\frac{4}{n-1}\right)^{2/n-1} = \Delta \frac{\phi(\sigma)}{k}, \tag{3.29}$$

where $\phi(\sigma)$ is the work required to separate two molecules attracting according to the law R_3/R^3 from a distance σ to infinity.

S has the same form whatever the attractive field for Sutherland's case, and the rule is valid not only to the inverse third power law. Then, if $\lambda_m R^{-m}$ is the attractive field, S will be given by:

$$S = \frac{\lambda_m}{(m-1)k\sigma^{m-1}} \Delta = \frac{\Delta'}{k^{(n-m/m-1)}} \frac{\lambda_m}{\lambda_n^{(m-1/n-1)}}, \tag{3.30}$$

where Δ' is a numerical factor. Thus, Lennard-Jones obtained that the coefficient of viscosity to general law of force $\lambda_n^{-n} - \lambda_m R^{-m}$ is given by Eq.(3.22). He applied these results to argon and obtained good agreement with experiment, and the repulsive field may have any index from 15 to 25, which led him to conclude that viscosity results alone are not sufficient to determine uniquely molecular fields [47].

In a subsequent paper, Lennard-Jones [46] begins to consider potential whose parameters are derived from the coefficients of second virial, more specifically B. This, however, can be applied only for two kinds of molecules: a van der Waals molecule and a molecule repelling according to an inverse power law, without attraction. First, he considered the equation of gas of moderately large dilution of the type:

$$pv = kNT\left(1 + \frac{B}{v}\right) \tag{3.31}$$

where, p, v, and T denote pressure, volume, and temperature respectively, k the Boltzmann gas constant, and B the second virial coefficient. The method aimed to determine the force constants, both attractive and repulsive, from a comparison of the theoretical and experimental values for B. For spherically symmetric molecules, B can be represented as [46]:

$$B = 2\pi N \int_0^\infty R^2(1 - e^{2j\phi(R)})dR, \tag{3.32}$$

where $2j = 1/kT$.

An alternative form B is:

$$B = \frac{2\pi N}{3kT}\int_0^\infty R^3 f(R) e^{2j\phi(R)}dR, \tag{3.33}$$

where $f(R)$ is the force between two molecules when separated by a distance R, now is given by:

$$f(R) = \frac{\lambda_n}{R^n} - \frac{\lambda_m}{R^m}. \tag{3.34}$$

and this is related to potential field $\phi(R)$, by the equation:

$$\phi(R) = -\int_0^\infty f(R)dR. \tag{3.35}$$

Lennard-Jones [46] obtained a general formula to B from which one can deduce the two special cases of molecules mentioned above. This is given by:

$$B = \frac{2}{3}\pi N\left(\frac{\lambda_n}{n-1}\frac{m-1}{\lambda_m}\right)^{3/(n-m)} F(y) \tag{3.36}$$

where

$$y = \frac{2j\lambda_m}{m-1}\left(\frac{n-1}{2j\lambda_n}\right)^{(m-1)/(n-1)} \tag{3.37}$$

and

$$F(y) = y^{3/(n-m)}\sum_{\tau=0}^{\infty}\frac{y^\tau}{\tau!}\left\{\Gamma\left(\frac{\tau\overline{m-1}+n-4}{n-1}\right) - \frac{m-1}{n-1}\gamma\left(\frac{\tau\overline{m-1}+m-4}{n-1}\right)y\right\}. \tag{3.38}$$

For molecules which repel according to an inverse power of distance $\lambda_n R^{-n}$, we have:

$$B = \frac{2}{3}\pi N \left(\frac{2j\lambda_n}{n-1}\right) \Gamma\left(\frac{n-4}{n-1}\right), \tag{3.39}$$

where was assumed $y = 0$ and $\lambda_m = 0$. For molecules which behave as rigid spheres of diameter σ, surrounded by an attractive field of force $\lambda_m R^{-m}$, we have:

$$B = \frac{2}{3}\pi N\sigma^3 \left\{1 - \sum_{\tau=1}^{\infty} \frac{3(2ju)^\tau}{\tau!(\tau\overline{m-1}-3)}\right\}. \tag{3.40}$$

observing that a rigid sphere molecules corresponds to a force $\lambda_n R^{-n}$ when $n \to \infty$, the diameter σ being given by:

$$\sigma = \lim_{n\to\infty} \lambda_n^{1/n-1}. \tag{3.41}$$

Lennard-Jones related the function B theoretical and experimentally, assuming that the values of B at various temperatures applied to a unit volume of a gas is given by expression

$$B_N = f(T) \tag{3.42}$$

while theoretically, we have as above:

$$B_N = \frac{2}{3}\pi\nu \left(\frac{\lambda_n}{n-1}\frac{m-1}{\lambda_m}\right)^{3/(n-m)} F(y) \tag{3.43}$$

being ν the molecular concentration.

He obtained two equation to determine λ_n and λ_m, given by [46]:

$$\frac{3}{n-1}\log\frac{\lambda_n}{n-1} = \frac{3}{n-m}X + Y - \log\frac{2\pi\nu}{3} + \frac{3}{n-1}\log k \tag{3.44}$$

and

$$\frac{3}{m-1}\log\frac{\lambda_m}{m-1} = \frac{3(n-1)}{(n-m)(m-1)}X + Y - \log\frac{2\pi\nu}{3} + \frac{3}{m-1}\log k, \tag{3.45}$$

where (X, Y) is a parallel transformation, which:

$$\log y + \frac{n-m}{n-1}\log T = X \tag{3.46}$$

and

$$\log B_N - \log F(y) = Y. \tag{3.47}$$

Lennard-Jones applied this method to the argon [46], helium and neon gases [48], and for hydrogen, nitrogen, and neon gases (with some corrections) [49]. Next, he considered the problem of determining the forces between molecules of different kinds of a gaseous mixture from second virial coefficients of a binary mixture [50]. In 1937, he observed that the interaction of neutral atoms at large distances can be represented by a potential function that varies as the inverse sixth power of the distance [51]. At smaller distances, he noted that the function is not so simple. Nevertheless, it was convenient to adopt the asymptotic form of the function as valid over the whole range and to make any necessary modifications in the repulsive field which must be used in conjunction with it. In this case, the interaction of neutral atoms at small distances can be represented by a potential function that varies as the inverse ninth, tenth, eleventh, or twelfth power of the distance. For this, he considered the equation of state for a gas of small concentration given by:

$$pv = KNT + \frac{B}{v} \tag{3.48}$$

or

$$pv = KNT + \frac{B'}{v} \tag{3.49}$$

where B and B' are functions of temperature. In terms of intermolecular fields they are given by:

$$B = B'kNT = 2\pi N^2 kT \int_0^\infty R^2[1 - \exp(-\phi(R)/kT)]dR \tag{3.50}$$

where $\phi(R)$ is the potential energy of two molecules at a distance R, given in Eq. (3.35). These equations are like that of van der Waals, only first approximations and valid only for dilute gases. When van der Waals equation is written in the form of equation (3.48), it appears that

$$B' = b - \frac{a}{kNT} \tag{3.51}$$

whereas the corresponding formula derived from (3.50) for molecules which behave as rigid spheres of diameter σ, surround by an attractive field, whose potential is $\lambda_m R^{-m}$, is:

$$B = \frac{2}{3}\pi N\sigma^3 \left\{ 1 - \sum_{\tau=1}^{\infty} \frac{3(\phi_0/kT)}{\tau!(\tau m - 3)} \right\}. \tag{3.52}$$

where

$$\phi_0 = \lambda_m \sigma^{-m} \tag{3.53}$$

and is the potential energy of two molecules in contact.

Equation (3.52) can be written as a more general formula which corresponds to interatomic forces whose potential is the sum of inverse power laws:

$$\phi = \lambda_n R^{-n} - \lambda_m R^{-m} \tag{3.54}$$

and this function can be written as [51]:

$$\phi = -|\phi_0| \left\{ \frac{1}{n} \left(\frac{R_e}{R} \right)^n - \frac{1}{m} \left(\frac{R_e}{R} \right)^m \right\} \Big/ \left(\frac{1}{n} - \frac{1}{m} \right) \tag{3.55}$$

where R_e is the distance between two molecules in equilibrium under the field (3.54), and $|\phi_0|$ is the energy required to separate them from this configuration (dissociation energy D).

The most appropriate values of n and m for the inert gases and some molecules have been given for $m = 6$, corresponding to the theoretical value for van der Waals forces, and a value of n between 9 and 12.The values of λ_n and λ_m were deduced from values of R_e and ϕ_0. For diatomic systems He_2, Ne_2, Ar_2, H_2, N_2, O_2 and CO the best value obtained for n was 12[51].

Then, the general potential LJ(m,n), as it is better known, is a two parameter potential energy function given by:

$$V_{LJ}(R) = \frac{D}{n-m} \left[m \left(\frac{R_e}{R} \right)^n - n \left(\frac{R_e}{R} \right)^m \right] \tag{3.56}$$

where R_e is the equilibrium distance and D is the dissociation energy. To have physical meaning, we must have $n > m > 0$, but neither m or n need be an integer. However, the function LJ(6,12) is the most widely used for diatomic systems in general.

Although it is still widely used in recent chemical research, mainly in computational simulations of liquids (see for example Ref. [52, 53]), the LJ(6,12) potential fails to describe the viscosity of the inert gases in a satisfactory manner [54] and measurements of the second virial coefficients of argon and krypton [55] at low temperatures indicated further the inadequacies of this model. Potential functions with more than two adjustable parameters were proposed in an attempt to overcome these defects (see Section 3.1.43).

3.1.3 The Morse function

In 1929, Morse [8] (MOR) proposed a function that served later as a reference to many other proposals. The functional form to describe diatomic potentials has well represented in at short interatomic distances, being quite adequate to represent atoms forming a chemical bond, providing greater precision in the region of the minimum potential.

The first potential energy functions proposed for $V(R)$ were very complicated functions [8]. Proposals for such a function were almost always based on the Dunham [24] method presented in the section 2.2, in which very general power series were obtained from the infinite polynomial:

$$E(\nu, J=0) = -D + \hbar\omega_e \left[\left(\nu + \frac{1}{2}\right) - x_e \left(\nu + \frac{1}{2}\right)^2 + K_3 \left(\nu + \frac{1}{2}\right)^3 - \cdots \right]. \quad (3.57)$$

These provide the energy levels accessible, whose spectroscopic constants x_e, ω_e, $K_3 \cdots$ were known, and E thus obtained empirically.

However, the use of V as these very general expansions bring some drawbacks. The terms in $(R - R_e)$ with power 3 or greater in the expansion of V must be calculated by perturbation methods since these are not small as Dunham had already pointed out [24]. Also, since V is obtained from known spectroscopic constants, it does not converge to large values of R.

Morse, based on experimental data, found the spectroscopic constants K_3 as well as the higher-order parameters in the expansion in $E(\nu, J=0)$ were very small compared to those in the first and second terms of the $E(\nu, J=0)$. Thus, he proposed to truncate such a series up to the second term. Considering also, the deficiencies of the thus far presented functions, Morse then proposed four criteria to be satisfied to obtain a simple and well-behaved function to describe these potentials [8]:

1. Converge asymptotically to a finite value when $R \to \infty$;
2. Possess minimum point only at $R = R_e$;
3. In $R = 0$, $V(R) \to \infty$;
4. Provide exactly the energy levels accessible as a finite polynomial $E(\nu, J=0)$, being given by

$$E(\nu, J=0) = -D + \hbar\omega_e \left[\left(\nu + \frac{1}{2}\right) - x_e \left(\nu + \frac{1}{2}\right)^2 \right]. \quad (3.58)$$

where D is the dissociation energy [2], R_e represents the equilibrium distance, $\omega_e = \frac{1}{2}\sqrt{\frac{f}{\mu}}$ is the vibration frequency, with μ the reduced mass of diatomic molecule. Also, $k_e = \left(\frac{d^2 V_{MOR}}{dR^2}\right)_{R=R_e}$ is the force constant and $\omega_e x_e = \hbar\omega_e^2/aD_e$ is the anharmonicity constant. The function proposed by Morse considering firstly only the vibrational levels, *i. e.*, for J equal to zero, has the form:

$$V_{MOR}(R) = D_e e^{-2a(R-R_e)} - 2D_e e^{-a(R-R_e)} \quad (3.59)$$

being D_e the depth of the well. Note that the criteria 3 does not necessarily true for the Morse proposal $V_{MOR}(R)$, because when $R \to 0$, $V_{MOR}(R)$ assumes the finite value $D_e(e^{2aR_e} - 2e^{aR_e})$.

[2] D should not be confused with the depth of the well D_e, since $D_e - D = \frac{1}{2}\hbar\omega_e$.

In the cases where the quantum rotational number J is different from zero, the term $V_J = J(J+1)\hbar^2/8\pi^2\mu {R_e}^2$ is added to the function (3.59). Morse showed his function reasonably satisfied all four criteria, still obtaining the first notable case of a one dimensional Schrödinger equation providing a finite number of discrete energy levels given by $E(\nu, J)$, this being the empirical form of (3.58). The vibrational energy levels in the harmonic approximation are given by:

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega_e, \nu = 0, 1, 2\cdots. \tag{3.60}$$

When dealing with realistic potentials, the distance between the energy levels decreases as the energy approaches the limit of dissociation. This is due to the anharmonicity of real molecules, not well described by the harmonic approach (3.60). Usually the vibrational and rotational energy levels of a diatomic molecule are expressed as a convergent double expansion in the variables $(\nu + \frac{1}{2})$ and $J(J+1)$ [56][3],

$$\begin{aligned}\frac{E(\nu,J)}{\hbar c} &= F(\nu, J) = \omega_e\left(\nu+\tfrac{1}{2}\right) - \omega_e x_e\left(\nu+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(\nu+\tfrac{1}{2}\right)^3 - \omega_e z_e\left(\nu+\tfrac{1}{2}\right)^4 \\ &+ \cdots + \left[B_e - \alpha_e\left(\nu+\tfrac{1}{2}\right) + \cdots\right]J(J+1) + \left[extslD_e + \beta_e\left(\nu+\tfrac{1}{2}\right) + \cdots\right]J^2(J+1)^2\end{aligned} \tag{3.61}$$

where ν is the vibrational quantum number defined by (3.60) and J, the rotational quantum number $(J = 0, 1, 2...)$.

At this point the Morse contribution becomes even more evident, not only with the functional form, but also providing a finite polynomial $E(\nu, J)$ suitable for the calculation of both vibrational and rotational energy levels given by:

$$\begin{aligned}E(\nu, J) = -D + \hbar\omega_e(\nu + 1/2)[1 - \hbar\omega_e\,(\nu + 1/2)\,/4D_e - \hbar^2 J(J+1)/16\pi^2 D_e\mu R_e^2] \\ +(\hbar^J(J+1)/8\pi^2\mu {R_e}^2)[1 - \hbar^2 J(J+1)/16\pi^4\mu^2 R_e^4\omega_e^2].\end{aligned} \tag{3.62}$$

Dunham [24] questioned the accuracy of this finite series, truncated in the second-order term, representing energy, since for light molecules like hydrogen, terms of order greater than two are not negligible. On the other hand, as for the other molecules the precision of the levels was considered good, this was not taken into account by Morse. Also, Rees [11] showed that in the case where $E(\nu, J)$ was expressed considering the cubics terms in $(\nu + 1/2)$, the calculations became much more difficult. Also, there was a dependence on the precision with which the second anharmonicity constant $\omega_e y_e$ was obtained, being the values of $\omega_e y_e$ are among the least reliable of the spectroscopic constants [31].

The Morse function was also known as a three-parameter potential function, D_e, a

[3] extslD$_e$ appearing in expression (3.61) represents the centrifugal distortion constant, should not be confused with D_e, the well depth in the Morse potential (3.59).

and R_e. D_e can be calculated by integrating exactly the Schrödinger equation, using Morse function $V_{MOR}(R)$, getting:

$$D_e = \omega_e^2/4\omega_e x_e. \tag{3.63}$$

Once ω_e and D_e are known, the a parameter is obtained as:

$$a = (8\pi^2 c\mu\omega_e x_e/\hbar)^{1/2} = 0.2454(\mu\omega_e x_e)^{1/2}, \tag{3.64}$$

or equivalently,

$$a = \sqrt{\frac{k_e}{2D_e}} \tag{3.65}$$

using that $k_e = 4\pi^2\mu c^2\omega_e^2 = 5.8883 \times 10^{-2}\mu\omega_e^2$ dyne/cm . Sometimes, this value of k_e is approximates by $k_e = \mu\omega_e^2$. This approximation is due to Dunham [24] with a slight correction being omitted, for simplicity.

The expression (3.63) usually gives values for the dissociation energy D, that are too large, so that it is better to use the experimental value when available [57].

To construct the potential energy curves, Morse used a different calculation for the molecular constant R_e. The relation used before his work was ${R_e}^2\omega_e = C_m$, where C_m has a different value for each molecule, and it was necessary to know at least one value of R_e before obtaining C. Morse [8] proposed an empirical law associating R_e and ω_e. Following Birges tests [58], where the values of R_e and ω_e for 21 molecules were known, and using the equation $\log\omega_e - p\log R_e = \log k$ it was estimated that $p = 2.95$ and $k = 2975$. To test its function, Morse assumed, even with a rather large error, $p = 3$, and then

$${R_e}^3\omega_e = 3000\text{Å}^3/cm. \tag{3.66}$$

He noticed that the values thus obtained reproduced well the experimental data, with an approximate error of 4%.

Morse tested its function in neutral diatomic molecules and ions, in ground electronic and excited states. Curves were calculated for the molecules BeO, BO, AlO, C_2, CN, CO, CO^+, F_2, H_2, H_2^+, I_2, N_2, N_2^+, NO_2, O_2,O_2^+ and SiN.

Many comparative studies involving the Morse function were done later, such as those by Varshni [14] or Royappa *et al.* [42]. Although the Morse function doesn't give a correct description of the potential in the long-range, this potential was still a reference for the most current ones.

Varshni [14] showed that the approximate expression for the vibrational rotational coupling constant α_e obtained by Pekeris [59], obtained solving the Schrödinger equation for the Morse potential by perturbation method is equivalent to the his expression:

$$\alpha_e = 6B_e x_e \left[\left(\frac{B_e}{\omega_e x_e} \right)^{1/2} - \frac{B_e}{\omega_e x_e} \right] = (\Delta^{1/2} - 1) \frac{6B_e^2}{\omega_e} \tag{3.67}$$

where $B_e = \hbar/(8\pi^2 \mu R_e^2 c)$ is the rotational constant and $\Delta = \frac{k_e R_e^2}{2D_e}$ is the Sutherland parameter. The anharmonicity constant $\omega_e x_e$ in (3.67) is given by:

$$\omega_e x_e = 8a^2 \frac{2 \times 2.1078 \times 10^{-16}}{\mu} = 8\Delta \frac{2 \times 2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.68}$$

However, the expression (3.63) obtained by Morse presented better results than the expression (3.68) as verified by Varshni. He analyzed 23 diatomic systems in their ground electronic states, and α_e and ω_e showed very poor results for these systems with the Morse function. The Rydberg [9] and Lippincott [43] potentials presented a much lower average percentage error than Morse.

On the other hand, in a more recent study, Royappa [42] *et al.* evaluated the behavior of the potential as a whole, and compared it with the experimental RKR [9–11] curve using the Z-test method of Murrell and Sorbie [60] (see details in Section: 3.1.26). He analyzed the average of the deviations of 21 potential energy functions for 14 diatomic systems in their ground electronic states, and obtained that the Morse function present lower error than Kratzer [16], Lippincott [43], Deng-Fan [41], Rydberg [9], Varshni III [14], Rosen-Morse [29], Linnett [61] and Posch-Teller [30] potentials.

3.1.4 The Rydberg function

The potential functions used before the Rydberg proposal described only the lowest vibrational levels and were not useful in the extrapolation to dissociation limit [9]. It was then necessary to seek more general analytical ways to describe potential energy functions for diatomic systems, to best fit also the dissociation region. Moreover, an accurate representation of the series of nuclear vibrations was not known, and nuclear vibrations are experimentally measured in terms of ΔE, being $\Delta E = E(\nu+1) - E(\nu)$, where $E(\nu)$ is the nuclear vibrational energy corresponding to the quantum number ν. Then ΔE is assumed to be a linear function of the quantum number ν, approximation valid only for the simple diatomic system H_2. For somewhat more complex systems like N_2 [62, 63], O_2 [64] and NO [65, 66], a function of the type $(\Delta E)^2$ was used, more properly describing the nuclear vibrations. However, such a function still depended only on the quantum number ν. Then, in 1931 Rydberg [9] developed a method for calculating potential curves which makes use of the experimental energy levels yourself and not depend on some derived formula for these levels. This a graphical method designed to produce a curve that will give the observed vibrational and rotational energies, when these are computed by Bohr theory with half-integral quantum numbers. It is a method of approximation to obtain the curves, and to this approximation, the energy levels depend only on the form of that part of the potential curve which lies between the classical motion of the system for the energy in question.

Rydberg [9] (RYD) suggested an empirical relationship between $(\Delta E)^2$ and B_ν:

$$(\Delta E)_\nu{}^2 = k_e \cdot B^3_{\nu+1} \tag{3.69}$$

where

$$B_\nu = \frac{\hbar}{8\pi^2\mu}\left(\frac{1}{R^2}\right)_\nu, \tag{3.70}$$

is the rotational constants, k_e is the force constant and μ is the reduced mass.

Rydberg showed that for the diatomic systems CdH and HgH, the relation (3.69) had a good fit at several vibrational levels [9]. Although with slightly greater straight-line deviations at the lower vibrational levels, acceptable representations were also obtained for NO and O_2 systems. These larger deviations were attributed to errors in the determination of rotational constants B_ν. Yet, the above-mentioned systems were considered as well represented in this frame. However, for the LiH and NaH, an unexpected behavior occurred, plotting Eq. (3.69) produces a curve towards the origin at the low levels, suggesting that for such systems, the relation (3.69) could be even applied for the highest vibrational levels [67].

Rydberg used a graphical method involving the action integral, together with another integral related to the spectroscopic constant B_ν. The action integral for a rotating vibrator is [31]:

$$I = \oint p_R dR = 2\int_{R_1}^{R_2} p_R dR = 2\int_{R_1}^{R_2} \sqrt{2\mu[U - V_{\text{eff}}(R)]}dR, \tag{3.71}$$

where p_R is the radial momentum of the particle, R_1 and R_2 are the classical turning points and R is the internuclear separation, μ is the reduced mass and U is the constant total energy given by:

$$U = \frac{p_R{}^2}{2\mu} + V_{\text{eff}}(R). \tag{3.72}$$

The term $V_{\text{eff}}(R)$ is the effective potential curve, given by sum of the potential $V(R)$ and the centrifugal potential:

$$V_{\text{eff}}(R) = V(R) + \frac{\kappa}{R^2}, \tag{3.73}$$

where

$$\kappa = \frac{p^2_{heta}}{2\mu}. \tag{3.74}$$

Here p_{heta} is the angular momentum which is a constant the motion. The quantization of the radial momentum, and therefore of the vibrational motion leads to:

$$I = 2\int_{R_1}^{R_2} \sqrt{2\mu[U - V_{\text{eff}}(R)]}dR = \hbar\left(\nu + \frac{1}{2}\right). \tag{3.75}$$

Here it is clear that the Rydberg method is based on the WBK approximation [25–27], since in this approximation the eigenvalues of the one-dimensional motion of a particle in a potential are given by phase integral condition (3.75). This is also known as Oldenberg's condition [68], in which the potential curve must be changed until the relation (3.75) is satisfied [9].

To obtain a relation for the rotational energy, we start from the relation of E_{rot} to a vibrating rotator [31], which will lead us to a more explicit relation for B_ν (3.70). We have:

$$E_{\text{rot}} = \kappa\left(\overline{\frac{1}{R^2}}\right)_\nu = \frac{\kappa}{\tau_\nu}\oint\frac{1}{R^2}dt = \frac{\kappa\mu}{\tau_\nu}\oint\frac{1}{R^2 p_R}dR \tag{3.76}$$

where τ_ν is the period of vibration. Again, the quantization of the angular momentum phase integral leads to

$$\kappa = \left(\frac{\hbar^2}{8\pi^2\mu}\right)J(J+1) \tag{3.77}$$

where J is the rotational quantum number, and the relation (3.77) is again a WKB approximation [31]. Here κ is the same of the Schrödinger equation (2.43) presented in the section 2.2, used to obtain the energy levels of a rotating vibrator.

Finally, replacing p_R and κ, for equations (3.72) and (3.74) respectively, we have the following relation to B_ν:

$$\frac{1}{\hbar^2\sqrt{2\mu}}\cdot\frac{1}{8\pi^2\tau_\nu}\oint\frac{dR}{R^2\sqrt{U - V_{\text{eff}}(R)}} = B_\nu, \tag{3.78}$$

which can now be obtained more easily than by expression (3.78), and these is know as condition of Hulthén [69]. This was of great importance in the work of Rydberg [9], since it was noticed when varying the values of the internuclear distance R, an infinity of solutions satisfied the action integral. Thus, to determine the potential curve clearly, a second condition other than Oldenberg [68] was required.

However, as the integrand of Eq. (3.78) becomes infinity at the classical turning points, graphical integration is not very accurate.

Then, in 1932, Klein [10] presented a method to solve the integral of condition (3.75) of Oldenberg [68]. Also, modified the Rydberg's procedure to calculate the classical turning points, led to the way to obtain PEC's of the RKR method, discussed earlier in section 2.3 this work.

The relation for $(\Delta E)^2$ (3.69), depends entirely on the behaviour of the potential curve, *i. e.*, the forces acting on the atomic nuclei. To construct the potential step by step, the energy $E(\nu)$ of the νth vibrational level and spacing of the rotational levels of that vibrational level provinding the above two conditions (3.75), (3.78) on the construction of the potential curve for energies between $E(\nu)$ and $E(\nu+1)$.

Seeking a potential simultaneously fulfilling both conditions, Rydberg [9] proposed the following potential function:

$$V_{RYD}(R) = -D_e(a(R-R_e)+1)e^{-a(R-R_e)} \tag{3.79}$$

where $a = (k_e/D_e)^{\frac{1}{2}}$, being k_e the force constant give for $k_e = \left(\frac{d^2V_{RYD}}{dR^2}\right)_{R_e}$. $V_{LJ}(R)$ becomes large, but not infinite when $R = 0$, similarly than Morse potential [8]. However, Rydberg showed that its potential provided best fitting compared to Morse function for the three diatomic systems mentioned before H_2, CdH and O_2.

From the third and fourth order derivatives of $V_{RYD}(R_e)$ it is possible to obtain the values for the spectroscopic parameters α_e and $\omega_e x_e$ as shown by Varshni [14]:

$$\alpha_e = \left[\frac{2\sqrt{2}}{3}\Delta^{\frac{1}{2}} - 1\right]\frac{6B_e}{\omega_e} \tag{3.80}$$

and

$$\omega_e x_e = \left[\frac{22}{3}\Delta\right] \cdot \frac{2.1078 \times 10^{-16}}{{R_e}^2\mu} \tag{3.81}$$

where B_e is the rotational constant and $\Delta = \frac{k_e {R_e}^2}{2D_e}$ the Sutherland parameter.

Years after Rydberg's work, his function was considered as good as the Morse function to represent various diatomic potentials, surpassing it in divergent cases. The mean error in calculating the parameter α_e for 23 diatomic systems was 28% with the Rydberg potential, whereas, for Morse, the error was about 33%. In the case of $\omega_e x_e$, the corresponding error was of 23% with Rydberg versus 31% with Morse, showing then a good improvement [14]. Additionally, the Rydberg function $V_{RYD}(R)$, as was shown by Murrell and Sorbie [60], was more easily extended to fit high order derivatives, adjusting the order of the polynomial in Equation (3.79).

3.1.5 The Born-Mayer function

In 1932, Born and Mayer [19] (BM) proposed a potential for diatomic systems with an extremely simple functional form, yet limited to repulsive states, *i. e.*, it is a potential to describe only the short-range region. They suggested the following functional form:

$$V_{BM}(R) = A\exp\{(-bR)\} \tag{3.82}$$

where A and b are constants. Note that the potential of Born-Mayer $V_{BM}(R) \to A$, when $R \to 0$, and $V_{BM}(R) \to 0$ if $R \to \infty$, presenting correct asymptotic behavior even for the long-range region of the potential.

In 1970, Gaydaenko and Nikulin [70] presented a method, based on statistical theory, to calculate the coefficients A and b for several pairs of neutral atoms in the ground state, with charges nucleus from $Z = 2$ to $Z = 16$. The method of least-squares fit of Born-Mayer potential (3.82) at intervals of internuclear separation in which the $V_{BM}(R)$ curve is approximately linear is used. The maximum error of fit in a given range was approximately 10%, and the mean error was approximately 4.8% for identical atom pairs.

To obtain the potential value for heteronuclear diatomic systems, Gaydaenko and Nikulin propose to use the rule of empirical combining proposed by Abrahamson [71] in which:

$$V_{12} \simeq (V_{11}V_{22})^{1/2} = (A_1A_2)^{1/2}\exp\left\{[-\frac{1}{2}(b_1+b_2)R]\right\} \tag{3.83}$$

where $(A_1, A_2)^{1/2}$ is the geometric mean of A_1;A_2 and $\frac{1}{2}(b_1+b_2)R$ is simply the arithmetic mean of b_1;b_2. As pointed out by Gaydaenko and Nikulin [70], this model of calculation of the Abrahamson [71] potential is quite accurate, with an error close to 1% only. The methods of Abrahamson and Gaydaenko-Nikulin are differentiated only by the fact that the first uses the Thomas-Fermi-Dirac approximation (TFD), while the second uses Hartree-Fock (HF) calculations to obtain the interaction energies.

The method presented by Abrahamson allows the calculation of the potential of interaction based on the potential of Born-Mayer to more than 5000 different diatomic systems, using the table presented by him in Ref. [71].

As pointed out by Murrell *et al.* [56], the Born-Mayer potential is a special case of the extended Rydeberg function that will be presented in section 3.1.26. Although we now have a few alternatives, the Born-Mayer role is extremely important in accurately describing short-range interactions. As pointed out in the recent work (2016) of Van Vleet, Misquitta, Stone and Schmidt [72], it is more than eighty years since the creation of the Born-Mayer function, and very little progress has been made in obtaining potentials with similar performance, especially in problems where molecular electron density overlap cannot be neglected (for more details see Ref. [72]).

The potential of Born-Mayer still appears in problems involving triatomic systems, especially in those where there is molecular ion interaction, and when the effect of the long-range attractive potential can be completely neglected (See for example Ref. [73]).

3.1.6 The Rosen-Morse function

Still in the year 1932, Rosen and Morse [29] (RM) proposed a functional functional form to describe the potential of a single atom, which might even seem a little strange. However, their intention was to create a potential that could be used to treat vibrational molecular energy from larger (polyatomic) systems:

$$V_{RM}(R) = Banh\left(\frac{R}{d}\right) - C\text{sech}^2\left(\frac{R}{d}\right), \tag{3.84}$$

where

$$B = -2Canh\left(\frac{R_e}{d}\right) \tag{3.85}$$

and

$$C = \frac{D_e}{\left[1 - anh\left(\frac{R_e}{d}\right)\right]^2}. \tag{3.86}$$

This potential function accomplish the conditions:

(i) $V_{RM}(R) \rightarrow B$ if $R \rightarrow \infty$;

(ii) $\left.\frac{dV_{RM}}{dR}\right|_{R=R_e} = \text{sech}^2\left(\frac{R_e}{d}\right)\left[B + 2Canh\left(\frac{R_e}{d}\right)\right]$, and then the depth of the well is given by $D_e = (B + 2C)^2/4C$;

(iii) $\left.\frac{d^2V_{FWJ}}{dR^2}\right|_{R=R_e} = \frac{1}{8d^2C^3(4C^2-A^2)^2} = k_e$.

Note that $V_{RM} \rightarrow -C$ if $R \rightarrow 0$, and then this potential does not attain the condition $V_{RM} \rightarrow \infty$ if $R \rightarrow 0$.

Varshni [14] suggested the introduction of a new parameter p, in order to obtain a better fit of the curve. Once the adjustable parameter p is obtained, it is possible to determine d. He defined:

$$\frac{R_e}{d} = p, \tag{3.87}$$

where the new parameter p is related with the Sutherland parameter $\Delta = k_e R_e^2/2D_e$:

$$\Delta = p^2(1 + anhp)^2. \tag{3.88}$$

From this parameter, Varshni obtained also the expressions to α_e and $\omega_e x_e$ spectroscopic parameters [14]:

$$\alpha_e = (2panhp - 1)\frac{6B_e^2}{\omega_e} \tag{3.89}$$

and

$$\omega_e x_e = 8\Delta(1 - e^{-2p} + e^{-4p})\frac{2.1078 \times 10^{-16}}{R_e^2\mu}. \tag{3.90}$$

Like the Morse [8] function, this potential was developed to satisfy exactly the Schrödinger equation, thus providing exact levels of energy for polyatomic systems. Rosen and Morse [29] obtained the energy levels given by:

$$E_\nu = -\frac{1}{4}\left[\left(4C+\frac{\hbar^2}{8\pi^2\mu d^2}\right)^{1/2}-\frac{\hbar}{\sqrt{8\mu}\pi d}(2\nu+1)\right]^2+\frac{B^2}{\left[\left(4C+\frac{\hbar^2}{8\pi^2\mu d^2}\right)^{1/2}-\frac{\hbar}{\sqrt{8\mu}\pi d}(2\nu+1)\right]^2} \tag{3.91}$$

where ν can be $0 \leq \nu \leq \left[\left(C\frac{8\pi^\mu d^2}{\hbar^2}+\frac{1}{4}\right)^{1/2}-\left(\frac{B8\pi^2\mu d^2}{2\hbar^2}\right)^{1/2}-\frac{1}{2}\right]$, being ν the quantum number.

In the case where $C\frac{8\pi^2\mu d^2}{\hbar^2} \gg 1$, the values of the energy become [29]:

$$E_\nu = V(R_e)+\hbar\omega_e\left(\nu+\frac{1}{2}\right)-\frac{\hbar^2}{8\pi^2\mu d^2}\left(1+\frac{3B^2}{8C^2}\right)\left(\nu+\frac{1}{2}\right)^2+\cdots \tag{3.92}$$

where ω_e is the classical frequency of oscillation about the minimum point R_m, being by:

$$\omega_e = \frac{(4C^2-B^2)}{4\pi d(2\mu C^3)^{1/2}}. \tag{3.93}$$

As an example, Rosen and Morse [29] used the ammonia molecule NH_3 and the vibration of the nitrogen in this molecule was chosen to be calculated by the potential (3.84).

The potential energy curve of nitrogen has two minimums and therefore two equilibrium positions, which may be symmetrical (see discussion in Ref. [29]) and in this case, the minimal points can be called $R_m = \pm R_e$. Since it is a peculiar case, the potential must be given by the joining of two potential fields to represent the symmetry of the problem:

$$V(R) = \begin{cases} Banh(R/d-k)-C\text{sech}^2(R/d-k), & R \geq 0 \\ -Banh(R/d+k)-C\text{sech}^2(R/d+k), & R \leq 0 \end{cases} \tag{3.94}$$

corresponding to half the distance between the minima $R_m = kd - anh^{-1}(B/2C)$.

One of the major difficulties of the Rosen-Morse method is to obtain the values for the parameters B, C, d, and k. These must be fitted satisfying the following conditions on potential: (i) V is reasonable in shape; (ii) $|B| < 2C$; (iii) the second level must be below the center hill and (iv) the hill should not be higher than the value of V at ∞. Thus it is possible to delimit intervals where these values are contained, being $2200 \leq C \leq 3000$ cm^{-1}, $0 \leq B \leq 1000$ cm^{-1}, $0.16 \leq d \leq 0.185$ Å and $2.20 \leq k \leq 2.24$. For the value of the dissociation D, it was assumed that it would be where $V(\infty)$ coincided with $V(+R_e)$, but not so precisely, could assume values within the range 2200 and 4000 cm^{-1} in the case of ammonia. The value of R_e and in turn must be a fixed value at 0.38 Å for ammonia, however assuming any value between 0.365 and

0.390 Å, the error is only 1% within spectroscopic accuracy [29].

In a comparative study of empirical potentials presented in 1962 by Steele, Lippincott, and Vanderslice [15], the Rosen-Morse potential presented good results for the spectroscopic constants and the potential as a whole. For example, spectroscopic constant calculated by Steele *et al.* $\omega_e x_e$ presented a average error lower than that of Morse [8], Pöschl-Teller [30], Frost-Musulin [74] and Varshni [14], some of these potential being more recent than Rosen-Morse [29].

In this same work, Steele, Lippincott, and Vanderslice proposed a criterion to evaluate the accuracy of potential energy curve from the RKR experimental curve, using as a parameter the dissociation energy D. The relationship $[|V_{RKR} - V|/D]_{all\ R}$ (or/and $[|V_{RKR} - V|/D]_{R>R_e}$) is known as the Lippincott criterion. This criterion was applied to evaluate the Rosen-Morse, and the average deviation of this potential from the curve obtained via RKR [9–11] for $R > R_e$ was lower than that obtained with the potential of Morse [8], Pöschl-Teller [30] and Linnett [61]. Also worth noting that the potential Rosen-Morse curve coincided exactly with the RKR experimental curve value in certain internuclear distances for the H_2 and N_2 molecules in the ground state $X^1\Sigma_g^+$, and for NO in the excited state $B^2\Pi$ [15].

3.1.7 The Davidson function

In 1932, Davidson [75] (DAV) begins his research for a potential that provide the correct vibrational levels of energy when using the Schrödinger equation (2.43). It was based upon an expansion in the neighborhood of $R = R_e$ such as that proposed by Dunham, given by:

$$V(\xi) = k\xi^2(1 + a\xi + b\xi^2 + c\xi^3 + d\xi^4 + \cdots) \tag{3.95}$$

where $\xi = \frac{R}{R_e} - 1$ and $k = 2\pi^2{\omega_e}^2\mu R_e c$.

In general, the potential can be determined with considerable precision if known:

(i) B_e, and therefore R_e by the relation $B_e = \frac{\hbar}{8\pi^2\mu R_e^2 c}$;

(ii) The approximate value of the dissociation energy D, to which V goes asymptotically;

(iiii) The constants in E_ν, where ω_e together with B_e determines the radius of curvature of V in R_e.

For Davidson [75], these data leave the constants a, b, $\cdots$ in the ξ series undetermined, though they determine k in (3.95). Thus, he proposes a functional form for the potential given by:

$$V_{DAV}(R) = \frac{k}{4}\left(\frac{R}{R_e} - \frac{R_e}{R}\right)^2 \tag{3.96}$$

and this relates to the series (3.95) as follows [75]

$$\frac{k}{4}\left(\frac{R}{R_e}-\frac{R_e}{R}\right)^2 = k\xi^2\left(1-\xi+\frac{5}{4}\xi^2-\frac{6}{4}\xi^3+\frac{7}{4}\xi^4\cdots\right) \tag{3.97}$$

so that in the series we will have only the first non-zero term, that is, $V_{DAV}(R)$ is compared to a harmonic oscillator. As the energy levels of a harmonic oscillator are given by the Eq.(3.60), we can already conclude that in Davidson's potential, the constant of anharmonicity $\omega_e x_e$ is zero.

Thus the exclusively vibrational part of the energy levels of $E_{\nu,J}$ in the Davidson potential contains only the first term, *i. e.* has only $\left(\nu{+}\frac{1}{2}\right)\hbar\omega_e$. However, in the rotational part of $E_{\nu,J}$, the same does not happen. The complete expression for the energy levels will be given by [75]

$$E_{\nu,J} = \left(\nu{+}\frac{1}{2}\right)\hbar\omega_e + \hbar B_e\left(J+\frac{1}{2}\right)^2 - \frac{4{B_e}^3}{{\omega_e}^2}\left(J+\frac{1}{2}\right)^4 + \cdots . \tag{3.98}$$

The Davidson potential also has the following characteristics:

(i) $V_{DAV} \to \infty$, when $R \to 0$;

(ii) $V_{DAV} \to \infty$, when $R \to \infty$, which is not desirable, since the curve does not have an asymptotic behavior, but was already expected due to its harmonicity;

(iii) $V_{DAV}(R)$ has a minimum in $R = R_e$.

In 1957, Varshni [14] further pointed out that the relationship

$$k_e {R_e}^2 = 8k = \text{constant} \tag{3.99}$$

where k_e is the force constant, leads to

$$\alpha_e = 0 \tag{3.100}$$

which is not valid for any molecule [14].

The Davidson function was also used to improve the precision of potential curves obtained experimentally, through the inverse perturbation analysis (see for example Ref. [76]).

3.1.8 The Pöschl-Teller function

Pöschl and Teller [30] (PT), following the steps of Klein [10] in the search for potentials, proposed two functions and investigated the extent to which there could be a relation between the frequencies of vibration of a diatomic molecule and the function $\Delta r(V)$, where $\Delta r(V)$ is the distance between two points of the potential curve that have the same energy, *i. e.*, the same potential value V.

The first potential proposed by Pöschl-Teller [30] was

$$V_1(R) = \frac{\hbar^2\alpha^2}{8\pi^2\mu}\left[\frac{\beta(\beta-1)}{\operatorname{sen}^2\alpha(R-R_0)} - \frac{\gamma(\gamma+1)}{\cos^2\alpha(R-R_0)}\right], \left(0 \leq \alpha(R-R_0) \leq \frac{\pi}{2}\right), \quad (3.101)$$

where μ is the reduced mass, R_0 is an adjustable real parameter, α is a reciprocal length, β and γ are two numbers greater than one, not necessarily integers.

The ansatz for the eigenfunctions that satisfy the Schrödinger equation proposed by Pöschl-Teller is given by [30]:

$$\psi = \operatorname{sen}^\beta \alpha(R-R_0) \cdot \cos^\gamma \alpha(R-R_0) \cdot z, \quad (3.102)$$

where z is given by the series

$$z = \sum_k a_k y^k \quad (3.103)$$

being y another independent variable in (3.102) given by

$$y = \operatorname{sen}\alpha(R-R_0). \quad (3.104)$$

Substituting this ansatz into the Schrödinger equation gives:

$$a_{k+2}[(k+\beta+2)(k+\beta+1)-\beta(\beta-1)]+a+k\left[-(\gamma+\beta+k)^2+\frac{8\pi^2}{\alpha^2}\frac{\mu}{\hbar^2}E\right] = 0, \quad (3.105)$$

which gives the following expression for the energy levels

$$E_\nu = \frac{\alpha^2\hbar^2}{8\pi^2\mu}(\gamma+\beta+2\nu)^2. \quad (3.106)$$

The first Pöschl-Teller potential $V_1(R)$ assumes infinite when $R-R_0 = 0$ and when $R-R_0 = \pi/2\alpha$, and has a minimum in a more flat region of the curve in the smaller value of $\gamma+\beta$. The energy levels depend on the sum $\gamma+\beta$, and if this value increases, for small quantic numbers ν, the energy levels become practically equidistant. The differences between the levels are more evident the higher the energy (or the greater ν), and the vibration frequencies will increase as the energy increases [30]. This potential is most useful in the discussion of high excitation vibrations of polyatomic molecules.

The most well-known and used potential form of Pöschl-Teller is the second, given by [30]

$$V_{PT}(R) = \frac{\hbar^2\alpha^2}{8\pi^2\mu}\left[\frac{\beta(\beta-1)}{\operatorname{senh}^2\alpha(R-R_0)} - \frac{\gamma(\gamma+1)}{\cosh^2\alpha(R-R_0)}\right], \left(0 \leq \alpha(R-R_0) \leq \frac{\pi}{2}\right), \quad (3.107)$$

where again $\beta > 1$ and $\gamma > 1$.

With the same treatment given to the first potential, the *ansatz* now so that the eigenfunctions remain finite, in the region where $\alpha(R - R_0) \leq 0$, it will be given by:

$$\psi = \operatorname{senh}^{\beta} \alpha(R - R_0) \cdot \cosh^{-\gamma} \alpha(R - R_0) \cdot z \tag{3.108}$$

and z is now developed according to the powers of $\operatorname{senh} \alpha(R - R_0)$. The condition to truncate this series becomes

$$E_n = -\alpha^2(-\gamma + \beta + 2\nu)^2. \tag{3.109}$$

Only when $-\gamma + \beta + 2\nu < 0$, the values of the energy for (3.107) are discrete.

Again, when $R \to R_e$, $V_{PT} \to \infty$. The curve has a minimum when $\gamma - \beta > 1$.

Now the distance between levels depends on $\gamma - \beta$, and if this value increases, for small quantic numbers ν, the energy levels become practically equidistant, just as occurred for the potential V_1.

Pöschl and Teller also pointed out that in quantum mechanics for potentials with the same energy levels one can have $\Delta r(V)$ different.

The rotational levels for potential $V_{PT}(R)$ are given by:

$$B_\nu = B_0 \left(1 - \nu\sqrt{2B_0} \frac{f_2}{(f_3)^{\frac{3}{2}}} \right), \tag{3.110}$$

where $f_2 = \left.\frac{d^2V_{PT}}{dR^2}\right|_{R=R_e}$ and $f_3 = \left.\frac{d^3V_{PT}}{dR^3}\right|_{R=R_e}$.

In this comparative study between the Morse [8], Rosen-Morse [29] and Pöschl-Teller [30] potentials, Davies [77] calculates the spectroscopic constants of hydrogen halide molecules. For this, he used as base for the data treatment, the expansion of the potentials in power series, centered in the equilibrium distance R_e, that is, doing:

$$V(R) = \frac{1}{2!}\left.\frac{d^2V_{PT}}{dR^2}\right|_{R=R_e}(R-R_e)^2 + \frac{1}{3!}\left.\frac{d^3V_{PT}}{dR^3}\right|_{R=R_e}(R-R_e)^3 + \left.\frac{d^4V_{PT}}{dR^4}\right|_{R=R_e}(R-R_e)^4 + \cdots \tag{3.111}$$

remembering that $\left.\frac{dV_{PT}}{dR}\right|_{R=R_e} = 0$.

When comparing the values of the derivative of the potentials, which provide relations between spectroscopic constants, obtained with the three potentials, taking the parameters calculated by Kirkwood [78], the Pöschl-Teller potential is the one that, in general, presents greater accuracy, being slightly better than Morse function. Both, as we have seen, depend on the same number of arbitrary constants, however, those derived from the Pöschl-Teller potential are more extensive. The Rosen-Morse potential was the worst performance among the three [77].

Varshni [14] analyzed the simplest version of $V_{PT}(R)$,

$$V_{PT}(R) = M \operatorname{cosech}^2(aR/2) - N \operatorname{sech}^2(aR/2) \tag{3.112}$$

where $a = \sqrt{k_e/4D_e}$, $N = D_e/[(1-y^2)^2]$, $M = Ny^4$ and $y = anh(aR_e/2)$.

Following the calculations of Davies [77], Varshni also obtained the spectroscopic constants derived from the potential, given by:

$$\alpha_e = [\Delta^{\frac{1}{2}} \coth \Delta^{\frac{1}{2}} - 1]\frac{6{B_e}^2}{\omega_e} \tag{3.113}$$

and

$$\omega_e x_e = 8\Delta \cdot \frac{2.1078 \times 10^{-16}}{{R_e}^2 \mu} \tag{3.114}$$

where $\Delta = k_e R_e^2/2D_e$ is the Sutherland parameter.

3.1.9 The Manning-Rosen function

In 1933, Manning and Rosen [79] (MR) proposed a new functional form to describe diatomic potentials given by:

$$V_{MR}(R) = \frac{1}{k\rho^2}\left[\frac{\beta(\beta-1)e^{-2R/\rho}}{(1-e^{-R/\rho})^2} - \frac{Ae^{-R/\rho}}{1-e^{-R/\rho}}\right] \tag{3.115}$$

where $k = 8\mu\pi^2/\hbar^2$, A and β are two dimensionless parameters [80], but parameter ρ has dimension of length. This potential remains invariant by mapping $\beta \leftrightarrow \beta - 1$, can be rewritten in simplified form as:

$$V_{MR}(R) = \frac{Be^{-R/\rho} + Ce^{-2R/\rho}}{(1-e^{R/\rho})^2} \tag{3.116}$$

where $B = A$ and $C = -A - \beta(\beta-1)$. However, this form of the Manning-Rosen potential is less well known.

The allowed values of the energy are given by [79]:

$$E_\nu = -\frac{1}{k\rho^2}\left[\frac{A-B}{2(\beta+\nu)} - \frac{\nu(\nu+2\beta)}{2(\beta+\nu)}\right]^2. \tag{3.117}$$

The potential (3.115) must satisfy the following conditions:

(i) $\left.\frac{dV_{MR}}{dR}\right|_{R=R_e} = 0$, *i. e.*, V_{MR} has a minimum in $R_e = \rho \ln\left[1 + \frac{2\beta(\beta-1)}{A}\right]$, for $\beta > 1$;

(ii) $V_{MR}(\infty) - V_{MR}(R_e) = D_e$, where D_e is the depth of the well;

(iii) $\left.\frac{d^2V_{MR}}{dR^2}\right|_{R=R_e} = k_e$, where k_e is the force constant .

Using conditions (i) and (ii), we have a relationship for D_e:

$$D_e = \frac{A^2\hbar^2}{32\mu\pi^2\rho^2\beta(\beta-1)} \tag{3.118}$$

or equivalently, a relationship for the parameter A:

$$A = \frac{16\mu\pi^2\rho^2}{\hbar^2}(e^{R_e/\rho}-1)D_e. \tag{3.119}$$

From these relationships, Wang *et al.* [81] suggested rewrite the Manning-Rosen potential as:

$$V_{MR} = D_e\left(1-\frac{e^{R_e/\rho}-1}{e^{R/\rho}-1}\right)^2, \tag{3.120}$$

where the term D_e was added to the function (3.115) so that $V_{MR}(R_e) = 0$, without affecting the physical properties of the potential function.

The expressions for the vibrational rotational coupling parameter α_e and anharmonicity parameter $\omega_e x_e$, can be obtained from Dunham's relations (2.57) and (2.58):

$$\alpha_e = \left\{\frac{R_e^3}{\rho^3\Delta}\left[\frac{e^{2R_e/\rho}(e^{R_e/\rho}+1)}{(e^{R_e/\rho}-1)^3}\right]+1\right\}\frac{6B_e^2}{\omega_e} \tag{3.121}$$

and

$$\omega_e x_e = \left\{\frac{15R_e^4}{\rho^3\Delta^2}\left[\frac{e^{2R_e/\rho}(e^{2R_e/\rho}+1)^2}{(e^{R_e/\rho}-1)^3}\right]-\frac{R_e^2}{\rho^4\Delta}\left[\frac{e^{2R_e/\rho}(7e^{2R_e/\rho}+22e^{R_e/\rho}+7)}{(e^{R_e/\rho}-1)^4}\right]\right\}\times W, \tag{3.122}$$

where $W = \frac{2.1078\times10^{-16}}{\mu}$, B_e is the rotational constant and Δ is the Sutherland parameter.

According to condition (iii), we have the parameter ρ given by:

$$\frac{2D_e e^{2R_e/\rho}}{\rho^2(e^{R_e/\rho}-1)^2} = k_e \tag{3.123}$$

or, using that $k_e = 4\pi^2\mu c^2\omega_e^2$, we have

$$\frac{e^{2R_e/\rho}}{\rho^2(e^{R_e/\rho}-1)^2} = \frac{2\pi^2\mu c^2\omega_e^2}{D_e}. \tag{3.124}$$

The dissociation energy D for the Manning-Rosen [79] potential differs from the value presented by Morse in the Eq. (3.63), increased by δ

$$D = \frac{\omega_e^2}{4\omega_e x_e}+\delta \tag{3.125}$$

which causes even greater problems than those obtained with the Morse potential in this region, and is still less asymptotic. Thus, the potential of Manning-Rosen is not considered adequate [14].

3.1.10 The Newing function

In 1935, based on Morse [8] potential, Newing [82] (NEW) begins his research by a functional form for the potential of diatomic systems. He assumed a potential with three adjustable parameters, $V(R, D_e, R_e, a)$ as well as Morse function, and with the same basic characteristics: V must be infinite at $R = 0$, V tend to a finite value when R tend to infinity and have a minimum value at $R = R_e$. For $0 \leq R \leq \infty$, the potential of Newing is given by:

$$V_{NEW}(R) = -D_e + D_e\beta^2 \left[\frac{1 - e^{-a(R-R_e)}}{\beta - e^{-a(R-R_e)}}\right]^2, \tag{3.126}$$

where $\beta = e^{aR_e}$, D_e is the depth of the well and the a parameter is different from what appears in the Morse function (3.59), and should be chosen to best agreement with experiment.

The vibrational levels are given by:

$$\begin{aligned} E_\nu = &-\tfrac{\left(2A-\frac{1}{4}\right)^2}{K[4A(\beta-1)+1]} + \tfrac{\left(2A-\frac{1}{4}\right)\left(2\beta A+\frac{1}{4}\right)}{2K\left[A(\beta-1)+\frac{1}{4}\right]^{\frac{3}{4}}}\left(\nu + \tfrac{1}{2}\right) \\ &-\tfrac{1}{4K}\left[\tfrac{3A^2(\beta+1)^2}{\left[A(\beta-1)+\frac{1}{4}\right]^2}\right]\left(\nu + \tfrac{1}{2}\right)^2 + \cdots \end{aligned} \tag{3.127}$$

where $K = 8\pi^2\mu/\hbar^2 a^2$ and $A = KD(\beta - 1)$.

Newing estimated that the constant a is of the order of 10^8. (UNITS) Comparing it with the expansion (3.57), he also observed that just like the Manning-Rosen potential [79], the value of the dissociation energy D differs little from the corresponding obtained by Morse (3.63), this value can be set as $D + \delta D$. Newing showed that δ/D is of the order of 10^{-16}, emphasizing that the difference with the energy of Morse dissociation is very small.

The great interest shown in the work of Newing was to obtain a relation between the nuclear distance of equilibrium R_e and the frequency of vibration of the molecule ω_e. In his work, he demonstrated such a connection between these parameters, obtaining [82]:

$$\begin{gathered} a = 9.507 \times 10^{18}\omega_e \left(\frac{\mu}{D}\right)^{\frac{1}{2}} \left(\frac{3}{2} - Y\right), \\ \beta = \frac{2}{(2Y-1)}, \quad Y = \left(X - \frac{3}{4}\right)^{\frac{1}{2}}, \quad X = \frac{4\omega_e x_e D}{{\omega_e}^2} \end{gathered} \tag{3.128}$$

for $1 < X < 3$.

For $X < 1$, Newing obtained [82]:

$$\begin{aligned} \beta &= \frac{[2X - 1 + \sqrt{(1 + 4X - 4X^2)}]}{4(1 - X)X}, \\ a &= \frac{3.8 \times 10^{19}\sqrt{(D\mu)} \cdot \omega_e x_e [1 - \beta + \sqrt{(\beta^2 - 1)}]}{\omega_e}. \end{aligned} \tag{3.129}$$

Since the relationships between R_e and ω_e are obtained by Newing involve D, further research was necessary to obtain a more definite relation, as was pointed out by Varshini [83].

3.1.11 The Huggins function

Huggins [20] (HUG) in 1935, was dedicated to modifying the potential proposed by Morse [8] and, like Newing [82], to obtain interesting relations between the spectroscopic constants. However, he was concerned with obtaining a potential and its constants only for diatomic systems composed of elements of the first row of the periodic table and having 12 or more electrons, except for Li.

First, he considered the Morse function (3.59) written in the form:

$$V_{HUG}(R) = Ce^{-a(R-R_e)} - C'e^{-a'(R-R_e)} \tag{3.130}$$

with $a = 2a'$ and $C' = 2C$. Here $C - C'$ is the dissociation energy.

To modify the Morse function, based on the Born-Mayer [19] repulsive potential, Huggins proposed that the repulsive part of the original potential be replaced by a term that would be the same for all electronic states of a particular diatomic system. Thus, he suggested the following change[4]:

$$C = ce^{-a(R_e-R_{12})} \tag{3.131}$$

and replacing in Eq.(3.130)

$$Ce^{-a(R-R_e)} = ce^{-a(R-R_{12})} \tag{3.132}$$

where c is taken as 10^{-12} erg, R,R_e and R_{12} measured in Angstroms units and a and a' in reciprocal Angstrom (10^8 cm^{-1}). Once the value of a is determined, it is possible to obtain the values of the constants a', C', C and R_{12} from the spectroscopic constants ω_e, $\omega_e x_e$ and R_e.

For the types of diatomic systems considered by Huggins, the value $a = 6$ is the

[4] $Ce^{-a(R_e-R_{12})}$ is used as a repulsive term to calculate lattice energies and interatomic distances for the alkali halide crystals, with the same value a for all these crystals (See for example Ref. [84]).

most usual, which leads him to conclude that this value of a leads to the same value of R_{12} (approximately) not only for different states of the same molecule but also for different molecules [20].

Huggins observed that using $a = 6$ to calculate the largest spectroscopic constants (*i. e.* except $\omega_e y_e$ and $\omega_e z_e$) and the dissociation energy $C - C'$ when $R \to \infty$, did not lead to correct values. This is probably explained by the fact that the Morse curve does not have an adequate behavior for large values of R [8].

In the case of the dissociation energy he used the value $a = 4$ and the relation:

$$D = 0.8(C' - C). \tag{3.133}$$

When compared to the experimental values, the energy of dissociation calculated by Huggins from this equation presented a result more accurate to that calculated by the original Morse equation for most of the diatomic systems in several electronic states. The results were lower than Morse only for O_2^+ in the states $b\ ^4\Sigma_g^-$ and $X\ ^2\Pi_g$, CN in the state $B\ ^2\Sigma^+$, BeO in the states $B\ ^1\Pi$ and $A\ ^1\Sigma^+$, CO in the states $F\ ^1\Pi$, $B\ ^1\Sigma$ and $X\ ^1\Sigma$, NO in the states D, $C\ ^2\Sigma^+$ and $A\ ^2\Sigma^+$ and for BeF in the ground state $X^2\Sigma^+$.

The value of $C - C'$ in (3.133), as well as a', is obtained from the spectroscopic constants ω_e, $\omega_e x_e$ and the a:

$$(C - C') = \frac{0.0585\mu\omega_e^2}{(33a^2/16 + 12\omega_e x_e/B_e R_e)^{\frac{1}{2}} a - 7a^2/4} \tag{3.134}$$

with

$$a' = (33a^2/16 + 12\omega_e x_e/B_e R_e^2)^{\frac{1}{2}} - 7a/4, \tag{3.135}$$

being B_e the rotational constant.

To obtain the values of R_e, Huggins used [20]:

$$(R_{12} - R_e) = (2.303/a)\log 10^{12} C. \tag{3.136}$$

For the diatomic systems tested, $a = 6$ provided practically constant R_{12} values, as desired, varying between 1.44Å e 1.45Å.

The rotational constant α_e was calculated from the relation:

$$\alpha_e = (2B_e^2/\omega_e)[(a + a')R_e - 3], \tag{3.137}$$

and the best value for a in this case is $a = 6$, with average deviation from the observed value of α_e of only 0.003 cm^{-1}. When compared to the Morse function the α_e values calculated by Huggins did not present more accurate results, showing only better for the state $X\ ^2{\Sigma_g}^+$ of N_2^+, for the states $B\ ^1\Pi$, $a\ ^1\Pi_u$ and $X\ ^1{\Sigma_g}^+$ of N_2, for the state $^1\Pi$ of F_2, for the state $A\ ^2\Pi$ of BO, for the states $A\ ^1\Pi$ and $a\ ^3\Pi$ of CO and for the state $B\ ^2\Pi$ of NO.

Finally, Huggins showed that the spectroscopic constant $\omega_e x_e$ is given by [20]:

$$\omega_e x_e = (1/\mu)(1.39a^2 + 4.89aa' + 1.398a'^2). \tag{3.138}$$

A year later, in 1936, Huggins [85] following the steps of Badger [86, 87] published a second paper on molecular constants, however the focus this time was the relationship between the equilibrium distance R_e and the constant force k_e. He further expanded the number of diatomic systems studied, now considering the first two lines of the periodic table.

Badger [87] showed that R_e is given approximately by the expression

$$R_e = d_{ij} + C_{ij}^{\frac{1}{3}}/{k_e}^{\frac{1}{3}}, \tag{3.139}$$

where C_{ij} and d_{ij} are constant depending only on the rows in the periodic table in which the two elements comprising the molecule are located.

Huggins then showed the relationship between his method and that of Badger to obtain R_e via k_e, and compared the methods. Firstly, he considered the constant force (in megadynes per centimeter) [85]:

$$k_e = 5.85 \times 10^{-8} \mu {\omega_e}^2 \tag{3.140}$$

and combining with Eqs. (3.134), (3.135) and (3.136), he obtained:

$$R_e = R_{12} - \frac{2.303}{a} \log\left(\frac{100k_e}{a^2 - aa'}\right) \tag{3.141}$$

which is equivalent to

$$R_e = \left[R_{12} + \frac{2.303}{a} \log\left(\frac{100k_e}{a^2 - aa'}\right) - K_{ij}\right] + \left[K_{ij} - \frac{2.303}{a} \log k_e\right] \tag{3.142}$$

where K_{ij} is any distance.

Through suitable choices for K_{ij}, Huggins notes that Eq.(3.142) is approximately equivalent to Eq.(3.139). Thus, he obtained a relation between the constants d_{ij} and C_{ij} of the Badger equation given by

$$d_{ij} = R_{12} + \frac{2.303}{a} \log\left(\frac{a^2 - aa'}{100k_e}\right) - \frac{{C_{ij}}^{\frac{1}{3}}}{f^{\frac{1}{3}}}. \tag{3.143}$$

In comparison with the experimental value of $R_{e_{(exp)}}$, the values obtained by Huggins are more accurate than those of Badger. In 35 different states of the 24 types of molecules tested, the $R_e - R_{e_{(exp)}}$ deviations were smaller using the Badger formulation, whereas, for 61 different states of 35 types of molecules, the Huggins formulation showed the smallest deviations (For more details see Ref [85]).

3.1.12 The Hylleraas function

In 1935, Hylleraas [88] (HYL) proposes what he called the general expression for the potential of a diatomic system, and ensures that the most important spectroscopic constants are theoretically derived from it. To build such a function, Hylleraas imposes basic conditions so that its function is minimally reasonable to describe diatomic potentials. Are they:

$$\left.\begin{array}{r} B_e = \frac{\hbar^2}{8\pi^2\mu_e^2}, \\ V(R_e) = -D,\ V'(R_e) = 0,\ V''(R_e) = \mu(2\pi\omega_e)^2 = \frac{\hbar^2\omega_e^2}{2B_eR_e^2}. \end{array}\right\} \tag{3.144}$$

He introduces a new ρ variable, making

$$F(\rho) = \frac{V(R)}{D},\ \rho = \frac{\hbar\omega_e}{2\sqrt{B_eD}}\frac{R-R_e}{R_e} \text{ or } \frac{R}{R_e} = 1 + \frac{2\sqrt{B_eD}}{\hbar\omega_e}, \tag{3.145}$$

where, is immediate that

$$F(0) = -1,\ F'(0) = 0,\ F''(0) = 2. \tag{3.146}$$

Like the others, it also treats the rotational energy of the problem separately, falling into a usual one-dimensional oscillation equation:

$$\left\{\left(\frac{\hbar\omega_e}{2D}\right)^2\frac{d^2}{d\rho^2} + \frac{E}{D} - F\right\}\psi = 0. \tag{3.147}$$

Hylleraas, firstly showed that the potentials Rosen-Morse [29], Manning-Rosen [79] and Pöschl-Teller [30], and their respective equivalents to calculate the vibrational energy, can be obtained in a much simpler and faster way. By transforming Eq.(3.147) in equations of the hypergeometric type, which can be solved in an elementary way associated with the three potentials, now written as:

$$\text{I. F} = -2\frac{1+\text{k}}{\text{e}^{(1+\text{k})\rho}+\text{k}} + \left(\frac{1+\text{k}}{\text{e}^{(1+\text{k})\rho}+\text{k}}\right)^2 \text{ (Rosen-Morse)} \tag{3.148}$$

$$\text{II. F} = -2\frac{1-\text{k}}{\text{e}^{(1-\text{k})\rho}-\text{k}} + \left(\frac{1-\text{k}}{\text{e}^{(1-\text{k})\rho}-\text{k}}\right)^2 \text{ (Manning-Rosen)} \tag{3.149}$$

$$\text{II. F} = -2\frac{(1+\text{k}^2)\text{e}^{\rho}-2\text{k}^2}{(\text{e}^{\rho}-\text{k})(\text{e}^{\rho}+\text{k})} + \left(\frac{(1+\text{k}^2)\text{e}^{\rho}-2\text{k}^2}{(\text{e}^{\rho}-\text{k})(\text{e}^{\rho}+\text{k})}\right)^2 \text{ (Pöschl-Teller).} \tag{3.150}$$

In solving the three hypergeometric differential equations associated with each of the three potentials, in which the same ansatz for the wave function can be used for the three cases, Hylleraas obtained the following formulas for the vibrational energy, respectively:

$$\text{I. } \frac{1}{\mathrm{k}}\sqrt{1+\frac{\mathrm{k}^2}{4}\left(\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\right)^2}-\frac{1}{1+\mathrm{k}}\sqrt{-\frac{\mathrm{E}}{\mathrm{D}}}-\frac{1}{1+\mathrm{k}}\sqrt{\frac{1}{\mathrm{k}^2}-\left(1+\frac{\mathrm{E}}{\mathrm{D}}\right)}=\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\left(\nu+\frac{1}{2}\right)$$
$$\Rightarrow \sqrt{-\frac{E}{D}}=\sqrt{1+\frac{k^2}{4}\left(\frac{\hbar\omega_e}{2D}\right)^2}-\frac{\hbar\omega_e}{2D}\left(\nu+\frac{1}{2}\right)-\frac{\frac{1}{2}(k-k^2)\left(\frac{\hbar\omega_e}{2D}\right)^2\nu(\nu+1)}{\sqrt{1+\frac{k^2}{4}\left(\frac{\hbar\omega_e}{2D}\right)^2-k\frac{\hbar\omega_e}{2D}\left(\nu+\frac{1}{2}\right)}} \tag{3.151}$$

$$\text{II. } \sqrt{-\frac{\mathrm{E}}{\mathrm{D}}}=\sqrt{1+\frac{\mathrm{k}^2}{4}\left(\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\right)^2}-\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\left(\nu+\frac{1}{2}\right)+\frac{\frac{1}{2}(\mathrm{k}+\mathrm{k}^2)\left(\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\right)^2\nu(\nu+1)}{\sqrt{1+\frac{\mathrm{k}^2}{4}\left(\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\right)^2+\mathrm{k}\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\left(\nu+\frac{1}{2}\right)}}$$
$$\Rightarrow -\frac{1}{k}\sqrt{1+\frac{k^2}{4}\left(\frac{\hbar\omega_e}{2D}\right)^2}-\frac{1}{1-k}\sqrt{-\frac{E}{D}}+\frac{1}{1-k}\sqrt{\frac{1}{k^2}-\left(1+\frac{E}{D}\right)}=\frac{\hbar\omega_e}{2D}\left(\nu+\frac{1}{2}\right) \tag{3.152}$$

$$\text{III. } \sqrt{-\frac{\mathrm{E}}{\mathrm{D}}}=\sqrt{\frac{(1+\mathrm{k})^4}{16\mathrm{k}^2}+\frac{1}{16}\left(\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\right)^2}-\sqrt{\frac{(1-\mathrm{k})^4}{16\mathrm{k}^2}+\frac{1}{16}\left(\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\right)^2}-\frac{\hbar\omega_{\mathrm{e}}}{2\mathrm{D}}\left(\nu+\frac{1}{2}\right)$$
$$\Rightarrow \sqrt{\frac{(1+k)^4}{16k^2}+\frac{1}{16}\left(\frac{\hbar\omega_e}{2D}\right)^2}-\sqrt{\frac{(1-k)^4}{16k^2}+\frac{1}{16}\left(\frac{\hbar\omega_e}{2D}\right)^2}+\sqrt{-\frac{E}{D}}=\frac{\hbar\omega_e}{2D}\left(\nu+\frac{1}{2}\right) \tag{3.153}$$

Observing that the above all energy formulas result in $\frac{\hbar\omega_e}{2D}\left(\nu+\frac{1}{2}\right)$, and therefore approximate according to the phase transition method (see details in section 2.3), Hylleraas obtained the following relation:

$$\frac{1}{2\pi i}\oint\sqrt{-\frac{E}{D}+F}d\rho=\frac{\hbar\omega_e}{2D}\left(\nu+\frac{1}{2}\right). \tag{3.154}$$

Analyzing the potential of Morse with three parameters, and considered one of the most accurate at the time, and that of Rosen-Morse that with four parameters showed a slight improvement, Hyleraas [88] proposes a potential that contains six adjustable parameters. If on the one hand this potential really should guarantee more accurate results and applicable to a greater number of different diatomic systems, on the other hand, a potential involving such a large number of parameters generally requires quite sophisticated calculations.

The potential proposed by Hylleraas is given by [89]:

$$V_{HYL}(R) = F + -D - D\xi^2, \quad 1 - \xi = \frac{(1+a)(1+c)(x+b)}{(1+b)(x+a)(x+c)},$$

$$x = e^{(1+k)\rho}, \quad \frac{1}{1+k} = \frac{1}{1+a} + \frac{1}{1+c} - \frac{1}{1+b}, \tag{3.155}$$

$$\rho = \frac{\hbar\omega_e}{2\sqrt{B_e D}} \frac{(R - R_e)}{R_e}$$

where D, B_e and $\hbar\omega_e$ are spectroscopic constants and R_e is the equilibrium distance.

For $b = a$, $c = -k$ we have the potentials of Manning-Rosen, for $b = a$, $c = 0$ the potential of Morse and for $b = a$, $c = k$ the potential of Rosen-Morse. Similarly, if we have $b = c$, $a = -k, 0, k$ we have the potentials of Manning-Rosen, Morse and Rosen-Morse respectively. Finally, if we have $a = -k$, $c = k$, $b = -2k^2/(1 + k^2)$, we get the potential of Pöschl-Teller.

For the potential $V_{HYL}(R)$, the energy equation will be calculated, using the same idea of (3.154), by:

$$\frac{1}{2\pi i} \oint \sqrt{-\left(1 + \frac{E}{D}\right) + \xi^2} d\rho = \sqrt{-\left(1 + \frac{E}{D}\right) + \xi^2} \frac{d\rho}{d\xi} d\xi = \frac{\hbar\nu_e}{2D}\left(\nu + \frac{1}{2}\right) \tag{3.156}$$

where $\frac{d\rho}{d\xi}$ is expanded in power series of ξ

$$\left.\begin{aligned} \tfrac{d\rho}{d\xi} &= 1 + a_1\xi + a_2\xi^2 + a_3\xi^3 + a_4\xi^4 + \cdots, \\ \rho &= \xi + \tfrac{a_1}{2}\xi^2 + \xi + \tfrac{a_2}{3}\xi^3 + \xi + \tfrac{a_3}{4}\xi^4 + \xi + \tfrac{a_4}{5}\xi^5 + \cdots \end{aligned}\right\}. \tag{3.157}$$

The energy formula can finally be expressed as [88]:

$$\begin{aligned} 1 - \sqrt{-\tfrac{E}{D}} &= \tfrac{\hbar\omega_e}{2D}\left(\nu + \tfrac{1}{2}\right) + \tfrac{1}{2}(1 - a_2)\left(\tfrac{\hbar\omega_e}{2D}\right)^2\left(\nu + \tfrac{1}{2}\right)^2 \\ &+ \left[\tfrac{1}{2}(a_2 - a_4) + \tfrac{1}{2}(1 - a_2)^2\right]\left(\tfrac{\hbar\omega_e}{2D}\right)^3\left(\nu + \tfrac{1}{2}\right)^3 + \cdots \\ &= \tfrac{\hbar\omega_e}{2D}\left(\nu + \tfrac{1}{2}\right) + \frac{\frac{1}{2}(1-a_2)\left(\frac{\hbar\omega_e}{2D}\right)^2\left(\nu+\frac{1}{2}\right)^2}{1 - \left[1 - a_2 + \frac{a_2 - a_4}{1 - a_2}\right]\frac{\hbar\omega_e}{2D}\left(\nu + \frac{1}{2}\right)} + \cdots. \end{aligned} \tag{3.158}$$

The coefficients a_1, a_2, a_3, a_4 may be derived from the expression:

$$\left.\begin{array}{c}\rho = \frac{1}{1+k}\log\frac{1}{1-\xi}\left\{1 + k\xi - \frac{2k_1k_2(1+k)\xi^2}{1+(k_1+k_2+2K_1k_2)+\sqrt{[1+(k_1+k_2+2k_1k_2)\xi^2]-4k_1k_2(1+k_1)(1+k_2)\xi^2}}\right\} \\ k_1 = \left(\frac{1}{1+b} - \frac{1}{1+a}\right)(1+k), \quad k_2 = \left(\frac{1}{1+b} - \frac{1}{1+c}\right)(1+k).\end{array}\right\} \tag{3.159}$$

or still,

$$\begin{cases} a_1 = 1 - k - 2k_1k_2 \\ a_2 = 1 - k + k^2 + 3k_1k_2[k + k_1 + k_2 + 2k_1k_2], \\ a_3 = 1 - k + k^2 - k^3 - 4k_1k_2\left[k(k + k_1 + k + 2 + 2k_1k_2) + (k + k_1 + k + 2 + 2k_1k_2)^2\right. \\ \left.+k_1k_2(1+k_1)(1+k_2) + \frac{1+k}{2}k_1k_2\right] \\ a_4 = 1 - k + k^2 - k^3 + k^4 + 5k_1k_2\{k(k + k_1 + k + 2 + 2k_1k_2) \cdot [(k + k_1 + k + 2 \\ +2k_1k_2)^2 + k^2 + (1+k)k_1k_2] + k_1k_2(1+k_1)(1+k_2)[k + 3(k_1 + k + 2 + 2k_1k_2)]\}. \end{cases} \tag{3.160}$$

As observed by Varshni [14], the potential of Hylleraas does not provide any relation between the spectroscopic constants, unlike the potential of Morse, Rosen-Morse, Manning Rosen, and Pöschl-Teller.

Soon after proposing its potential function, Hylleraas [90] uses it to calculate the curves for the diatomic systems N_2 and CdH, both in the ground state. In the case of N_2 the accuracy that Hylleraas obtained for the series of the vibrational energy E_ν, with only two terms, is remarkable.

When comparing the Morse (N_2) and Rydberg (CdH) curves, he sees a good agreement with Rydberg. However, when compared to Morse, the potential curve of Hylleraas presents good agreement for the vibrational levels of 0 to 10, presenting a very poor result in the long-range region (and in the levels $\nu > 21$), where the Hylleraas curve tends to be less infinity [90].

3.1.13 The Extended Morse function

In 1938, Coolidge, James, and Vernon [32] (CJV) based on the Dunham [24] theory, have established that any potential curve of a diatomic system, which has an asymptotic value D, can be written as

$$V(\xi) = DF(\xi), \quad \xi = (R - R_e)/R_e. \tag{3.161}$$

Furthermore, for CJV all potential energy functions must have at least three parameters, that is, in addition to D and R_e, a third parameter β would always be present to ensure a good fit of the curve. The energy formulas will be related to the Dunham coefficients (3.163) and will be expressed in terms of the constant C, given by:

$$C^2 = \frac{4R_\infty m_e \beta^2}{\mu R_e} \tag{3.162}$$

where R_∞ is the Rydberg constant[5] and m_e is the mass of the electron. The Y'_{lj} will be related follow:

$$\begin{aligned} Y'_{10} &\sim \omega_e \quad -Y'_{20} \sim \omega_e x_e \\ Y'_{01} &\sim B_e \quad -Y'_{11} \sim \alpha_e \end{aligned} \tag{3.163}$$

To obtain terms of highest order, *i. e.*, up to Y''_{20}, Y'_{40}, Y''_{11}, Y'_{31}, Y''_{02}, Y'_{22}, Y'_{13} and Y'_{04}, CJV [32] opted to determine by numerical integration the values R_ν and B_ν for large ν, and so adjusting the values the higher $Y's$ as to reproduce these values.

The potential proposed by CJV is an extension of the Morse function, being known as Extended Morse (EM) potential. Using the formulation (3.161), this potential is given by:

$$F(\xi) = \sum_{n=2}^{8} c_n[1 - e^{-2\beta\xi}]^n \tag{3.164}$$

or in terms of R,

$$V_{EM}(R) = \sum_{n=2}^{8} c_n[1 - e^{-2\beta\frac{R-R_e}{R_e}}]^n \tag{3.165}$$

where c_n are adjustable parameters. These can be obtained from the relationships with the coefficients of Dunham:

$$\begin{aligned} a_0 &= 4\beta^2 D c_2 \\ a_0 a_1 &= 4\beta^2 D(-2c_2 + 2c_3) \\ a_0 a_2 &= 4\beta^4 D(7/3c_2 - 6c_3 + 4c_4) \\ a_0 a_3 &= 4\beta^5 D(-2c_2 + 10c_3 - 16c_4 + 8c_5) \\ a_0 a_4 &= 4\beta^6 D(62/45c_2 - 12c_3 - 342/3c_4 - 40c_5 + 16c_6) \\ a_0 a_5 &= 4\beta^7 D(-4/5c_2 - 1121/45c_3 - 531/3c_4 + 1062/3c_5 - 96c_6 + 32c_7) \\ a_0 a_6 &= 4\beta^8 D(127/315c_2 - 91/5c_3 + 645/5c_4 - 200c_5 - 304c_6 - 224c_7 + 64c_8). \end{aligned} \tag{3.166}$$

The parameter β may be chosen to satisfy the auxiliary condition, $\sum_n c_n = 1$, if it is desired to reproduce the observed dissociation energy D, or as an adjustable parameter to satisfy other condition.

CJV exhibited potentials and energy formulas for the potential of Morse, Pöschl-Teller, and Hylleraas, in addition to the one proposed by them, and presented a comparative study for the H2 system in the excited state $1s\sigma 2s\sigma\ {}^3\Sigma_g$.

The curve obtained with the potential Extended Morse function reproduces the

[5]The Rydberg constant is given by $R_\infty = \frac{m_e e^4}{8\epsilon_0{}^2 h^3 c} = 1.0973731 \times 10^7 m^{-1}$ for heavier elements and $R_H = 1.09677576 \times 10^7 m^{-1}$ for the hydrogen molecule.

values of the coefficients $Y_{10} \cdots Y_{40}$, $Y_{01} \cdots Y_{31}$ given by Sandeman [91], who a priori used the H_2 system in the state $1s\sigma 2s\sigma\ ^3\Sigma_g$ in his work. The curve presents correct behavior, both short and long range with deviations within the spectroscopic limit for R between 1.5 ${a_H}^6$ and 2.5 a_H, and only one deviation of 2 cm^{-1} for $R = 2.7\ a_H$ and of 8 cm^{-1} for $R = 2.9\ a_H$.

Concerning the energy formulas, both vibrational and rotational, the function of CJV was much higher than that of Morse, Poschl-Teller, and Hylleraas. The errors in the reproduction of energy levels by the potential curve using Dunham's terms supplemented by results of numerical integrations are practically zero in the first levels $(0 \leq \nu \leq 3)$ [32].

Among the comparative potentials, the one closest to the extended Morse is the Hylleraas, however, this occurs only when it is constructed by the method proposed by CJV.

3.1.14 The Mecke-Sutherland function

Firstly, in 1927, Mecke [92] based on the work of Born and Handb, used a well known analytical expression in those time to develop his diatomic potential:

$$V = -e^2 \left[\frac{c_1}{R^p} - \frac{c_2}{R^q} \right]. \tag{3.167}$$

Here, the first term represents the potential of attractive forces in the molecular association, since they are supposed to be purely radial forces, they may, in any case, be inversely proportional to an initially arbitrary power p of the central distance R. The second term represents the repulsive part of the potential. The inequality $p < q$ must be maintained. For dimensional reasons, the total expression was multiplied by the square of the elemental charge e. The constants in (3.167) are related with spectroscopic parameters (R_e, a, b and D).

For Mecke, the equilibrium position, that is, the distance R_e from the nuclei, caused by the compensation of the repulsive and attractive forces that prevail in it, and thus corresponds to a minimum of the potential energy, was given by

$$R_e^{q-p} = \frac{q \cdot c_2}{p \cdot c_1}. \tag{3.168}$$

To obtain the elastic potential (3.167), he developed the expression for vibrations with a small amplitude x ($R = R_e \pm x$) in power of x, obtaining:

$$V = -\left(\frac{e^2 c_1 (q-p)}{R_e^p \cdot q} \right) + \frac{e^2 c_1 \cdot p(q-p)}{2R_e^{p+2}} x^2 \cdots \tag{3.169}$$

[6] Here a_H is the ray of the first circle of Bohr, and $a_H = \frac{\hbar^2}{4\pi^m e^2 = 0{,}529 \cdot 10^{-8}}$

or more generally,

$$V = -D + \frac{D_2}{2!}\left(\frac{x}{R_e}\right)^2 - \frac{D_3}{3!}\left(\frac{x}{R_e}\right)^3 + \frac{D_4}{4!}\left(\frac{x}{R_e}\right)^4 \cdots \tag{3.170}$$

where D_j is a product of dissociation energy D by a simple (p, q) function. In particular, $D_2 = p \cdot q \cdot D$, and as is well known, the x^2 coefficient immediately gives us the value of the molecule's natural vibration

$$2\pi\nu = \sqrt{\frac{D_2}{J}} = \sqrt{\frac{e^2 c_1 p(q-p)}{R_e^p J}} \tag{3.171}$$

which the two constants in (3.167) can be determined by ν (=a from oscillation equation $an - bn^2$) and J.

Analyzing the expression (3.167) Mecke [92] observed that the values $p = 1$ and q from 3 to 4 were adequate for most hydrides, and $p = 1$ or $q = 4$ were adequate for oxides and nitrides spectra. In particular, for most hydride the potential curve in the immediate neighborhood of the equilibrium position is best characterized by particularly simple approach:

$$V = -\frac{e^2}{R} + \frac{e^2}{qR_e}\left(\frac{R_e}{R}\right)^q. \tag{3.172}$$

Years later, Sutherland [44] suggested an analogous functional form to express the mutual potential energy, known as Mecke-Sutherland (MS) potential, given by:

$$V_{MS} = \frac{\alpha}{R^m} - \frac{\beta}{R^n}, \tag{3.173}$$

where, since $\left(\frac{dV_{MS}}{dR}\right)_{R=R_e} = 0$, the relationship

$$m\alpha = n\beta R_e^{m-n} \tag{3.174}$$

can be obtained.

Sutherland derived the relations between force constant k_e, equilibrium distance R_e and the dissociation energy D. He expanded V_{MS} about R_e in powers of $(R - R_e)$, such the coefficient of $(R - R_e)^2$, *i. e.*, the force constant k_e was obtained by:

$$k_e = \frac{n\beta}{R_e^{n-1}}\left(\frac{n+1}{R_e} - \frac{m+1}{R_e}\right) \tag{3.175}$$

and using the relationship (3.174)

$$k_e = \frac{m\alpha(n-m)}{R_e^{m+2}} = \frac{n\beta(n-m)}{R_e^{n+2}}. \tag{3.176}$$

The dissociation energy was obtained by Sutherland [44] from (3.174)

$$D = \frac{\alpha}{R_e^m}\left(1 - \frac{m}{n}\right) \tag{3.177}$$

or from (3.176)

$$D = \frac{k_e R_e^2}{mn} = 2\Delta, \tag{3.178}$$

where Δ is the Sutherland parameter.

This result once reminiscent of the rule of Mecke was presented during a congress in Leipzig (Leipziger Vorträge 1931). In this congress, Mecke was criticized by prominent physicists that only normal vibrations involving all atoms of the molecule are possible, but not vibrations of isolated groups of the molecule. However, Mecke's opponents were wrong. They did not consider the large difference in the stretching frequencies of CH, OH, or NH groups due to the low weight of the H atom (as compared to frequencies where no H atoms are involved), nor the influence of the great differences between single, double, and triple bonds and their respective frequencies, effects which allow a mathematical separation solution in the respective eigenvalue equations. Thus the Mecke's concepts are adequate and clear even today [93].

More some spectroscopic parameters can be obtained using the relation (3.178) [14]:

$$\alpha_e = (m + n)\frac{2B_e^2}{\omega_e} \tag{3.179}$$

and

$$\omega_e x_e = \left[\frac{2}{3}m^2 + \frac{7}{3}mn + \frac{2}{3}n^2 + 4(m + n) + 4\right]\frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.180}$$

3.1.15 The Hulburt-Hirschfelder function

The Morse function was considered limited because is not flexible due to the reduced number of parameters, which initially seemed to be an advantage, because it made the functional form simpler. To tackle this limitation, in 1940, Hulburt and Hirschfelder [7] (HH) suggested the addition of two parameters, *i. e.*, functions involving five spectroscopic constants. These two parameters to be added in a so-called correction term were easily determined, and the five-parameter functions proved satisfactory for a large majority of diatomic molecules. However, the problem to obtain the potential $V(R)$ already reported in the Morse function for large internuclear distances was not solved with this correction. Since the high levels of vibrational energy are unknown for many molecules, it is virtually impossible to find a unique potential that could be universally used for diatomic systems.

For Hulburt and Hirschfelder [7], any functional form intended to describe a potential energy function must have as basic characteristics a value close to infinity when nuclei approach each other, passing then through a minimum at the equilibrium distance and a value close to the dissociation energy when the nuclei become distant. They analyzed the best-known functions with three, four, five, and six spectroscopic constants, and concluded that a function with five parameters would be ideal, being able to be used by the largest possible number of diatomic systems.

From the fact that the spectroscopic constants ω_e, $\omega_e x_e$, B_e and α_e are known for most diatomic molecules, where $B_e = \hbar/(8\pi^2\mu R_e^2 c)$, the function proposed by them had three parameters used to recover the usual Morse function plus two parameters, b and c, which corrected the curve of Morse, and at the same time were obtained by means of the known constants. The function of Hulburt and Hirschfelder has the form:

$$V_{HH}(R) = D_e[(1 - e^{-x})^2 + (1 + bx)cx^3 e^{-2x}] \tag{3.181}$$

where $x = \frac{\omega_e}{2(B_e D_e)^{\frac{1}{2}}}\left[\frac{R - R_e}{R_e}\right]$, and the constants b and c are given by the relation

$$c = 1 + a_1(D_e/a_0)^{\frac{1}{2}}, \tag{3.182}$$

$$b = 2 + \frac{\left[\frac{7}{12} - \frac{D_e a_2}{a_0}\right]}{c} \tag{3.183}$$

being a_0, a_1 and a_2 the Dunham coefficients given by expansion [24]

$$a_0 = \omega_e^2/4B_e \tag{3.184}$$

$$a_1 = -1 - \alpha_e\omega_e/6{B_e}^2 \tag{3.185}$$

$$a_2 = \frac{5}{4}{a_1}^2 - \frac{2}{3}\frac{\omega_e x_e}{B_e}. \tag{3.186}$$

What made HH believe the potential they presented with five parameters was ideal, were tests performed with selected diatomic molecules in certain states which were not analytically well described until then, but when using $V_{HH}(R)$ as potential function presented good results. They are: H_2 in $1s\sigma 2s\sigma {}^3{\Sigma_g}^+$ state, CdH and N_2 both in the ground electronic state.

For H_2 in $1s\sigma 2s\sigma {}^3\Sigma_g^+$ state the HH potential was the one that best fitted the curve, not better only than the potential by Hylleraas [88] with six parameters or than the Pöschl-Teller [30] that have the same vibrational levels of the Morse function, but on account of a fourth parameter, provides better fitting for the rotational levels.

For the CdH, the maximum deviation from the Rydberg curve [9], which is a reference in the fitting of this molecule, remains very small (of the order of 0.35 kcal mol^{-1}).

For N_2 molecule, when compared with the Hylleraas [88] fitting for the first 22 vibrational levels, the HH potential again showed good agreement. Also comparing with the Extended Morse curve of Coolidge, James, and Vernon [32], it presents the same results, however, these are more easily obtained by the HH potential as parameters can more easily be determined in terms of Eq. (3.181).

For the H_2 molecule, the required corrections to the Morse curve are rather small. With the constants b and c introduced, the Morse curve was corrected for small and large nuclear separations, and with the potential HH, the curve is much smoother, providing an improvement in the description of the asymptotic limit.

The potential of HH was conceived with the purpose of giving the best fit for the spectroscopic constants. However, it is difficult to find a suitable polynomial to express both the lowest and the highest vibrational energy levels. Then, the polynomial function should also be multiplied by an exponential term, such as:

$$E_\nu = A[1 - exp(-1/2(\nu + 1/2))]\left[1 + 0,1\left(\nu + \frac{1}{2}\right) - 0.005\left(\nu + \frac{1}{2}\right)^2\right]. \quad (3.187)$$

Thus, there are two different series for each case, the difference is because exponentials with large negative values converge asymptotically to zero. For small values of $(\nu + 1/2)$, the energy levels are calculated by the series [7]:

$$E_\nu/\text{kcal mol}^{-1} = 0,5\left(\nu + \frac{1}{2}\right) - 0.075\left(\nu + \frac{1}{2}\right)^2 + \cdots \quad (3.188)$$

and for large values, the series in kcal mol^{-1}

$$E_\nu/\text{kcal mol}^{-1} = 1 + 0,1\left(\nu + \frac{1}{2}\right) - 0.005\left(\nu + \frac{1}{2}\right)^2 + \cdots . \quad (3.189)$$

The method to obtain the corresponding energy levels would replace (3.181) in the Schrödinger equation and perform numerical integrations.

In 1961, Hulburt and Hirschfelder [94] perceived an error in the first sign of the expression referring to parameter b, the correct signal is negative and not positive, *i. e.*:

$$b = 2 - \frac{\left[\frac{7}{12} - \frac{D_e a_2}{a_0}\right]}{c}. \quad (3.190)$$

This led researchers as Tawde [95] and Herzberg [96] to question the fit of their potential function, being considered poorly fitted because of this error.

In a paper published in 1954, Tawde and Gopalakrishnan [95] even stated that the fitting of the HH function was good only for distances larger than the equilibrium distance, *i. e.*, for $R > R_e$ in the case of the C_2 molecule. However, after re-counting with the correct sign of parameter b, Tawde and Katti, who first notice it and communicated the authors about the error in b, concluded that the function by Hulburt and Hirschfelder was indeed a good representation [97]. They also verified for other diatomic molecules the function HH is far superior to several others even more known than the Morse function considering the prediction of molecular constants.

3.1.16 The Linnett function

After analyzing the Morse[8] and Mecke-Sutherland[44, 92] potentials, the former being an double-exponential function of type $V = a \cdot e^{-mR} - b \cdot e^{-nR}$, and the latter a double-reciprocal function of type $V = \frac{a}{R^m} - \frac{b}{R^n}$, Linnett[61] proposed a two terms function containing elements from both. Its intention was to improve the fitting of the potential energy curve for several diatomic systems and to obtain satisfactory connections between the parameters k_e and R_e, which did not occur in the Mecke-Sutherland[44, 92] potential.

It was then that in 1940, Linnett [61] (LIN) introduced a potential function more generic than the thus far proposals, involving four adjustable parameters, given by:

$$V_{LIN}(R) = \frac{a}{R^m} - b \cdot e^{-nR}. \tag{3.191}$$

He called this potential of reciprocal-exponential function, consisting of two terms, both going to zero when R becomes infinite. The first term represents the repulsion between atoms, going to $+\infty$ when $R = 0$, and the second term represents the attraction of two atoms, going to $-\infty$ when $R = 0$. Thus, the behavior of the total function will depend on the values assigned to the parameters that compose it.

Linnett devoted himself to testing its potential for diatomic systems composed of atoms belonging to the second period of the periodic table. First, considering the relationships $\left(\frac{dV_{LIN}}{dR}\right)_{R_e} = 0$ e $\left(\frac{d^2V_{LIN}}{dR^2}\right)_{R_e} = k_e$, the following relationships were obtained for the dissociation energy D and for the constant force k_e[61]:

$$D = \frac{a}{{R_e}^m}\left(\frac{m - nR_e}{nR_e}\right) \tag{3.192}$$

and

$$k_e = \frac{a}{{R_e}^{m+2}} \cdot m(m + 1 - nR_e) \tag{3.193}$$

combining (3.192) and (3.193), and by eliminating nR_e is obtained

$$k_e{R_e}^{m+2} = ma + \frac{m^2 \cdot D{R_e}^m}{1 + \frac{D{R_e}^m}{a}}. \tag{3.194}$$

One of his major concerns was to explain the relationship between k_e and R_e since the functions of the double-reciprocal type could not do so. For this, it was necessary to assume the parameters m and a constants for all states of the same molecule, with n and b calculated and fitted for each state conveniently from two other parameters. Linnett [61] used $m = 3$ for all studied molecules in his tests, since $k_eR_e^5$ according to Fox and Martin [98] was approximately constant, and when analyzing the behavior of this same expression when $m = 4$ came to the conclusion that if a is constant, the expression $k_eR_e^6$ does not significantly change, that is, it can be considered constant as well.

The probable reason for Linnett to have used the values m =3 and $m = 4$ in his tests is that when calculating parameters such as vibration frequency and harmonicity, the potential is usually expanded in a series of powers around the equilibrium interatomic distance and this series is truncated in 3^{rd} or 4^{th} power, the other terms being generally negligible. Thus, it was reasonable to consider only such m values.

To the parameter a was given a different value for each molecule, taking into account the atoms involved, the charge of the molecule, among other aspects.

Linnett [61] calculated R_e from the observed values of k_e and D for certain states of the following diatomic systems: Li_2, C_2, N_2, O_2, BeF, BO, CN, CO, NO, N_2^+, O_2^+ and CO^+.

By using $k_e R_e^5 = a$ and $k_e R_e^6 = a$, being a constant chosen for each molecule, Linnett [61] came to the conclusion that in general, the expression with the 6th power of the interatomic distance provided better results than the 5th. For the states of the molecules in general, the mean error in the calculation of R_e using $k_e {R_e}^6 = a$ was 0.9% while using $k_e {R_e}^5 = a$ was 1.5%.

For the calculation of $\omega_e x_e$ from k_e and D, Linnett expanded the potential function (3.191) on power series in $(R - R_e)$ in the neighborhood of R_e, neglecting the highest terms in the series to be able to use the Kratzer [16] method, obtaining a value for $\omega_e x_e$ in function of m, n and R_e given by:

$$\omega_e x_e = \frac{\hbar}{64\pi^2 c\mu {R_e}^2} \left\{ \tfrac{5}{3}\left[\tfrac{(m+1)(m+2)-(nR_e)^2}{(m+1)-nR_e}\right]^2 - \left[\tfrac{(m+1)(m+2)(m+3)-(nR_e)^3}{(m+1)-nR_e}\right] \right\} \quad (3.195)$$

where μ is the molecule reduced mass.

Except for Li_2 and O_2, $\omega_e x_e$ values were better reproduced by the Linnett potential than by any other known before, with an average error on all states of 16%, largely improving the corresponding error obtained with the Morse potential, of about 46%[61].

When the values of $\omega_e x_e$ were calculated using the same parameter a, but now starting from k_e and R_e, the average error increases very little, being at the 18%, already the calculated average error for the dissociation energy D stands at 28%, not so good, but slightly better than the calculated via Morse potential[61].

Also, the spectroscopic parameter α_e can be obtained from equation:

$$\alpha_e = \frac{6B_e^2}{\omega_e}\left[\frac{(m+1)(m-1)-(nR_e)^2+3nR_e}{3(m+1-nR_e)}\right] \quad (3.196)$$

but this was not evaluated by Linnett in his paper published in 1940. Subsequent work, such as Varshni [14] and of Steele *et al.* [15] approached this calculations for Linnett potential. Varshni [14] analyzed the behavior of α_e for 23 diatomic systems and concluded that this was unsatisfactory for most of them, adequate only for CO, N_2, NO and O_2. However, Steele *et al.* [15] obtained very different results, for the diatomic systems in their ground and some excited electronic states: H_2, I_2, N_2, O_2, CO, NO, OH and HF. The average error for α_e using the Linnett potential was less than for the Morse [8], Rydberg [9], Rosen-Morse [29], , Pöschl-Teller [30], Frost-Musulin [74], Lippincott [43] and Varshni (III) [14] potentials.

Still, in the same work, Steele *et al.* [15] showed that for the 8 diatomic systems above cited, the average error for $\omega_e x_e$ relative to Linnett potential was practically half of the error presented relative to Morse [8], Rydberg [9], Rosen-Morse [29], Pöschl-Teller [30], Frost-Musulin [74] and Varshni (III) [14] potentials.

Then, the Linnett potential provided a good representation of the potential energy curve, superior to many others functions that were known at that time, obtaining the best results for the diatomic systems O_2 and CO[61], especially when using the observed values of k_e e D.

In more recent research, such as Royappa *et al.* [42], has shown that if the parameters of the Linnett potential are well fitted, using, for example, the Mathcad (Mathsoft Inc.), this function has fewer deviations from the RKR [9–11] curve than the Kratzer [16], Lippincott [43], Deng-Fan [41] and Rosen-Morse [29] potentials.

3.1.17 The Heller function

In 1941, Heller [21] (HEL) proposed a functional form for specific diatomic systems known as van der Waals molecules. They present a very flat potential minimum at relatively large interatomic distances. He was interested in the diatomic system, in the gaseous phase and for the lowest energy state: HgHe, HgNe, HgAr, HgKr, HgXe, Hg_2 and in the polyatomic systems $(O_2)_2$ and $(NO)_2$ which can be treated as consisting of two bodies since the two atoms in each normal O_2[NO] diatomic molecule are fairly tightly bound and their internuclear separation 1.21[1.15]Å [96] is much smaller than intermolecular distance, R_0 say, of $(O_2)_2[(NO)_2]$.

The potential energy function is constituted by an attractive part, $\Delta E^{(2)}$, being considered the dispersion forces only, and a repulsive part $A(\rho)e^{-R/\rho}$ in the form of Born-Mayer's potential, given by:

$$V_{HEL}(R) = A(\rho)e^{-R/\rho} - \left(\frac{c_1}{R^6} + \frac{c_2}{R^8} + \frac{c_3}{R^{10}} + \frac{c_4}{R^{12}}\right). \tag{3.197}$$

where $\Delta E^{(2)} = -\frac{c_1}{R^6} - \frac{c_2}{R^8} - \frac{c_3}{R^{10}} - \frac{c_4}{R^{12}}$ and $A(\rho)e^{-R/\rho}$ is the same kind of function used in Born-Mayer's potential [19] to treat the alkali-halide crystals (see section 3.1.5).

The coefficient of the first term, c_1 is calculated by London general expression (see Ref. [99]) and the remaining coefficients are found using perturbation calculation using the Margenau harmonic oscillator model (see Ref. [100]).

Heller observed the well depth D_e of the potential (3.197) at R_m (minimum) is given by:

$$V_{HEL}(R_m) = -\left[\frac{c_1}{R_m^6}\left(1-\frac{6\rho}{R_m}\right)+\frac{c_2}{R_m^8}\left(1-\frac{8\rho}{R_m}\right)+\frac{c_3}{R_m^{10}}\left(1-\frac{10\rho}{R_m}\right)+\frac{c_4}{R_m^{12}}\left(1-\frac{12\rho}{R_m}\right)\right] = D_e. \tag{3.198}$$

However, this would be the minimum if and only if:

$$A(\rho) = \frac{2}{R_m^7}\left(3c_1 + 4\frac{c_2}{R_m^2} + 5\frac{c_3}{R_m^4} + 6\frac{c_4}{R_m^6}\right)\cdot \rho e^{R_m/\rho}, \tag{3.199}$$

being ρ bounded by

$$\rho < \frac{c_1 + \frac{4}{3}\frac{c_2}{R_m^2} + \frac{5}{3}\frac{c_3}{R_m^4} + 2\frac{c_4}{R_m^6}}{c_1 + \frac{12}{7}\frac{c_2}{R_m^2} + \frac{55}{21}\frac{c_3}{R_m^4} + \frac{26}{7}\frac{c_4}{R_m^6}}\frac{R_m}{7} \tag{3.200}$$

For the eight diatomic systems considered by Heller, ρ was considered equal to 0.28Å, ensuring that the energy of dissociation was in good agreement with experimental data.

The interatomic distance R_m considered by Heller was not identical to the equilibrium distance R_e. Using a graphic procedure that identifies the midpoint of the classical range of oscillation of the lowest vibrational level with the equilibrium distance R_e (for more details see Ref. [101]).

The coefficient of term R^{-12} is many times neglected, and when this is considered zero, the error for the well depth's is only 2.1 percent or less, assuming $\rho = 0.28$Å, for the analyzed systems. However, although the contribution of the term R^{-12} is small, it is important when $R = R_m$ [21].

The type of function (3.197) was firstly proposed in 1938, by Buckingham [102] for to treat diatomic system composed by rare gases, such as helium, neon and argon. He obtained the potential energy interaction $V_{BUC}(R)$ for rare gas atoms from the observed virial coefficients, using the classical equation of state:

$$V_{BUC}(R) = Ae^{-bR} - \left(\frac{C_6}{R^6} + \frac{C_8}{R^8}\right) \tag{3.201}$$

being A and b constant, C_6 and C_8 parameters evaluated by Lennard-Jones and Ingham [103]. However, function (3.201) has a deficiency. Although the exponential term increases rapidly as R decreases, it remains finite when $R = 0$, so that the long-range term is dominant at $R \to 0$ when then $V_{BUC}(R) \to -\infty$. These problems were fixed damping the dispersion term by Tang-Toennies potential [104].

3.1.18 The Wu-Yang function

In 1944, although intending to cover the most diverse types of diatomic systems, and not just rare gases or crystals forces, Wu and Yang [105] (WY) proposed a potential function similar to Heller [21], which is also based on the potential of Born-Mayer [19] and Buckingham [102]. They have applied their relation to diatomic systems composed by elements of HH, KH, LH, KK, KL, and LL periods.

The potential used by Wu-Yang is given by:

$$V_{WY}(R) = ae^{-R/p} - \frac{b}{R^m} \tag{3.202}$$

being a, b, p and m constants within a molecular period (see table 1 on p.296 in Ref. [105]).

When a new analytical form was proposed, the first concern was to obtain relations to calculate the spectroscopic constants related to the proposed potential. In particular, Wu and Yang [105] sought a correct relationship between Re and the constant force k_e. To this end, they analyzed the proposals that had been successful such as that of Clark [106], Badger [86](see section 3.1.11), Allen-Longair [107] and Sutherland [44](see section 3.1.14).

Through the potential (3.202), with $\left(\frac{\partial V_{WY}}{\partial R}\right)_{R_e} = 0$ and $\left(\frac{\partial^2 V_{WY}}{\partial R^2}\right)_{R_e} = k_e$, Wu and Yang obtained the follows relations:

$$\frac{a}{p}e^{-R_e/p} = \frac{b_m}{R^{m+1}} \tag{3.203}$$

and

$$k_e = \frac{1}{e^{R_e/p}}\left[\frac{a}{p^2} - \frac{a(m+1)}{pR_e}\right] = \frac{1}{R_e^{m+1}}\left[-\frac{bm(m+1)}{R_e} + \frac{bm}{p}\right]. \tag{3.204}$$

They plotted $k_e e^{R_e/p}$ against $1/R_e$ for various diatomics systems of the HH, KH, LH, KK, KL, and LL molecular periods, in their ground and excited states. For diatomic molecules of HH, KH, LH periods, they obtained a good result for $m = 4$, and for systems in other periods, the best value obtained was $m = 6$. As these constant values of m ensured a straight line for each period, they concluded that the values of b and p also remained constant in each period.

The average errors in k_e calculated from R_e for the periods HH, KH, LH, KK, KL and LL obtained for Wu and Yang [105] were 7.1%, 5.3%, 4.5%, 12.0%, 13.1% and 19.0% respectively.

With asymptotic characteristics similar Buckingham's function [102], the Wu-Yang potential presented the same deficiency when $R = 0$, where $V = -\infty$. However, this was not the only problem with the potential proposed by them. As observed by Varshni [108], in 1959, the Wu-Yang assumption that the values of m, p, and b were constant for different states of diatomic molecules from the same molecular period is not true even when $R = Re$.

Using the Wu-Yang rule for obtain k_e, Varshni [108] calculated others spectroscopic constants, α_e and $\omega_e x_e$ for diatomic systems from KK period. To this end, Varshni first obtained:

$$\alpha_e = -\left(\frac{XR_e}{3} + 1\right)\frac{6B_e^2}{\omega_e} \tag{3.205}$$

and

$$\omega_e x_e = \left(\frac{5}{3}X^2 - Y\right)\frac{2.108 \times 10^{-16}}{\mu_A} \tag{3.206}$$

where

$$X = -\frac{\frac{1}{p}^2 R_e^2 - (m+1)(m+2)}{\frac{1}{p}R_e^2 - (m+1)R_e} \qquad \text{and} \qquad Y = \frac{\frac{1}{p}^3 R_e^3 - (m+1)(m+2)(m+3)}{\frac{1}{p}R_e^3 - (m+1)R_e^2}. \tag{3.207}$$

Varshni [108] showed that, mainly, the values of the anharmonicity $\omega_e x_e$ were very different from the experimental values. Besides, the average error in calculating the constant force for diatomics of that period was 12.1%, which is not at all attractive. Varshni considers that even for the other diatomic systems, large deviations in the values of α_e and $\omega_e x_e$ should occur.

3.1.19 The Lippincott function

In 1953, Lippincott [43] (LIP) proposed a functional form for diatomic potentials still in the Hulburt-Hirschfelder and Morse-type, involving an exponential of the interatomic distances, given by:

$$V_{LIP}(R) = D_e(1 - e^{-n(\Delta R)^2/2R})(1 + aF(R)), \tag{3.208}$$

where D_e is the depth of the well and R has the usual meaning, a and n are constants. $\Delta R = R - R_e$ and $F(R)$ is a function internuclear distance so that $F(R) = \infty$, when $R = 0$ and $F(R) = 0$, when $R = \infty$. In many cases, $F(R)$ has no great relevance, and can only be considered $V_{LIP}(R)$ as the first term of the product.

Considering $a = 0$ and using the relation for the constant force $k_e = \left(\frac{d^2V_{LIP}}{dR^2}\right)_{R_e}$ in its function $V_{LIP}(R)$, the dissociation energy D is obtained from:

$$D(ergs/molecule) = k_e R_e/n \tag{3.209}$$

where n is empirically given by:

$$n = 6.32 \times 10^8 (I/I_0)_A^{\frac{1}{2}} (I/I_0)_B^{\frac{1}{2}}\ cm^{-1} \tag{3.210}$$

with $(I/I_0)_A^{\frac{1}{2}}$ and $(I/I_0)_B^{\frac{1}{2}}$ corresponding to the ionization potentials of the atoms A and B respectively relative to those of the corresponding atoms in the same row and first column of the periodic table.

Lippincott [43] pointed out that most researchers were always in search of a good analytical way to represent potential curves of diatomic systems, however, these were little used to predict the energy of bond dissociation D and anharmonicity constants. He calculated D using the relation (3.209) for 22 diatomic molecules and obtained good results compared to spectroscopically obtained values. The resulting mean deviation of 4.5%, was considered large when compared to the experimental error for R_e, k_e and (I/I_0) (around 0.1%).

For the calculation of the anharmonic constants, such as $\omega_e x_e$, a second-order perturbation theory was used. The potential (3.208) was expanded in power series, taking $a = 0$, so that the cubic and quartic terms of this expansion represent the perturbation potential in the Schrödinger equation. The quadratic (harmonic) term of this potential stands for the unperturbed potential. In this way, he obtained :

$$\omega_e x_e = 3\hbar(n/R_e + 1/{R_e}^2)/64\pi^2 c\mu. \tag{3.211}$$

He calculated the value of $\omega_e x_e$ employing (3.211) for 22 different diatomic molecules, and compared with the values obtained spectroscopically, reaching an average deviation of 5.7%. This was considered as a good result compared to the same process using the Morse function[8] (46%), or even compared with the Linnett [61] reciprocal-exponential function (16%).

Now, D can be obtained as a function of known parameters, through (3.209) and (3.211):

$$D(ergs/molecule) = k_e/[(64\pi^2 c\mu\omega_e x_e/3\hbar) - 1/{R_e}^2] \tag{3.212}$$

and the results obtained from this method showed an average error of 4.8% in relation to the D values obtained spectroscopically for 17 diatomic molecules.

In 1955, Lippincott and Schroeder [109] presented a more detailed study on the function (3.208). First, they considered the simple function already analyzed by Lippincott with $a = 0$, *i. e.*:

$$V_{LS}(R) = D_e(1 - e^{-n(\Delta R)^2/2R}), \tag{3.213}$$

where, if $R \to 0$, then $V_{LS}(R) = D_e$, not satisfying $V_{LS} \to \infty$. However, for them this was not a serious problem. The biggest problem with this function is that it provides $\alpha_e = 0$ for all molecules, which is not correct. Then, they concluded that this function would not be the most suitable to represent a generic potential.

Another important contribution by Lippincott and Schroeder was on the calculation of parameter n. This parameter may be calculated through the following empirical relation:

$$n = n_0(I/I_0)_A^{\frac{1}{2}}(I/I_0)_B^{\frac{1}{2}}\ cm^{-1} \tag{3.214}$$

with $(I/I_0)_A^{\frac{1}{2}}$ and $(I/I_0)_B^{\frac{1}{2}}$ corresponding to the ionization potentials of the atoms A and B, as well as in the Eq. (3.210). For H atoms I/I_0 they assigned the value 0.88 and for most molecules where the binding is primarily covalent and including all molecules of the fourth, fifth, sixth, and seventh columns of the periodic table, n_0 has the value 6.32×10^8. For the diatomic alkali metal and alkali hydrides, n_0 had the value of 4.21×10^8 [109].

Now, since n was calculated separately it may be used to predict $\omega_e x_e$ from R_e values in the Eq. (3.211), without needing k_e or D. The average error for $\omega_e x_e$ calculated from n for diatomic systems As_2, Br_2, C_2, CH, ClBr, Cl_2, ClF, CLI, CO, F_2, HBr, HCl, H_2, HI, IBr, I_2, N_2, NO, OH, O_2, P_2, S_2, SO and Se_2 is only 5.5% [109].

Lippincott and Schroeder [109] pointed out that the simple potential (3.213), which provided $\alpha_e = 0$, could be used as a first approximation to an overall potential. Furthermore, they observed that since bonds in polyatomic systems usually have values of α_e are much smaller than the corresponding α_e values for diatomic molecules, it may be that Eq. (3.213) represents an improved approximation to potential curves for the bond in polyatomic systems. They used this function for this, see for example the Ref. [110] and [111].

Next, Lippincott and Schroeder [109] considered the complete potential (3.208), *i. e.*, with $a \neq 0$. The term $(1 + aF(R))$ was chosen such that $V_{LS} \to \infty$ when $R = 0$ and a way that the resulting function will allow a prediction of vibrational-rotational coupling constants. At large distances it should give a Van der Waals energy of interaction. To accomplish this, they used three terms of power series in the quantity $[1 - \exp(-b^2 n\Delta R^2 R^{11}/2R_e^{12})]^{\frac{1}{2}}$:

$$\begin{aligned} 1 + aF(R) = 1 + (-1)a \times (R_e/R)^6[1 - \exp\big(-b^2 n\Delta R^2 R^{11}/2R_e^{12}\big)]^{\frac{1}{2}} \\ -(R_e/R)^{12}[1 - \exp\big(-b^2 n\Delta R^2 r^{11}/2R_e^{12}\big)] \end{aligned} \qquad (3.215)$$

or for the general function

$$\begin{aligned} V_{LS}(R) = D_e[1 - \exp\big(-n\Delta R^2/2R\big)] \\ \times\{1 + (-1)a \times (R_e/R)^6[1 - \exp\big(-b^2 n\Delta R^2 R^{11}/2R_e^{12}\big)]^{\frac{1}{2}} \\ -(R_e/R)^{12}[1 - \exp\big(-b^2 n\Delta R^2 r^{11}/2R_e^{12}\big)]\}. \end{aligned} \qquad (3.216)$$

For large values of R this function takes the form

$$V = D_e[1 - \exp\big(-n\Delta R^2/2R\big)\{1 + a[-(R_e/R)^6 + (R_e/R)^{12}]\}, \qquad (3.217)$$

where $F(R)$ takes form of a Lennard-Jones(6,12) Van der Waals potential (see section 3.1.2). This fact ensures that the curve from Eq. (3.216) is in good agreement with the observed curve.

From Eq. (3.216), the spectroscopic parameters D, α_e and $\omega_e x_e$ now are give by:

$$D = \omega_e^2/2nR_eB_e \qquad (3.218)$$

$$\alpha_e = 0 \tag{3.219}$$

$$\omega_e x_e = 1.5B_e[0.25 + nR_e/4 + ab(nR_e/2)^{\frac{1}{2}} + (5a^2b^2 - ab^2)nR_e/2]. \tag{3.220}$$

Note that Eq. (3.218) is equivalent to relation (3.209), since $Be = \hbar/8\pi^2\mu R_e^2 c$ and $k_e = 4\pi^2\mu\omega_e^2 c^2$. Studies such as Somayajulu [112] have suggested that in the relation (3.209), n could be a constant not depending on the ionization potential of each molecule. However, Lippincott, Schroeder and Steele [113] have shown that such a relationship was not valid for diatomic molecules in electronic excited states.

Although the function (3.216) is a function of 5 parameters, more complicated to calculate than (3.213), the parameters ab and b can be considered as constants for most molecules, simplifying the computation of α_e and $\omega_e x_e$, for example. Thus, the potential (3.216) was considered a good general approximation to the "true" potential function.

3.1.20 The Frost-Musulin function

In 1954, Frost and Musulin [114] (FM) initially proposed, a general potential energy function for diatomic molecules. This kind of potential considers the possible relation between a "reduced" potential energy and a "reduced" internuclear distance, analogous to a reduced equation of state. For this, they considered V the potential energy of a diatomic molecule in the ground state or in any attractive excited state taking the zero of the energy at infinite separation of the nuclei. At the potential energy minimum $V = -D_e$, being D_e the depth of the well. Then, the reduced potential is defined by:

$$V'(\rho) = \frac{V(\rho)}{D_e} \qquad \text{with} \qquad \rho(R) = (R - R_{ij})/(R_e - R_{ij}) \tag{3.221}$$

where R and R_e are the usual distances and R_{ij} is a constant for a given molecules and is a measure of inner shell radii of atoms i and j. Note that the minimum is $V' = -1$ and $\rho = 1$, since $R = R_e$.

Frost and Musulin [114] assumed V' as a universal function of ρ for any diatomic system. At the minimum this function, we have:

$$\left(\frac{d^2V'}{d\rho^2}\right)_{\rho=1} = K \tag{3.222}$$

being K a dimensionless parameter. Since the force constant is given by $k_e = (d^2V/dR^2)_{R=R_e}$, it follows that:

$$k_e(R_e - R_{ij})^2/D_e = K \tag{3.223}$$

or that

$$R_{ij} = R_e - (KD_e/k_e)^{1/2}. \tag{3.224}$$

For to analyze the behavior of reduce potential, Frost and Musulin [114] chose 23 diatomic systems: H_2, H_2^+, CH, OH, HCl, HCl^+, KH, ZnH, HBr, CdH, HI, HgH, Li_2, O_2, O_2^+, ClF, Na_2, P_2, Cl_2, K_2, Br_2, ICl and I_2. Firstly, they calculated the value of K for the diatomic systems H_2 and H_2^+, assuming that $R_{ij} = 0$, obtaining $K = 4.14$ and $K = 3.96$, respectively. For the other diatomic systems, they assumed the mean value $K = 4.00$.

To check the validity of this properties, Frost and Musulin [114] examined the coefficients of the higher terms such as $L/6$ and $M/24$ in the expansion:

$$V'(\rho) = -1 + (K/2)(\rho - 1)^2 + (L/6)(\rho - 1)^3 + (M/24)(\rho - 1)^4 + \cdots \tag{3.225}$$

where

$$L = \left(\frac{d^3V'}{d\rho^3}\right)_{\rho=1} \quad \text{and} \quad M = \left(\frac{d^4V'}{d\rho^4}\right)_{\rho=1}. \tag{3.226}$$

For L and M they obtained the follow relations:

$$L = \frac{(R_e - R_{ij})^3}{D_e}\left(\frac{d^3V}{dR^3}\right)_{R=R_e} \tag{3.227}$$

and

$$M = \frac{(R_e - R_{ij})^4}{D_e}\left(\frac{d^4V}{dR^4}\right)_{R=R_e}. \tag{3.228}$$

The average values for 23 molecules were $L = -15.06$ and $M = 43.48$. The mean deviations of L and M from their averages were 13.2 and 42%, respectively. These results, although not very satisfactory, led Frost and Musulin to believe that their universal potential was approximately correct. However, in 1961, Varshni and Shukla [115] showed that this "universal" potential energy function does not exist. They still claim that it is possible to obtain universal relations for spectroscopic parameters α_e and $\omega_e x_e$ in terms of the Sutherland parameter $\Delta = k_e R_e^2/2D_e$ [14].

While Frost and Musulin [114] used the third and fourth derivatives to obtain α_e and $\omega_e x_e$, Varshni and Shukla [115] using a different method, obtained these parameters in terms of L, M and K:

$$\alpha_e = \left[-\frac{L}{3K}\frac{R_e}{(R_e - R_{ij})} - 1\right]\frac{6B_e^2}{\omega_e} \tag{3.229}$$

and

$$\omega_e x_e = \left[\frac{5}{3}\left(\frac{L}{K}\right)^2 - \frac{M}{K}\right]\left[\frac{R_e}{R_e - R_{ij}}\right]^2 \frac{2.1078 \times 10^{-16}}{\mu R_e} \tag{3.230}$$

where μ is the reduced mass. The calculated values by Frost and Musulin [114] for α_e and $\omega_e x_e$ presented the average percent errors corresponding to 24.9 and 17.7, respectively, whereas with Varshni [14] method we have 22.1 and 11.1 for 23 diatomic systems, being 18 common with the analyzed by Frost and Musulin. Varshni and Shukla still guarantee that the relatively low error for $\omega_e x_e$ is nothing more than a happy cancellation of the errors [115].

In the same year, Frost and Musulin [74] suggested a semi-empirical potential energy function aiming to overcome difficulties found in previous potentials, such as Morse [8], Hulburt-Hirschfelder [7], Lippincott [43]. For this, they imposed more conditions to be fulfilled by an adequate function. They are:

(i) The potential energy for nuclear motion V is the algebraic sum of two parts given by:

$$V = \frac{e^2}{R} + V_e \tag{3.231}$$

where the first term is the nuclear repulsive potential corresponding to Coulomb force $Z_1 Z_2 e^2/R$, with e the electronic charge, Z_1 and Z_2 the atomic numbers, and R the interatomic distance; and the second term is the purely electronic energy defined as V_e, which is also a function of R.

(ii) V becomes infinite as R approaches zero, being due to the nuclear repulsion term e^2/R, assuming therefore that V_e does not become infinite in equal and opposite sense.

(iii) V_e is finite in $R = 0$ and assumes $V = V_e^0$, being V_e^0 the known "united" atom energy.

(iv) $V_e \propto -e^2/R$ for R large. This is based upon the choice of $V = 0$ as $R \to \infty$ and is the required condition to cancel the nuclear repulsion potential since the total V goes to zero faster than inversely as the first power of R.

(v) V must be capable of going through a minimum as R varies.

The potential energy function with two adjustable parameters that accomplish these criteria presented by FM [74]:

$$V_{FM}(R) = e^{-aR}\left(\frac{1}{R} - b\right) \tag{3.232}$$

being a and b these parameters.

In principle, the parameters a and b were fixed by demanding the function provides any two of the known experimental quantities such as R_e, equilibrium internuclear distance; D_e, dissociation energy from the minimum of the curve (depth well);k_e, force constant for infinitesimal amplitudes, which is related to the spectroscopic constant α_e; and $\omega_e x_e$, anharmonicity constant. Again, they applied this function to the diatomic systems H_2 and H_2^+ in their ground states, so that the corresponding electronic energy is given by:

$$V_e = -\frac{1}{R}\left(1 - e^{-aR}\right) - be^{aR}. \tag{3.233}$$

with the limiting value as $R \to 0$:

$$V_e^0 = -(a + b). \tag{3.234}$$

For these systems, they calculated the usual parameters above described: R_e, D_e, k_e, α_e, $\omega_e x_e$ and also the critical distance R_c which is the value of R, less than R_e, at which $V = 0$, or the same as at infinite separation. For this parameter R_c, in particular for the diatomic H_2^+, they obtained (1.136a$_0$) [74] in good agreement with the experimental values(1.12a$_0$) [116].

Varshni [14] showed that the spectroscopic parameters α_e and $\omega_e x_e$ are best represented in terms of a parameter s, related to Sutherland parameter Δ, defined by:

$$\Delta = s^2/2 + s \quad \text{or} \quad s = -1 + (1 + 2\Delta), \tag{3.235}$$

so that,

$$\alpha_e = \left[\frac{2s^2 + 3s}{3(s + 2)}\right] \frac{6B_e^2}{\omega_e} \tag{3.236}$$

and

$$\omega_e x_e = \left[\frac{11s^4 + 66s^3 + 156s^2 + 144s + 36}{3(s + 2)^2}\right] \frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.237}$$

Analyzing the behavior of these expressions in terms of s, Varshni [14] concluded that the FM function is very close to the Morse potential [8], being FM slightly more complex.

In 1957, Chen, Geller and Frost [117] (CGF) provided a generalization of the function (3.232) for to be applied in a more kinds of diatomic systems, being V now given by:

$$V_{CGF} = e^{-aR}\left(\frac{c}{R} - b\right) \tag{3.238}$$

where the new parameter c is:

$$c = Z_1 Z_2 \tag{3.239}$$

with Z_1 and Z_2 some kind of effective nuclear charges of the two atoms.

With this new potential, the three parameters a, b and c can be now obtained by direct algebraic evaluate from spectroscopic constants D_e, R_e and k_e, using the relations:

$$a = p/R_e \tag{3.240}$$

$$b = D_e(1 + p)\exp\{p\} \tag{3.241}$$

$$c = D_e R_e p \exp\{p\} \tag{3.242}$$

where

$$p = \left(1 + \frac{fR_e^2}{D_e}\right)^{1/2} - 1. \tag{3.243}$$

Although the potential V_{CGF} is more flexible than the original potential $V_{FM}(R)$, it does not present better results. Steele *et al.* [15] in a comparative study for systems H_2, I_2, N_2, O_2, CO, NO, OH and HF in their ground and excited states, showed that the CGF potential does not give any appreciable improvement over the Morse [8] curve. They observed also that the average errors for the quantities α_e and $\omega_e x_e$ for the diatomic systems above cited were bigger using this more general of Frost-Musulin potential than with the Rose-Morse [29], Rydberg [9], Linnett [61] and Lippincott [43] potentials.

However, recent work such as Royappa, Suri and McDonough [42] has shown that if the parameters of the V_{CGF} potential are well fitted, using for example the Mathcad (Mathsoft Inc.), on the whole this function present good results. They observed that the new Frost-Musulin potential (3.238) showed average error less from RKR [9–11] curves than the Kratzer [16], Lippincott [43], Rydberg [9], Morse [8], Rose-Morse [29], Linnett [61] and Pöschl-Teller [30] curves for C_2, CF, CH, CN, CO, H_2, HF, Li_2, LiH, N_2, N_2^+, NO, O_2, and OH in their ground electronic states.

3.1.21 The Varshni function

Although already quite convinced that a universal analytical function to represent "all" diatomic potentials did not exist, as proposed by Frost and Musulin [114], Varshni [14], in 1957, presented a comparative study of the more relevant functions known at that time. He analyzed the behavior of potentials energy functions from Morse [8] to Frost and Musulin [74] for 23 molecules in their ground and excited electronic states. In addition, he calculated the rotational α_e and vibrational $\omega_e x_e$ constants for these systems. From this analysis, Varshni concluded that it is not possible to have an exact "universal" potential energy function for all diatomic systems, but it is possible to have a function for molecules with similar linkages. As a result, Varshni (VAR) proposed seven different potentials.

For to construct his potentials $V_{VAR}(R)$, Varshni [14] established the criteria that a good potential must satisfy, such as the potentials presented before. He divided them into criteria that are necessary and desirable:

1. Necessary:

   (a) $V_{VAR}(R)$ should come asymptotically to a finite value as $R \to \infty$;

   (b) $V_{VAR}(R)$ should have a minimum at $R = R_e$;

(c) $V_{VAR}(R)$ should become infinite at $R = 0$, but this need not be very strict, because if $V_{VAR}(R)$ becomes very large in $R = 0$ it is enough.

2. Desirable:

(a) The potential function should be capable of giving rise to a least one maximum under certain conditions;

(b) V_e is finite at $R = 0$;

(c) $V_e = V_e^0$ at $R = 0$, where V_e^0 is the known "united" atom energy;

(d) $V_e \propto -e^2/R$ for R large;

(e) $\frac{dV_e}{dR} = 0$ at $R = 0$;

(f) Van der Waals terms should introduce terms of the form $1/R^n$.

The desirable criteria (b), (c), (d) and (e), were based on the Frost-Musulin [74] potential (see previous section 3.1.20), and the criteria (a) to (f) need not be exactly true.

The First potential proposed by Varshni [14] was a function similar to Morse [8]:

$$V_{VAR_I}(R) = D_e\{1 - \exp\{[-b(R^2 - R_e^2)]\}\}^2, \tag{3.244}$$

where b is given by:

$$b = \left(\frac{k_e}{8D_eR_e^2}\right)^2 = \Delta^{1/2}/2R_e^2. \tag{3.245}$$

being $\Delta = k_eR_e^2/2D_e$ the Sutherland parameter.

The potential (3.244) satisfies the criteria 1.(a) and 1.(b), and as well as the Morse potential, $V_{VAR_I}(R)$ becomes large at $R = 0$. Varshni obtained also expressions to calculate the spectroscopic parameters, α_e and ω_ex_e, from his potential:

$$\alpha_e = (\Delta^{1/2} - 2)\frac{6B_e^2}{\omega_e} \tag{3.246}$$

and

$$\omega_ex_e = [8\Delta - 12\Delta^{1/2} + 12]\frac{2.1078 \times 10^{-16}}{R_e^2\mu}. \tag{3.247}$$

For the 23 diatomic systems analyzed, this potential gives much lower values for α_e than the Morse [8] function. On the other hand, $V_{VAR_I}(R)$ gives lower values for ω_ex_e, but these presented average error (18.2%) lesser than that Morse [8](31.2%) and Rydberg [9](23.1%) potentials.

The Second potential proposed by Varshni [14] was:

$$V_{VAR_{II}}(R) = D_e\left\{1 - \frac{R_e}{R}\exp\{[-\alpha(R - R_e)]\}\right\}^2 \tag{3.248}$$

where

$$\alpha = \frac{\Delta^{1/2} - 1}{R_e}. \tag{3.249}$$

The potential (3.248) accomplish the three criteria 1.(a), 1.(b) and 1.(c). The parameters α_e and $\omega_e x_e$ are given by:

$$\alpha_e = \left[\Delta^{1/2} + \frac{1}{\Delta^{1/2}} - 1\right] \frac{6B_e^2}{\omega_e} \tag{3.250}$$

and

$$\omega_e x_e = \left[8\Delta + 12 - \frac{8}{\Delta^{1/2}} + \frac{12}{\Delta}\right] \frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.251}$$

In this case, the values α_e and $\omega_e x_e$ were higher than those obtained from Morse [8] potential, being considered unsuitable by Varshni.

Since the First potential provides low values and the Second provides very high values, Varshni bet on a Third option that mixed the two functions.

Then, the Third potential energy function proposed by Varshni was a mixture of the first (3.244) and the second potentials (3.248), given by:

$$V_{VAR_{III}}(R) = D_e \left\{1 - \frac{R_e}{R} \exp\{[-\beta(R^2 - R_e^2)]\}\right\}^2 \tag{3.252}$$

where

$$\beta = \frac{1}{2R_e^2}[\Delta^{1/2} - 1]. \tag{3.253}$$

This potential obeys the three necessary criteria, and in fact it was a good bet. The expressions for α_e and $\omega_e x_e$ are given by:

$$\alpha_e = \left[\Delta^{1/2} + \frac{2}{\Delta^{1/2}} - 2\right] \frac{6B_e^2}{\omega_e} \tag{3.254}$$

and

$$\omega_e x_e = \left[8\Delta + 12\Delta^{1/2} + 66 - \frac{111}{\Delta^{1/2}} + \frac{73}{\Delta}\right] \frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.255}$$

For α_e, the average error from $V_{VAR_{III}}(R)$ (22.9%) potential is significantly lower than that obtained from Morse [8] (33.1%) and Rydberg [9] (28.0%) potentials. In relation to $\omega_e x_e$, the Third potential $V_{VAR_{III}}(R)$ presented a similar behavior to that of Frost-Musulin [74].

The Fourth function proposed by Varshni was:

$$V_{VAR_{IV}}(R) = B(A + \exp\{(b/R)\})^2 \tag{3.256}$$

with the conditions

$$A = \exp\{(b/R_e)\}, \tag{3.257}$$

$$B = \frac{D_e}{[\exp\{(b/R_e) - 1]^2\}} \tag{3.258}$$

$$b = R_e \ln A \tag{3.259}$$

and, here,

$$\Delta = \left[\frac{\ln A}{1 - 1/A}\right]^2. \tag{3.260}$$

For this function, α_e and $\omega_e x_e$ are given by:

$$\alpha_e = (\ln A + 1)\frac{6B_e^2}{\omega_e} \tag{3.261}$$

and

$$\omega_e x_e = [8(\ln A)^2 + 24\ln A + 64]\frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.262}$$

The Fourth potential fulfills the three necessary criteria. However, this function was discarded because this gives much higher values for α_e and $\omega_e x_e$ than the Morse [8] function.

The Fifth potential proposed by Varshni is a generalization of Kratzer [16] function and a special case of the Mecke-Sutherland [44, 92] potential, being given by:

$$V_{VAR_V}(R) = D_e \left[1 - \left(\frac{R_e}{R}\right)^n\right]^2. \tag{3.263}$$

Here, we have:

$$n^2 = \Delta \tag{3.264}$$

and the spectroscopic parameters are given by:

$$\alpha_e = \Delta^{1/2}\frac{6B_e^2}{\omega_e} \tag{3.265}$$

and

$$\omega_e x_e = [8\Delta + 12\Delta^{1/2} + 4]\frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.266}$$

As well as the Fourth potential, the $V_{VAR_V}(R)$ function gives higher values than the Morse for the parameters α_e and $\omega_e x_e$, being therefore considered inadequate.

The Sixth potential proposed was similar to second $V_{VAR_{II}}$:

$$V_{VAR_{VI}}(R) = D_e \left\{1 - \frac{R_e}{R}\exp\{[-a(R - R_e)]\}\right\}^2 [1 + Kf(R)] \tag{3.267}$$

where $f(R)$ is a function such that:

$$f(R) = \begin{cases} \infty, & \text{at} \quad R = 0 \\ 0, & \text{at} \quad R = \infty \end{cases}$$

This function attain the tree necessary criteria. Note that if $f(R) = 0$, we have the function very similar to Second function:

$$V_{VAR_{VI}}(R) = D_e \left\{ 1 - \frac{R_e}{R} \exp\{[-a(R - R_e)]\} \right\}^2 \tag{3.268}$$

which provides $V_{VAR_{VI}} = D_e$ at $R = 0$. For this function, we have:

$$aR_e = \Delta^{1/2} \tag{3.269}$$

and the spectroscopic vibrational rotational α_e and anharmonicity $\omega_e x_e$ parameters given by:

$$\alpha_e = \left[\Delta^{1/2} - \frac{1}{\Delta^{1/2}} - 1 \right] \frac{6B_e^2}{\omega_e} \tag{3.270}$$

and

$$\omega_e x_e = \left[8\Delta - 12 + \frac{8}{\Delta^{1/2}} + \frac{12}{\Delta} \right] \frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.271}$$

The behavior of α_e is not suitable for the Sixth potential. However, $\omega_e x_e$ is very close to the Rydberg function.

The Seventh and last potential proposed by Varshni is similar to Lippincott [43] potential:

$$V_{VAR_{VII}}(R) = -AR^n \exp\{(-aR)\}[1 + Kf(R)] \tag{3.272}$$

and, as before, $f(R) = \infty$ at $R = 0$, and at $R = \infty$, $f(R) = 0$.

This function satisfies the tree necessary criteria, and as before, if $f(R) = 0$, we have:

$$V_{VAR_{VII}}(R) = -AR^n \exp\{(-aR)\} \tag{3.273}$$

where,

$$a = \frac{n}{R_e} \tag{3.274}$$

$$A = \frac{D_e}{R_e^2 e^n} \tag{3.275}$$

$$n = 2\Delta. \tag{3.276}$$

The constants α_e and $\omega_e x_e$ are given by:

$$\alpha_e = -\frac{1}{3} \frac{6B_e^2}{\omega_e} \tag{3.277}$$

and

$$\omega_e x_e = \left[6\Delta + \frac{2}{3} \right] \frac{2.1078 \times 10^{-16}}{R_e^2 \mu}. \tag{3.278}$$

This potential gives a negative value to α_e, which is absurd. On the other hand, the values of $\omega_e x_e$ obtained from the Seventh potential were slightly lower than that of the Lippincott [43] function, with the average error (13.6%) very near to that of

Lippincott (12.9%).

Varshni concluded that for the overall representation of the potential energy curves, the Third and Sixth functions were the most useful [14].

In 1962, Steele *et al.* [15] in a comparative study of potential functions, analyzed 8 of the 23 diatomic systems in their ground and excited electronic states previously treated by Varshni [14]. The average error for the quantity α_e calculated from Third Potential (3.252) was less (15.57%) than from Morse [8] (19.67%), Rydberg [9] (17.45%), Rosen-Morse [29] (22.33%), Pöschl-Teller [30] (18.47%) and Frost-Musulin [74] (23.55%). On the other hand, the average error for $\omega_e x_e$ was the largest among the analyzed potentials.

Steele *et al.* [15] also compared the average error from RKR [9–11] curves for all R and for $R > R_e$. For all R, the Third potential by Varshni presented lower deviation (2.28%) than Morse [8] (3.68%), Rydberg [9] (2.94%), Rosen-Morse [29] (3.71%), Pöschl-Teller [30] (3.48%), Frost-Musulin [74] (3.41%) and Linnett [61] (4.18%). Still, for $R > R_e$ the Third potential by Varshni presented lower deviation (1.68%) than Morse [8] (3.20%), Rydberg [9] (2.27%), Rosen-Morse [29] (2.80%), Pöschl-Teller [30] (3.28%), Frost-Musulin [74] (3.30%) and Linnett [61] (5.07%), showing that $V_{VAR_{III}}(R)$.

In a more recent, and similar to Steele *et al.* comparative study [42], the Third potential by Varshni again showed to be more accurate than the potentials before cited, and also more accurate that the Kratzer [16], Lippincott [43] and Deng-Fan [41] potentials.

3.1.22 The Deng-Fan function

It is possible to note that for the various potentials analyzed until now, the Morse [8] function is still a benchmark, although, as we have seen, it is not the ideal potential because it does not present correct asymptotic behavior when $R \to 0$.

In an attempt to correct this failure, in 1957, Deng and Fan [41] (DF) propose a simple modification in Morse potential:

$$V_{DF}(R) = D_e \left[1 - \frac{e^{aR_e} - 1}{e^{aR} - 1}\right]^2 \tag{3.279}$$

where a is the Morse parameter (3.64). This potential is called a generalized Morse potential.

The function $V_{DF}(R)$ has three parameters as the Morse potential. However, this function has correct physical boundary conditions at $R = 0$ and ∞. Note that, when $R \to 0$ we have $V_{DF} \to \infty$, which was not the case with Morse potential. Furthermore, when used as a potential function for the vibration of diatomic molecules, the Schrödinger equation is exactly soluble as well as Morse (see in detail in Ref. [118]).

Using the relations, established by Dunham [24], we can obtain the spectroscopic parameters vibrational rotational α_e and anharmonicity $\omega_e x_e$, in terms of the derivatives of the potential function $V_{DF}(R)$:

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{R_e f_3}{3k_e}\right) \tag{3.280}$$

and

$$\omega_e x_e = \frac{B_e}{8}\left[-\frac{R_e^2 f_4}{k_e} + 15\left(1 + \frac{\omega_e \alpha_e}{2B_e^2}\right)^2\right] \tag{3.281}$$

where B_e and k_e have theirs usual meanings

$$B_e = -\frac{\hbar}{8\pi^2 c\mu R_e^2}, \qquad k_e = 4\pi^2\mu c^2\omega_e^2 \tag{3.282}$$

and f_3 and f_4 are given by:

$$f_3 = \left.\frac{d^3V_{DF}}{dR^3}\right|_{R=R_e} = -\frac{12a^3D_e e^{3aR_e}}{(e^{aR_e}-1)^3} + \frac{6a^3D_e e^{2aR_e}}{(e^{aR_e}-1)^2} \tag{3.283}$$

and

$$f_4 = \left.\frac{d^4V_{DF}}{dR^4}\right|_{R=R_e} = \frac{72a^4D_e e^{4aR_e}}{(e^{aR_e}-1)^4} - \frac{12a^4D_e e^{3aR_e}}{(e^{aR_e}-1)^3} + \frac{14a^4D_e e^{2aR_e}}{(e^{aR_e}-1)^2}. \tag{3.284}$$

As the potential of Deng Fan brings supposedly greater accuracy than the Morse [8] function, many researchers have conducted comparative studies involving both potentials.

For example, in 2003, Rong *et al.* [119] presented a comparative study between Morse and Deng-Fan potentials involving only X-H bonds in small molecules. They observed that for several molecules the Morse model leads to better agreement with the experiment while for other the reverse is true, which is somewhat inconclusive. However, they easily obtained a set of Morse potential parameters while for the DF potential different sets of parameters lead to similar frequencies and intensities. In the molecular systems considered the Deng-Fan potential does not predict observed energy levels and intensities significantly better than Morse's potential despite its correct asymptotic behavior.

In 2006, Royappa *et al.* [42] presented a comparative study involving many more potentials than Morse and Deng-Fan (21 in total). They analyzed the average error of these potentials related to the RKR [9–11] curve using Murrell and Sorbie's Z-test (see Section: 3.1.26) for 14 diatomic systems in their ground electronic state. The Deng-Fan [41] potential present the has a deviation 3 times greater than the Morse potential, and with one of the worst results, it is only more accurate than the potentials of Kratzer [16] and Lippicott [43].

Still, in a more recent comparative study, Wang *et al.* [81] calculated the anharmonicity ω_e and vibrational rotational coupling parameter α_e for 16 molecules in their ground electronic states. Although the proposal of Deng-Fand [41] was an improvement of Morse function, Wang*et al.* showed that by choosing the experimental values of dissociation energy D, equilibrium bond length R_e and vibrational frequency ω_e as input, the Deng-Fan potential is not better than the Morse potential in simulating the atomic interaction for diatomic molecules. Furthermore, Wang *et al.* concluded also that the Manning-Rosen [79], Deng-Fan [41] are the same potential energy function, actually (see details in Ref. [81]).

3.1.23 The Tietz-Hua function

Whenever a new potential energy function was proposed, it was also analyzed whether this potential exactly solved the Schrödinger equation, or if this new potential was just another approximate solution. Since few potentials had this property until that time, in 1963, Tietz [120] (TIE) sought to obtain potentials that were an exact solution to the Schrödinger equation (at least for the quantum number $L = 0$) and that at the same time were mathematically simple functions, such as the Morse [8] potential.

The first proposal by Tietz [120] was a potential energy function with five parameters, given by:

$$V_{TIE_I}(R) = D_e + D_e \frac{(a+b)e^{-2\beta R} - be^{-2\beta R}}{(1+ce^{-\beta R})^2} \tag{3.285}$$

where D_e is the depth of the well. This potential, fulfill three standard conditions:

(i) $\left.\frac{dV_{TIE_I}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{TIE_I}(\infty) - V_{T_I}(R_e) = D_e;$

(iii) $\left.\frac{d^2V_{TIE_I}}{dR^2}\right|_{R=R_e} = k_e.$

where k_e and R_e have their usual meanings. These conditions are also necessary to determine a, b, c and β, which are constants. In addition, these constants depend that the Tietz potential curve give correct values for the vibrational-rotational coupling constant α_e, given by:

$$\alpha_e = -\left[\frac{1}{3}\left(\frac{d^3V_{TIE_I}(R_e)}{dR^3}\right)\frac{R_e}{k_e} + 1\right]\left(\frac{6B_e^2}{\omega_e}\right) = F_e\left(\frac{6B_e^2}{\omega_e}\right) \tag{3.286}$$

where ω_e is the vibrational frequency and B_e is the rotational constant.

Tietz [120] showed that the four constants β, c, b and a can be express using the Sutherland parameter $\Delta = \frac{k_e R_e^2}{2D_e}$ and the quantity $\Gamma = \left[1 + \left(\frac{\alpha_e \omega_e}{6B_e^2}\right)\right]^2$:

$$\begin{aligned}
\beta R_e &= 2\Delta^{1/2} - \Gamma^{1/2}, \\
c &= -\left[\tfrac{\exp\{(\beta R_e)\}}{\Delta^{1/2}}\right](\Gamma^{1/2} - \Delta^{1/2}), \\
b &= 2\exp\{(\beta R_e)\}\left[2 - \left(\tfrac{\Gamma}{\Delta}\right)^{1/2}\right], \\
a &= 2b\left[-2 + \left(\tfrac{\Gamma}{\Delta}\right)^{1/2}\right]\exp\{(\beta R_e)\}.
\end{aligned} \tag{3.287}$$

From Γ and Δ, Tietz also showed that the anharmonicity $\omega_e x_e$ is given by:

$$\begin{aligned}
\omega_e x_e &= \tfrac{8[\Delta^{3/2} - (\Gamma^{1/2} - \Delta^{1/2})^3]}{(2\Delta^{1/2} - \Gamma^{1/2})} \tfrac{2 \times 1078 \times 10^{-16}}{\mu R_e^2} \\
&= \tfrac{8[\Delta^{3/2} - (\Gamma^{1/2} - \Delta^{1/2})^3]}{\beta R_e} \tfrac{2 \times 1078 \times 10^{-16}}{\mu R_e^2}.
\end{aligned} \tag{3.288}$$

Tietz [121] calculated the anharmonicity using Eq. (3.288) and compared his values with the values obtained from Eq. (3.68), for the Morse potential, and also compared with the experimental values for 23 diatomic systems in their ground electronic states: H_2, ZnH, CdH, HgH, CH, OH, HF, HCl, HBr, HI, Li_2, Na_2, K_2, N_2, P_2, O_2, SO, Cl_2, Br_2, I_2, ICl, CO and NO. For 16 these, the results obtained by Tietz presented less deviation from experimental values. The Morse function showed better only for the systems HCl, HBr, HI, N_2, O_2, SO, I_2 and NO.

In an attempt to obtain a more general potential, Tietz [122] suggest a function with more parameters, and therefore more flexible, given by:

$$V_{TIE_{II}}(R) = D_e \left(\frac{R - R_e}{R}\right)^2 \frac{\left(\frac{H^2 B}{AF} + HR\right)}{(F + HR)} \tag{3.289}$$

where D_e and R_e have their usual meanings, and A, B, F and H are constants. This potential is demanded to satisfy the conditions (i), (ii) and (iii).

One of the advantages this potential (3.289) over the first proposed by Tietz (3.285) is that the potential $V_{TIE_{II}}(R)$ can solve the Schrödinger equation exactly for arbitrary L and both discrete and continuous energy parameters E.

As before, the requirement that the second Tietz's potential (3.289) give the correct experimental values of F_e and G_e is warranted by:

$$-\left[\frac{1}{3}\left(\frac{d^3 V_{TIE_I}(R_e)}{dR^3}\right)\frac{R_e}{k_e} + 1\right] = F_e = \frac{\alpha_e \omega_e}{6B_e^2} \tag{3.290}$$

and

$$\left[\frac{5}{3}\left(\frac{1}{k_e}\frac{d^3V_{TIE_I}(R_e)}{dR^3}\right)^2-\left(\frac{1}{k_e}\frac{d^4V_{TIE_I}(R_e)}{dR^4}\right)\right]R_e^2=G_e=\frac{\omega_e x_e\mu R_e^2}{2\times 1078\times 10^{-16}}. \quad (3.291)$$

The accuracy of potential (3.289) can be determined by calculating F_e and G_e from Eq. (3.290) and (3.291) and comparing them with the experimental values. The values of F_e calculated by Tietz from potential (3.289) have shown to be in good agreement with experimental values for most of the evaluated systems [122]. However, in this potential, the parameters A, B, and H don't have a simple physical interpretation. Furthermore, curves generated by this function showed unphysical features at very large or very small values of R. Then, the first Tietz's potential (3.285) is better known and used than the second Tietz's potential.

In 1990, Hua [123] conducted a comparative study with the potentials of Morse [8], Varshni [14] and Levine [124]. These three potentials had a common characteristic: all showed large deviations from the RKR curve [9–11] when the domain of the potential extended to the limit of dissociation. Moreover, for the potentials of Varshni and Levine the Schrödinger equation can be solved exactly, but with very difficult calculations [123]. With this in mind, Hua proposes a potential of four parameters, in order to meet both characteristics:

$$V_{TH}(R)=D_e\left[\frac{1-e^{-b(R-R_e)}}{1-ce^{-b(R-R_e)}}\right]^2,\ |c|<1 \quad (3.292)$$

with

$$b=a(1-c) \quad (3.293)$$

being a the same of the Morse equation.

The parameter c is fitted to provide smaller absolute mean deviations. Hua calculated c for the systems: Li_2, Na_2, K_2, Rb_2, Cs_2, Cl_2, ICl, H_2 all in the state $X^1\Sigma_g^+$, HF and CO in the state $X^1\Sigma^+$, XeO in the state $d^1\Sigma_g^+$, ICl in the states $A^3\Pi_1$ and $A'^3\Pi_2$, I_2 in the state XO_g^+ and Cl_2 in the state $B^3\Pi(O_u^+)$. Comparing the value of the absolute mean deviation provided by the potential Hua with those provided by the Morse, Varshni and Levine potentials, only Cl_2 and ICl, both in the state $X^1\Sigma_g^+$, with values of 1.89% and 1.97% respectively, generated slightly larger variances with Hua than with Varshni (1.08% and 1.30% for Cl_2 and ICl respectively) and Levine (1.11% and 1.44% for Cl_2 and ICl respectively), which are much smaller than those provided by the Morse potential (6.06% and 5.68% for Cl_2 and ICl respectively) [123].

Still, the average general of the mean absolute deviation for the molecular states above was 1.63% using the $V_{TH}(R)$, while it was 7.72% using Morse, 4.74% using Varshni, and 4.67% using Levine [123].

For large-amplitude vibrations and for the extended potential domain, the Hua function (3.292) yielded a much lower absolute mean deviation compared to Morse, Varshni, and Levine, as shown for ICl in the state $A'^3\Pi_2$, Cs_2 in the state $X^1\Sigma_g^+$ and CO in the state $X^1\Sigma^+$ [123].

In addition to showing a better fit potential for the cited systems, the function of Hua $V_{TH}(R)$ has the advantage that when inserted into the Schrödinger equation, it can be solved exactly when the angular momentum J is zero and can be treated precisely for $J \neq 0$, allowing to calculate the corresponding ro-vibrational energy levels for a given system.

The four parameters potential of Hua gained prominence because it presented a good fit for the systems verified [123] in the overall potential, both in the spectroscopic region and in the dissociation limit. Such results were obtained even for large domains, dispensing a piecewise fitting of the potential without requiring spline functions associated or other functions, as is the case of the Morse potential (see for example [56]).

Royappa [42] *et al.* compared the two Tietz's potentials (3.285) and (3.289), and also the Tietz-Hua potential with others 18 functions for 14 diatomic systems in their ground electronic states, 9 of which are in common with those analyzed by Tietz [122]. Using the Z-test method of Murrell and Sorbie [60], Royappa verified that the average error of the second Tietz potential (3.289) was more than twice the average error of the first potential (3.285).

Royappa *et al.* further observed that the first Tietz potential was one of the most accurate. The Tietz potential (3.285) gives an average error less than of the Kratzer [16], Morse [8], Rydberg [9], Rosen-Morse [29], Pöschl-Teller [30], Linnett [61], Lippincott [43], Frost-Musilin [74], Deng-Fan [41], Varshni III [14], Levine [124] and Noorizadeh [125]. In addition, Royappa showed that the first Tietz potential (3.285) proved to be even more accurate than Tietz-Hua's own potential [123].

Currently, the Hua potential is known as the Tietz-Hua potential, and so we have used the TH index in the V function. The function proposed by Hua (3.292) corresponds exactly to the first Tietz's potential, according to Jia *et. al* [126]. They observed that the Tietz potential in Eq. (3.285) defined with five parameters, actually only has four independent parameters, and this potential can be rewritten as an improved representation so that the similarity to Hua's potential is evident (see more details in Ref. [126]).

3.1.24 The Levine function

Considering the relative accuracy obtained with the Varshni III [14] potential, in 1966, Levine [124] (LEV) proposed a similar function, but more general. This function can be considered a modified version of $V_{VAR_{III}}$ (3.252), being given by:

$$V_{LEV}(R) = D_e \left\{ 1 - \left(\frac{R_e}{R} \right) \exp\{[-a(R^p - R_e^p)]\} \right\}^2 \tag{3.294}$$

where p is a function of known spectroscopic parameters k_e, R_e and D_e. Levine defined p so that it vary for different molecules, being obtained by:

$$p = 2 + \frac{1}{4}\frac{(\Delta^{1/2} - 4)(\Delta^{1/2} - 2)}{(\Delta^{1/2} - 1)}, \tag{3.295}$$

where $\Delta = k_e R_e^2/2D_e$ is the Sutherland parameter.

The parameter a in Eq. (3.294) depends of p, and can be obtained by:

$$a = \frac{(\Delta^{1/2} - 1)}{pR_e^p}. \tag{3.296}$$

The potential $V_{LEV}(R)$, such as that of Varshni III reach the necessary conditions (see Section 3.1.21). Furthermore, we have:

$$\frac{d^2V_{LEV}}{dR^2}(R_e) = k_e \tag{3.297}$$

where k_e is the constant force.

In this case, the vibrational-rotational coupling constant α_e and the anharmonicity $\omega_e x_e$ are given by:

$$\alpha_e = \left[\Delta^{1/2} + \frac{p}{\Delta^{1/2}} - p\right]\frac{6B_e^2}{\omega_e} = \frac{3}{4}\Delta - \frac{1}{2} \tag{3.298}$$

and

$$\omega_e x_e = \left[8\Delta - 12(p-1)\Delta^{1/2} + 8p^2 + 4 - \left(\frac{20p^2 - 12p}{\Delta^{1/2}}\right) + \frac{12p^2}{\Delta}\right]. \tag{3.299}$$

Note that these expressions are identical to (3.254) and (3.255) respectively, replace 2 by p.

To check the accuracy of potential (3.294), Levine [124] calculated the average percent error using the relation $|V_{LEV} - V_{RKR}|/D_e$, where the V_{RKR} represents the experimental data curve from RKR [9–11]. He analyzed the diatomic systems: H_2, I_2, N_2, O_2, CO, NO, OH and HF in 19 states, and compared his results with the Lippincott [43] and Varshni [14] potentials. The Levine potential can be considered a potential with three parameters because p is obtained from k_e, R_e and D_e. This is the reason for choosing the potentials of Varshni III and Lippincott to make the comparison, both have three adjustable parameters too. Besides, these are considered the most accurate (with three parameters) in the comparative study by Steele *et al.* [15].

The Levine potential presented an average error in $|V_{LEV} - V_{RKR}|/D_e$ for the 19 states of 1.99%, while for Varshni III is 2.31% and for Lippincott is 2.21%. Moreover, the values obtained by Levine for α_e were also more accurate compared to the others, with an average error of 11.1%, against 15.6% of Varshni and 13.8% of Lippincott. For $\omega_e x_e$, the Levine potential showed a slightly smaller error (14.5%) than Varshni (14.6%), while the Lippincott gave only 12.2%.

In 1974, in a comparative study, Blinkova [127] calculated the vibrational levels for N_2, N_2^+, O_2, O_2^+ and CO in 31 electronic states using the Levine [124], Morse [8], Lippincott [43] and Varshni III [14] potentials, and compared them with experimental levels. The Levine and Varshni potentials presented intermediate results, being the Lippincott and Morse the best functions. However, it is verified only for some states of some diatomic systems. For example, the relative errors in the vibrational levels for $\mathrm{A}^3\Sigma_\mathrm{u}$ state of N_2 are: Lippincott 0.31%, Varshni 0.57%, Levine 0.77% and Morse 2.09%. In this case, the Morse potential is the least accurate among the others. On the other hand, for $\mathrm{a}^1\pi_\mathrm{g}$ state of N_2, we have the relative errors: Morse 0.39%, Levine 0.60%, Varshni 0.77% and Lippincott 1.0%, showing now, that Lippincott is the least accurate among the others. Then, Blinkova concluded that not is possible to describe equally well all the electronic states of various molecules using a single potential function of three parameters.

More recently, in 2006, in the comparative study by Royappa *et al.* [42], the Levine potential proved to be one of the most accurate for the 14 diatomic systems analyzed. This potential given less average error than the Kratzer [16], Morse [8], Rydberg [9], Rosen-Morse [29], Pöschl-Teller [30], Linnett [61], Frost-Musulin [74], Deng-Fan [41] and Varshni III [14].

3.1.25 The Simons, Parr and Finlan function

The Dunham expansion (3.61) to obtain potential energy for diatomic systems was one of the most frequently used in the 1970s and even in later years [24]. Essentially, the Dunham expansion is based on the calculation of the potential $V_{DUN}(R)$:

$$V_{DUN}(R) = a_0[(R - R_e)/R_e]^2 \left\{ 1 + \sum_{n=1}^{\infty} a_n[(R - R_e)/R_e]^n \right\} \tag{3.300}$$

as a Taylor series expansion in powers of the variable $(R - R_e)/R_e$, where the coefficients of this series are usually calculated via the Rayleigh-Schrödinger [128] perturbation theory. However, the Dunham expansion presented some convergence problems, especially in the long range region, making difficult to calculate the dissociation energy and also converging very slowly when $R \to R_e$ [129].

Looking for corrections to these problems, in 1973, Simons, Parr and Finlan [129] (SPF) decided to make a seemingly minor modification in the expansion of Dunham, replacing $(R - Re)/R_e$ and $(R - Re)/R$, by placing the potential as a series of powers in the variable $(R - R_e)/R$:

$$V_{SPF}(R) = b_0[(R - R_e)/R]^2 \left\{ 1 + \sum_{n=1}^{\infty} b_n[(R - R_e)/R]^n \right\}. \tag{3.301}$$

The expansion in the new variable given by (3.301) was properly justified and validated by SPF based on the perturbation theory. They also showed the upper limit for the radius of convergence of the new potential was infinite, while that of Dunham cannot converge to $R > 2R_e$[129].

For the calculation of the coefficients in equation (3.301), SPF used and adapted the procedure proposed by Dunham [24]. In the region where both potentials $V_{DUN}(R)$ and $V_{SPF}(R)$ converge, the coefficients of the new potential b_n and the potential of Dunham a_n are related as follows:

$$\begin{aligned} a_0 = b_0,\ a_1 = b_1 - 2,\ a_2 &= b_2 - 3b_1 + 3, \\ a_3 &= b_3 - 4b_2 + 6b_1 - 4; \\ a_n = b_n + \sum_{i=1}^{n-1} (-1)^i b_{n-i} \binom{n+1}{i} &+ (-1)^n (n+1). \end{aligned} \tag{3.302}$$

SPF compared their potential with Dunham expansion by analyzing the diatomic systems CO and HF, both in the ground electronic state, taking as reference the curve obtained by the known Rydberg-Klein-Rees [9–11] (RKR) method, considered to date as the most accurate curves for diatomic systems. In order to compare the convergence rates, they established a potential expansion of order N, set the N^{th} order term of the potential as:

$$V^N{}_D(R) = a_0[(R - R_e)/R_e]^2 \left\{ 1 + \sum_{n=1}^{N} a_n [(R - R_e)/R_e]^n \right\} \tag{3.303}$$

$$V^N{}_{SPF}(R) = b_0[(R - R_e)/R]^2 \left\{ 1 + \sum_{n=1}^{N} b_n [(R - R_e)/R]^n \right\}. \tag{3.304}$$

When testing $V^N{}_{SPF}$ for zero-order potential ($N = 0$) of the CO system, the SPF potential showed correct asymmetry, going to a finite value, when R becomes large, quite different from Dunham potential approaching a harmonic oscillator, going to infinity to large R. When $N = 1$, the Dunham expansion was very different from the RKR potential for $R > 1.2R_e$, where the function presents a maximum in $1.2R_e$ and goes to negative infinity for large R. The SPF potential was well behaved for R up to $1.5R_e$, assuming a finite value for a large R. Also for the CO diatomic system, when $N = 4$, $V^N{}_{SPF}$ fitted almost perfectly to the curve provided by RKR, especially in the region where R assumes larger values, while $V^N{}_D$ showed to be quite different, still close to that of a harmonic oscillator [129].

For the HF diatomic system, SPF used an expansion up to the fifth-order to compare the potentials $V^N{}_{SPF}$ and $V^N{}_D$, using as reference the potential obtained by the RKR method. Once again the SPF potential presented a good fit to the RKR curve [130], whereas the Dunham potential showed a maximum when $R \to \infty$, similarly than for CO, indicating such series truncation provided a reliable result. However, for short-range, $R \leq \frac{1}{2}R_e$, ${V^N}_{SPF}$ has an oscillatory behavior, converging slowly. This latter problem was not considered as relevant since the curve in the other regions converges quickly and smoothly as is desired [129].

Another advantage over the Dunham expansion is that due to the good behaviour of the potential expansion of the equation (3.301) for large R, the following boundary conditions are valid:

$$\lim_{R\to\infty} \{[R^2(d/dr)]^p V_{SPF}(R)\} = 0,\ p = 1, \cdots, 5 \tag{3.305}$$

from which the following relations are obtained

$$\begin{aligned}
\left[2 + \sum_{n=1}^{\infty}(n+2)_1 b_n\right] &= 0,\\
\left[2 + \sum_{n=1}^{\infty}(n+1)_2 b_n\right] &= 0,\\
\left[\sum_{n=1}^{\infty}(n)_3 b_n\right] &= 0,\\
\left[\sum_{n=1}^{\infty}(n-1)_4 b_n\right] &= 0,\\
\left[\sum_{n=1}^{\infty}(n-2)_5 b_n\right] &= 0,
\end{aligned} \tag{3.306}$$

where $(X)_N$ is the Pochhammer function, with $(X)_0 = 1,\ (X)_N = X(X+1)\cdots(X+N-1)$.

These relationships are valid for the infinite expansion (3.301), however SPF [129] suggest that they can also be used for truncated expression (3.304), using b_N instead of b_n, such coefficients being calculated only from b_{N+1} to b_{N+5}, neglecting others. To test their potential in this case, SPF performed the calculation of the dissociation energy D for CO and HF again.

When assuming the convergence at $R = \infty$, the equation (3.301) provides:

$$D = b_0 \left(1 + \sum_{n+1}^{\infty} b_n\right). \tag{3.307}$$

For the potential of the CO system, SPF used the first two conditions of (3.306) to calculate two additional coefficients, b_5 and b_6, and used these two extra coefficients to obtain the dissociation energy for CO. The value of D differed by only 7% of its value obtained experimentally. Furthermore, the sixth order potential fitted well again compared to the curve provided by RKR. For the HF system the result was not so good. When calculated for large values of R, the coefficients b_6 and b_7, and these coefficients used to obtain the dissociation energy D, differed by 44% from the corresponding value. In this case, the maximum values that occur in higher-order expansions can be used in the dissociation energy calculation, differing between 10 and 15% of the experimental values [129].

3.1.26 The Extended Rydberg function

In 1974, the Morse [8] potential was still considered one of the most popular to describe the PES of diatomic systems, and that of Hulburt and Hirschfelder [7] was also well known for its improved Morse potential as it corrected the long region of the function, making it more asymptotic. Furthermore, the Rydberg [9] potential, largely used by spectroscopists, with its simple functional form, differing little from the potential of Morse, was also a reference at the time to describe such systems.

Taking these three potentials into consideration, seeking for a functional shape best representing various diatomic systems, Murrell and Sorbie [60] proposed a modification of the Rydberg function. They then compared this new potential with results obtained using Morse and Hulburt and Hirschfelder functions, taking as reference the fitting obtained by the RKR method [9–11]. This was done for eight benchmark diatomic systems: HF, H_2, I_2, O_2, N_2, OH, CO and NO.

The original potential function of Rydberg [9]:

$$V_{RYD}(R) = -D_e[1 + a(R - R_e)] \exp\{[-a(R - R_e)]\} \tag{3.308}$$

where D_e is the depth of the well

$$a = (k_e/D_e)^{1/2} \tag{3.309}$$

being the derivatives of order n are given by the relation

$$k_e{}^{(n)} = k_e(-1)^n(n-1)a^{(n-2)} \tag{3.310}$$

where k_e is the constant force.

MS began to investigate the properties of the modified potentials of Rydberg,

$$V = \left(-D_e\frac{[\sum_n a_n R^n]}{[\sum_m b_m R^m]}\right) e^{-\gamma(R)}. \tag{3.311}$$

For the calculation of a_n and b_n in (3.311), MS assumed $a_0 = b_0 = 1$, and for the others they used the following spectroscopic expansion:

$$V = -D_e + \frac{1}{2}\sum_{n=2} f_n(R)^n = -D_e \sum_{n=0} g_n R^n; \quad f_n = 2k_e{}^{(n)}/n!, \quad g_n = -f_n/2D_e \text{ and } g_0 = 1,\ g_1 = 0 \tag{3.312}$$

or more conveniently

$$a_n = \sum_{s=0}^{n} g_{n-s} \sum_{t=0}^{s} b_t \gamma^{s-t}/(s-t)!. \tag{3.313}$$

Since $f_1 = 0$, and the spectroscopic parameters f_2, f_3 and f_4 are known, MS [60] imposed three conditions warrantying the solutions of Eq. (3.313) are physically acceptable. There are:

(i) γ shall be positive;

(ii) There shall be no zeros of the b-polynomial in the region physically significant R (*i. e.* all positive and small negative R);

(iii) There shall be no maxima in the attractive branch of the potential.

Murrell and Sorbie analyzed all cases of potential (3.311) which had the following non-zero coefficients: (a_1, a_2, a_3); (a_1, a_2, b_1); (a_1, a_3, a_4); (a_1, a_3, b_1); (a_1, b_1, b_2); and (b_1, b_2, b_3). The only one of these that led to satisfactory potential to describe the long-range region was the first. The function (3.311) then takes the form:

$$V_{MSorb}(R) = D_e(1 + a_1(R) + a_2(R)^2 + a_3(R)^3)e^{-\gamma R} \tag{3.314}$$

where the constants a_1, a_2 and a_3 and γ are obtained through the relations:

$$\begin{aligned} a_1 &= \gamma \\ a_2 &= g_2 + \gamma^2/2 \\ a_3 &= g_3 + \gamma g_2 + \gamma^3/6 \\ 0 &= g_4 + \gamma g_3 + \gamma^2 g_2/2 + \gamma^4/24. \end{aligned} \tag{3.315}$$

In 1983, Huxley and Murrell [131] improved the Murrel-Sorbie potential, using $(R - Re)$ instead R in Eq. (3.314), obtaining:

$$V_{ER}(R) = D_e(1 + a_1(R - R_e) + a_2(R - R_e)^2 + a_3(R - R_e)^3)e^{-\gamma(R-R_e)}. \tag{3.316}$$

This function became known as Extended Rydberg (ER) potential. The coefficients of this function can be obtained in the same way as for the Murrel-Sorbie potential.

The last equation in (3.315) has at least one positive root, as condition 1 demands. Its solution is obtained numerically. However, Huxley and Murrell [131] derived more explicit relations for the expansion coefficients a_n from f_n, which are the nth derivative of the potential (3.314) at the equilibrium distance R_e, known as the Dunham's expressions for the nth force constant (Section 2.2). For this, first they solved the quartic polynomial for a_1:

$$D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 - f_4 = 0 \tag{3.317}$$

and, as before, if the roots are all real, since f_4 is always positive, there must be one or three positive roots. For a physical acceptable (3.314), a_1 must be positive. Now, if a_1 is known, a_2 and a_3 can be obtained from expressions:

$$a_2 = \frac{1}{2}\left(a_1^2 - \frac{f_2}{D_e}\right) \tag{3.318}$$

and

$$a_3 = a_1 a_2 - \frac{1}{3}a_1^3 - \frac{f_3}{6D_e}. \tag{3.319}$$

Using the Dunham's expressions for the nth force constants, where $f_n = \left(\frac{d^n V}{dR^n}\right)_{R=R_e}$, we have the a_n in terms of spectroscopic parameters:

$$\begin{aligned} f_2 &= 4\pi^2\mu c^2\omega_e^2 \\ f_3 &= \tfrac{-3f_2}{R_e}\left(1 + \tfrac{\alpha_e\omega_e}{6B_e^2}\right) \\ f_4 &= \tfrac{f_2}{R_e^2}\left[15\left(1 + \tfrac{\alpha_e\omega_e}{6B_e^2}\right)^2 - \tfrac{8\omega_e x_e}{B_e}\right]. \end{aligned} \tag{3.320}$$

To quantify the accuracy of their potential relative to that of Hulburt and Hirschfelder [7], using the potential of RKR, Murrell, and Sorbie [60] calculated the deviation of $V_{MSorb}(R)$ and $V_{HH}(R)$ relative to V_{RKR}, using the following function:

$$Z = \frac{1}{n_i \Delta R}\sum_i \left(V_{RKR} - V_i\right)^2 \tag{3.321}$$

where n_i is the number of RKR points, and ΔR is the range covered by these points and V_i is the calculated potential.

The Z function was calculated for three potential regions, namely: the attractive region, the repulsive region, and the potential as a whole. This Z-test method was employed for eight selected diatomic systems HF, H_2, I_2, O_2, N_2, OH, CO and NO, using the potential functions V_{MSorb} and $V_{HH}(R)$ in place of V in (3.321).

For the repulsive part of the potential, Murrell and Sorbie [60] function $V_{MSorb}(R)$, provided a more precise fitting of Hulburt and Hirschfelder [7] $V_{HH}(R)$ in five of the eight diatomic systems, offering a worse fitting only for the HF, I_2 and N_2 systems. In the attractive branch of the potential, $V_{ER}(R)$ showed better results for practically all systems except I_2 and NO.

In the overall potential, the Extended Rydberg function performed better on all systems except for I_2, thus showing that the $V_{MSorb}(R)$ potential offers, in general, a better fit to the systems tested [60]. However, this analytical empirical potential does not produce accurate vibrational eigenvalues and eigenfunctions for highly vibrational excited states in the asymptotic region of a stable diatomic system.

3.1.27 The Thakkar function

Usually, curves of potential energy for diatomic systems were obtained by one of four forms: by a table of points; by an empirical function; by a series of powers truncated or through the Padé approximants [22]. Expansions in power series are very interesting because they provide an analytical form for the potential curve, facilitating the interpretation. In 1975, Thakkar [22] (THA) proposes a new and generalized power series expansion, with a nonlinear parameter p, containing both Dunham [24] and SPF [129] expansions as special cases corresponding to the particular choices of p in

$$V_{THA}(R) = e_0(p)\lambda^2 \left[1 + \sum_{n=1}^{\infty} e_n(p)\lambda^n\right] \tag{3.322}$$

where

$$\lambda(R, p) = s(p)[1 - (R_e - R)^p] \tag{3.323}$$

being p a nonzero number, R_e the equilibrium internuclear separation and $s(p)$ an abbreviated notation for the *sgn* function defined for:

$$s(p) = sgn(p) = \begin{cases} +1, & p > 0 \\ -1, & p < 0 \end{cases} . \tag{3.324}$$

For $p = -1$, the equation (3.322) becomes:

$$V(R) = a_0[R - R_e/R_e]^2 \left\{1 + \sum_{n=1}^{\infty} a_n[R - R_e/R_e]^n\right\} \tag{3.325}$$

where $a_n = e_n(-1)$, and the equation (3.325) is exactly the Dunham expansion (3.300).

For $p = +1$, the equation (3.322) becomes:

$$V(R) = b_0[R - R_e/R]^2 \left\{1 + \sum_{n=1}^{\infty} b_n[R - R_e/R]^n\right\} \tag{3.326}$$

where $b_n = e_n(1)$, and the equation (3.326) is exactly the SPF expansion (3.301).

Still, for $p > 0$ and $e_n(p) = 0(p \geq 1)$ the equation (3.322) becomes:

$$V(R) = e_0(p) + e_0(p)[(R_e/R)^{2p} - 2(R_e/R)^p] \tag{3.327}$$

which is simply the Lennard-Jones $(2p, p)$ potential [46] (see section 3.1.2).

The radius of convergence of the equation (3.322) is determined by the singularity of $V_{THA}(R)$ closest to $R = R_e$ in the complex R plane. For $p < 0$, the singularity occurs at $(R^{|p|} - R_e^{|p|})/R_e^{|p|} = -1$, which implies that for $p < 0$ the potential (3.322) cannot converge for $R > 2^{1/|p|}R_e$ [22]. In the case of Dunham potential ($p = -1$), as appointed in SPF [129], the expansion can not converge to $R > R_e$. For $p > 0$, the pole at $R = 0$ occurs at $(R^p - {R_e}^p)/R^p = -\infty$, and therefore the radius of convergence of (3.322) is bounded by infinity.

Thakkar [22] conjectured that the equation (3.322) converges to R in the interval $(0, 2^{1/|p|}R_e)$ for $p < 0$ and converges to R in the interval $(0, \infty)$ for $p > 0$, converging faster only in the interval $(R_e/2^{1/|p|}, \infty)$ for $p > 0$. For the calculation of the coefficients $e_n(p)$ in the expansion (3.322), Thakkar adapted the Dunham [24] procedure, and obtained a relation between $e_n(p)$ and a_n [22].

Regarding the choice of p, $p > 0$ values lead to a better result since the potential converges rapidly in the long-range region, which is of great interest when one wants to study molecular dynamics. Thakkar [22], proposes

$$p = -a_1 - 1 \tag{3.328}$$

and estimates some values for p through the extensive Calder and Reudenberg analysis of the Dunham coefficients for 160 diatomic molecules [22].

Thakkar analyzed the behaviour of the potential $V_{THA}(R)$, with p given by the relation (3.328) for the CO and HF systems, both in the ground state. He compared the results obtained with the Dunham and SPF potentials, using the truncated expansion:

$${V_{THA}}^N(R) = e_0(p)\lambda^2 \left[1 + \sum_{n=1}^{N} e_n(p)\lambda^n\right]. \tag{3.329}$$

For CO, Dunham potential proved to be well below that of SPF and ${V_{THA}}^N(R)$, showing that they agree with the RKR curve [130] for $N = 3$ or 4. In the calculation of the dissociation energy, the difference between SPF and Thakkar potential is very significant, since while SPF provides a 229% error, the calculation of D via Thakkar has an error of only -3.9% calculated via [22]:

$$D^N = e_0(p)\left[1 + \sum_{n=1}^{N} e_n(p)\right], \; p > 0 \tag{3.330}$$

being p calculated by (3.328).

For the HF system, the result is similar to CO, with Dunham potential once again diverging from the RKR and SPF curve, about 1193% deviation from the RKR curve for $N = 4$. In the calculation of the dissociation energy, the truncated function of Thakkar, for $N = 5$, presents the best fit with a maximum error of only 7.2%, while the SPF expansion with the same number of terms presented an error of 204% [22].

Thakkar still calculated the values of the dissociation energy for 20 alkali halides: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, CsCl, CsBr and CsI. For these systems, in comparison with experimental values, only NaBr had smaller deviation using SPF than Thakkar, being that in average the deviation of SPF was in 122%, whereas by the Thakkar model the average deviation was only 28% [22].

3.1.28 The Huffaker function

As we can see, until the 1970s, most research involving potential energy functions was based on either the Dunham potential [24] or the Morse potential [8]. However, although Morse presented a good approximation for real diatomic systems and the Dunham (theoretically) could be applied to any system, both have some disadvantages. The Dunham series has a poor convergence whereas the Morse function fails to describe finer spectroscopic details and the introduction of rotational effects is complicated [132].

Thinking about that, in 1976, Huffaker [133] presented a formula for the rotational-vibrational energy levels of a diatomic system using a perturbed Morse potential along with additional perturbations describing rotational energy.

The potential function of the perturbed Morse oscillator (PMO) used by Huffaker (HUF) is given by:

$$V_{HUF}(R) = D_e[(1 - e^{-a(R-R_e)})^2 + \sum_{n=4} b_n(1 - e^{-a(R-R_e)})^n] \tag{3.331}$$

where R_e and D_e have their usual means. This series converges for all R, except for a singularity at $R = 0$, and it is related with the dissociation energy D by:

$$D + \hbar c F_{\nu=0,J=0} = D_e(1 + b_4 + b_5 + \cdots) \tag{3.332}$$

where $F_{\nu,J} = \sum_{lj} Y_{lj} \left(\nu + \frac{1}{2}\right)^l J^j (J+1)^j$ as in Eq.(2.48) (see Section 2.2).

Note that the potential (3.331) does not have the cubic term. This is possible only if the unperturbed Morse potential is specified by the location of its minimum and its second and third derivatives there. Huffaker described, for convenience, the unperturbed Morse potential by the three parameters ρ, σ and τ, given by:

$$\rho = aR_e \tag{3.333}$$

$$\sigma = \frac{\sqrt{2\mu D_e}}{a\hbar} \tag{3.334}$$

$$\tau = \frac{D_e}{\hbar c}. \tag{3.335}$$

The parameter σ is approximately the number of bound states of the Morse oscillator, then $\sigma \approx \frac{\omega_e}{2\omega_e x_e}$. Then, as a result of the perturbation calculation, Huffaker [133] obtained expressions for Dunham coefficients Y_{ij}, with $i + j \leq 4$, as function of these ρ, σ, τ and $b_4, \cdots, b_8$. He modified slightly the Dunham notation, expressing each Y_{ij} as $Y_{ij} = Y_{ij}^{(0)} + Y_{ij}^{(2)} + Y_{ij}^{(4)} + \cdots$, where the lowest-order term, of order $i+j-1$ is given by $Y_{ij}^{(0)}$ and the terms of higher order are $Y_{ij}^{(2)}$, $Y_{ij}^{(4)}$, etc. Some of these coefficients for rotational-vibrational energy levels of a PMO are given by:

$$\begin{aligned}
Y_{10}^{(0)} &\equiv \omega_e^{(0)} = \tfrac{2\tau}{\sigma} \\
Y_{10}^{(2)} &\equiv \omega_e^{(2)} = \tfrac{au}{8\sigma^3}\left(-3b_4 - 15b_5 + 25b_6 - \tfrac{67b_4^2}{4}\right) \\
Y_{20}^{(0)} &\equiv -\omega_e x_e^{(0)} = -\left(\tfrac{\tau}{\sigma^2}\right)\left[\tfrac{1-3b_4}{2}\right] \\
Y_{01}^{(0)} &\equiv B_e^{(0)} = \tfrac{\tau}{\sigma^2\rho^2} \\
Y_{01}^{(2)} &\equiv B_e^{(2)} = \left(\tfrac{\tau}{8\sigma^4\rho^6}\right)\left[\tfrac{-5\rho^3}{6} + \tfrac{21\rho^2}{4} - 14\rho + 15 - \rho^2(7\rho+9)b_4 + 15\rho^3 b_5\right] \\
Y_{20}^{(2)} &\equiv -\omega_e x_e^{(2)} = \left(\tfrac{5\tau}{16\sigma^4}\right)\left[9b_5 - 15b_6 - 35b_7 + 49b_8 + \tfrac{237b_4^2}{20} + \tfrac{143b_4b_5}{2} - \tfrac{177b_4b_6}{2} - \tfrac{217b_5^2}{4}\right. \\
&\qquad \left. + \tfrac{1707b_4^3}{40}\right] \\
Y_{11}^{(0)} &\equiv -\alpha_e^{(0)} = -\left(\tfrac{3\tau}{\sigma^3\rho^4}\right)[\rho - 1] \\
Y_{11}^{(2)} &\equiv -\alpha_e^{(2)} = \left(\tfrac{\tau}{8\sigma^5\rho^8}\right)\left[\tfrac{-3\rho^5}{2} + \tfrac{43\rho^4}{3} - \tfrac{411\rho^3}{6} + \tfrac{1135\rho^2}{6} - 285\rho + 175\right. \\
&\qquad -\rho^2\left(\tfrac{13\rho^3}{12} - \tfrac{103\rho^2}{8} - 79\rho + \tfrac{335}{2}\right)b_4 + 5\rho^3\left(\tfrac{29\rho^2}{6} - 15\rho + 38\right)b_5 \\
&\qquad \left. -15\rho^4(17\rho - 15)\tfrac{b_6}{2} + 175\rho^5 b_7 + \rho^4(1043\rho + 1005)\tfrac{b_4^2}{8} - 715\rho^5\tfrac{b_4b_5}{2}\right] \\
Y_{30}^{(0)} &\equiv \omega_e y_e^{(0)} = \left(\tfrac{\tau}{2\sigma^3}\right)\left[-b_4 + 5b_5 + 5b_6 - \tfrac{17b_4^2}{4}\right] \\
Y_{21}^{(0)} &\equiv \gamma_e^{(0)} = \left(\tfrac{3\tau}{2\sigma^4\rho^6}\right)\left[-7\tfrac{\rho^3}{6} + \tfrac{23\rho^2}{4} - 10\rho + 5 + \rho^2(\rho - 1)b_4 - +5\rho^3 b_5\right]
\end{aligned} \tag{3.336}$$

where $\omega_e^{(0)}$ and $B_e^{(0)}$ correspond to Dunham's ω_e and B_e and have the values:

$$\omega_e^{(0)} = \frac{2\tau}{\sigma} \tag{3.337}$$

and

$$B_e^{(0)} = \frac{\tau}{\sigma^2\rho^2}. \tag{3.338}$$

Making power series expansion of the exponentials in Eq.(3.331) and comparing with Dunham expansion (2.46), Huffaker obtained the relations between the a_i Dunham coefficients and his b_i coefficients:

$$\begin{aligned}
a_0 &= \tau\rho^2, \\
a_1 &= -\rho, \\
a_2 &= \rho\left(b_4 + \tfrac{7}{12}\right), \\
a_3 &= \rho^3\left(b_5 - 2b_4 - \tfrac{1}{4}\right), \\
a_4 &= \rho^4\left(b_6 - \tfrac{5b_5}{2} + \tfrac{13b_4}{6} + \tfrac{31}{360}\right), \\
a_5 &= \rho^5\left(b_7 - 3b_6 + \tfrac{10b_5}{3} - \tfrac{5b_4}{3} - \tfrac{1}{40}\right), \\
a_6 &= \rho^6\left(b_8 - \tfrac{7b_7}{2} + \tfrac{19b_6}{4} - \tfrac{25b_5}{8} + \tfrac{81b_4}{80} + \tfrac{127}{20160}\right).
\end{aligned} \tag{3.339}$$

Ignoring the higher-orders correction $\omega^{(2)}$, etc., Huffaker obtained the Morse parameters ρ, σ and τ from experimental values of ω_e, B_e and α_e, given by:

$$\rho = \frac{(\alpha_e\omega_e + 6B_e^2)}{6B_e^2} \tag{3.340}$$

$$\tau = \frac{\omega_e^2}{4B_e\rho^2} \tag{3.341}$$

$$\sigma = \frac{2\tau}{\omega_e}, \tag{3.342}$$

and with similar approximations, the first three perturbation parameter of Eq. (3.331) are given from $\omega_e x_e$, γ_e and $\omega_e y_e$:

$$b_4 = \frac{2}{3}\left[1 - \frac{\sigma^2\omega_e x_e}{\tau}\right] \tag{3.343}$$

$$b_5 = \frac{1}{5\rho^3}\left[\frac{2\sigma^4\rho^6\gamma_e}{3au} + \frac{7\rho^3}{6} - \frac{23\rho^2}{4} + 10\rho - 5 - 3\rho^2(\rho - 1)b_4\right] \tag{3.344}$$

$$b_6 = \frac{1}{5}\left[\frac{2\sigma^3\omega_e y_e}{\tau} + b_4 - 5b_5 + \frac{17b_4^2}{4}\right]. \tag{3.345}$$

To evaluate the convergence properties of the Y_{ij}, Huffaker compared his method with Dunham's formulas, and concluded that his method was not only most convenient (mathematically), but also the most accurate.

Huffaker chose the $(^1\Sigma^+)$ CO diatomic system for testing the perturbed potential Morse $V_{HUF}(R)$. He compared his results with the RKR [9–11] experimental curves. For this diatomic system, the eight parameters σ, ρ, τ, b_4, $cdots$, b_8 were calculated using the equations from (3.340) to (3.345). Then, the higher-order corrections $\omega_e^{(2)}$, $B_e^{(2)}$, $\alpha_e^{(2)}$ and $\omega_e x_e^{(2)}$ also were calculated. Although of these to be practically negligible, these small corrections were included to obtain the eight parameters before cited.

To compare the accuracy of his analytical potential with others existing at the time, Huffaker chose those that were also given by a power-series expansion, such as Dunham [24], SPF [129] and Thakkar [22] potentials. The unperturbed Morse potential obtained by Huffaker showed to be superior to all others with a series using only 3 parameters, presenting the smallest mean absolute deviation from the carbon monoxide RKR potential. Moreover, the percent deviation of predicted dissociation energy for CO, from the experimental value, was much smaller using the Huffaker potential than using SPF, Thakkar, or Dunham potential.

Camacho *et al.* [134] in 1994, confirms the good accuracy of Huffaker potential for $(^1\Sigma^+)$ CO. Huffaker showed again to be more accurate than Dunham and SPF and obtained similar results to Thakkar.

In a second paper, Huffaker [135] extended the calculations of PMO parameters up through b_{12} from spectral data and applied this potential to some more diatomic systems: HF, HCl and CO (again) in their electronic ground states and also for the $B(^3\Pi_{0u}^+)$ excited state of I_2. Then, knowing that the highest PMO parameters to contribute with $Y_{ij}^{(2k)}$ is $b_{2i+j+2k}$, he obtained the following modified Dunham coefficients: $Y_{i0}^{(0)}$ for $i \leq 6$; $Y_{i1}^{(0)}$ for $i \leq 5$; $Y_{i0}^{(2)}$ for $i \leq 4$; $Y_{i1}^{(2)}$ for $i \leq 3$; $Y_{i0}^{(4)}$ for $i \leq 2$, and $Y_{i1}^{(4)}$ for $i \leq 1$. Thus, using an iterative approach Huffaker calculated all twelve parameters: ρ, σ, τ, $b_4, \cdots, b_{12}$.

Huffaker [135] showed that of the diatomic systems chose, CO was the most suited for a PMO analysis including the twelve parameters, with maximum discrepancy from RKR of only about 2 cm^{-1} at the $\nu = 19$ vibrational level, whereas, for HF, the error was about 200 cm^{-1} at the $\nu = 16$. For HCl, the results were similar to HF, but problems of convergence and truncation were not as bad. For the excited state of I_2, he obtained that the values of $b_n's$ were so large that the perturbation finally became bigger than the Morse potential, and because of the very large value of σ, convergence properties were good. Huffaker claims that an accurate PMO analysis through b_{12} should be possible for the ground state of any diatomic system, and for excited states, consistent results should be obtained.

However, in 1979, Goble and Winn [136] obtained a potential function for the $X^2\Sigma^+$ and $A^2\Pi$ of the weakly bound system NaAr and the $A^2\Pi_{3/2}$ state of NaNe derived by inverting spectral data to analytic potential functions. For NaNe($A^2\Pi_{3/2}$), the Huffaker function presented an inadequate behavior, similarly for NaAr, which led the authors to believe that this performance was general for weakly bound molecules when the Huffaker potential is used. For these cases, the Thakkar [22] function is more appropriate.

3.1.29 The Ogilvie function

Ogilvie presented his first potential for diatomic systems at the Canadian Spectroscopy Symposium, in Ottawa, 1974. He stated that although there are many potential functions which can be fit to R_e and k_e, and other parameters derived from vibrational-rotational spectra, for a lower portion of the potential well a flexible and accurate function which will reliably reproduce all the fitting procedures by which the spectroscopic parameters are derived, is still the Dunham [24] potential function given by Eq. (2.44). Most of the potential functions purposed by Ogilvie was Dunham type, because he believed that the general form of the potential energy of a diatomic system should be given as a function of some general parameter related to internuclear separation R to be represented as a truncated polynomial or power series of ξ (see Eq. (2.44)). Also, Tipping and Ogilvie [137] derive matrix elements appropriate to a generalized (Dunham potential), and these were the most accurate analytic results to date and were computed in detail for HCl (see details in Ref. [137]). The Ogilvie potentials are known as the Ogilvie-Tipping series (O-T).

In 1976, Ogilvie and Koo [138] calculated the Dunham potential coefficients a_i, $0 \leq i \leq 6$ (except 4 for HI), derived from spectroscopic data of diatomic systems HF, HCl, HBr, HI and CO in their electronic states. For this, they used the Dunham potential function:

$$V_{DUN} = \hbar c a_0 \xi^2 (1 + \sum_{i=1}^{\infty} a_i \xi^i) \tag{3.346}$$

where $\xi = \frac{R-R_e}{R_e}$. This function has the following properties:

(i) $V = 0$ at $R = R_e$;

(ii) $\left. \frac{dV_D^2}{dR^2} \right|_{R=R_e} = k_e$, being k_e the constant force.

The coefficient a_0 is related to the force constant according to equations:

$$a_0 = \frac{\omega_e^*}{4B_e^*} = \frac{k_e R_e}{2\hbar c}. \tag{3.347}$$

being ω_e^* and B_e^* adjusted parameters where Dunham corrections to Y_{01} and Y_{10} were applied. The other Dunham coefficients are determined by iterative procedure from equations (given by Dunham) using the energy level equation (2.48). These coefficients a_i, $i \geq 1$ determine the manner in which the lower portion of the potential function, $V \leq \frac{1}{2}D_e$, deviates from the parabolic form of the limiting case, $a_i = 0$, for all $i \geq 1$, of the harmonic oscillator [138]. The results obtained by Ogilvie and Koo were in good agreement with the previous sets of a_i existing at the time.

They computed correlation matrices for the coefficients a_i, ω_e^*, and B_e^* and also for energy coefficients Y_{lj} for all diatomic systems. In general, the coefficients a_i were not strongly correlated with each other and ω_e^* and B_e^* (absolute values of off-diagonal elements less than 0.9) except that a_1 was fairly anti-correlated with a_2 (matrix element ≤ -0.95). The calculated coefficients Y_{lj} also were not correlated with each other, except Y_{04} and Y_{12} for which the matrix elements ~ 0.99. Nevertheless, the calculated Y_{lj} are generally in good agreement with observed values. Ogilvie and Koo observed also that for the hydrogen halide molecules the coefficient a_0 varied little in this group and the other potential coefficient a_1 to a_4 (except a_4 of HI) showed a smooth monotonic increase as the halogen mass increases [138].

Still in 1976, Ogilvie [139] following the suggestion of Tipping, examined the series expansion (3.346) in the variable $\xi = \frac{R-R_e}{R+R_e}$, with $\xi = -1$ when $R \to 0$, and $\xi = 1$ when $R \to \infty$. Note that, in this case, $V(R) \to \infty$ at $R = -R_e$ and $V(R) = 0$ at $R = R_e$, and at $R = 0$ we have $V(R)$ defined (or regular), what allows one to introduce correct behavior near the origin by Coulomb subtraction, *i. e.*, without the Coulomb repulsion (For more details see section B of Ref. [140]). Then, the truncated Coulomb-subtraction Ogilvie-Tipping series (CS-OT) yield finite values $V(R)$ at both limits $R = 0$ and $R \approx \infty$.

Engelke [140] in 1978, compared the O-T and CS-OT functions with Thakkar [22] and SPF [129] potentials, because all have the same feature: are a Dunham-type power series. He considered O-T function as:

$$V_{OT}(R) = c_0\xi^2 \left(1 + \sum_{i=1}^{\infty} c_i \xi^i\right) \tag{3.348}$$

where $\xi = \frac{R-R_e}{R+R_e}$ and the coefficients c_i are related with Dunham coefficients. The first five coefficients are given by:

$$\begin{aligned} c_0 &= 4a_0 \\ c_1 &= 2(a_1+1) \\ c_2 &= (4a_2+6a_1+3) \\ c_3 &= (4a_3+8a_2+6a_1+2) \\ c_4 &= (16a_4+40a_3+40a_2+20a_1+5). \end{aligned} \tag{3.349}$$

He calculated these coefficients c_i for $(1s\sigma_g)^2$ state of H_2^+ and obtained that for

$R/R_e > 1$ both Thakkar and SPF were slight better than O-T when a_0, a_1 and a_2 Dunham coefficients were known. On the other hand, the CS-OT series was superior to all the other series in this region. Now, for $R/R_e < 1$, the O-T series was more accurate than Thakkar and SPF potentials, and CS-OT is again better than all the other series [140].

The similar situation occurred when a_0, a_1, a_2, a_3 and a_4 were known. In the region $R/R_e > 1$ the Thakkar potential was slightly superior and the SPF potential slightly inferior to the O-T series. On the other hand, for $R/R_e > 1$ the O-T series was more accurate than both potentials. For $0 < R/R_e < 5$ the CS-OT series was better than the all other, while for $R/R_e > 5$ the Thakkar potential became better [140].

In 1981, Ogilvie [141] proposed a general potential energy function for diatomic systems. This function more flexible is showed as a family of functions including previous polynomial functions having more restricted validity, like those presented before.

As before, Ogilvie considered the general form of potential energy as a function of internuclear separation R being given by a truncated polynomial or power series of argument w:

$$V_{OGI}(R) = d_0 w^2 \left(1 + \sum_{i=1}^{k} d_i w^i \right), \tag{3.350}$$

He considered that w can assumes three forms, and therefore $V_{OGI}(R)$ can be three different potentials series:

(i) if $w \to x = \frac{R-R_e}{R_e}$, $V_{OGI}(R)$ is the Dunham potential (3.346), and then, the coefficients d_i, $0 \le i \le k$, are written as a_i;

(ii) if $w \to y = \frac{R-R_e}{R}$, $V_{OGI}(R)$ is the SPF potential (3.301), and the coefficients are written as b_i;

(iii) if $w \to z = \frac{2(R-R_e)}{(R+R_e)}$ is the new form proposed by Ogilvie, and the coefficients are written as c_i (actually, this is the same form presented by Ogilvie in 1976 [140], but using the 2ξ variable).

In all cases, the expansion series is made about $R = R_e$, and thus $z = \frac{2x}{2+x} - \frac{2y}{2-y}$. Note also that for $R \sim R_e$, $x \sim y \sim z$ and $a_0 \equiv b_0 \equiv c_0$, and for $R \to 0$ and $R \to$ only z remains finite at both limits, with $z = -2$ and $z = 2$ respectively.

For convenience, Ogilvie [141] considered a potential energy function of a general type of truncated polynomial that could represent $V(x)$, $V(y)$ and $V(z)$ in a single expression. This is given by:

$$V(w_{mn}) = d_0^{mn} w_{mn}^2 \left(1 + \sum_{i=1}^{n} d_i^{mn} w_{mn}^i \right), \tag{3.351}$$

where the argument w_{mn} becomes a function of two integer parameters m and n as well as R and R_e:

$$w_{mn} = \frac{(m+n)(R-R_e)}{(mR+nR_e)}. \tag{3.352}$$

Note that these relations define a family of functions which, as earlier:

(i) if $n = 0$ we have $V(x)$;

(ii) if $m = 0$ we have $V(y)$;

(iii) if $m = m \neq 0$ we have $V(z)$.

To check the accuracy of your family potentials, Ogilvie [141] chose the diatomic system Ar_2 in $X^1\Sigma_g^+$ state. For this, he used a sample of 85 points in the range $2.5 < R/10^{-10}m < 6.7$, with geometrically increasing interval, in a general routine LMM1 for fitting parameters in the same initial estimates of parameters d_i^{mn} were applied to each set of m and n. Two sets of coefficients, numbering either seven ($d_0^{mn} - d_6^{mn}$) or nine ($d_0^{mn} - d_8^{mn}$), were tested. The data demonstrated that the $V(y)$ was slightly superior in these cases than $V(z)$, but four times as many iterations were required.

Ogilvie highlighted that $V(y)$ and $V(z)$ were not the best, but the case $m = 4$, $n = 1$ was the best for determination of seven coefficients, whereas the case $m = 4$ and $n = 3$ was best for the set of nine coefficients.

The coefficients d_i^{mn} are related with c_k coefficients in V(z) by equations:

$$c_0 = d_0^{mn}$$

$$c_1 = d_1^{mn} + \tfrac{n-m}{n+m} \tag{3.353}$$

$$c_k = (k+1)\left[\left(\tfrac{-m}{m+n}\right)^k - \tfrac{1}{(-2)^k}\right] + d_k^{mn} + \sum_{i=1}^{k-1} \binom{k+1}{i+1} \left[\left(\tfrac{-m}{m+n}\right)^{k-i} d_i^{mn} - \tfrac{c_i}{(-2)^{k-i}}\right],$$

where $\binom{m}{n}$ is the combinatorial $\frac{m!}{(n!(m-n)!)}$ and $k > 1$.

Thus, the $V(z)$ function defined according to the equation for $V(w_{mn})$ is a useful function, and among the others, it is the only one in which the $w_{11} = z$ parameter possesses the desirable equivalence of magnitude of limiting values, corresponding to $R = 0$ and $R \to \infty$, that ensure convergence within the entire range of accessible, real nuclear separation [141]. The same result was obtained by Engelke [140] as cited before, in which the function CS-OT corresponds to $V(z)$ without the Coulomb repulsion.

3.1.30 The Mattera function

From the 1970s, potentials began to present functional forms in power series expansions of Dunham-type, and closed formulas began to appear less frequently. Simons *et al.* [129], Thakkar [22], Huffaker [133] and Ogilvie [138] are some of the potentials presented earlier that are given in this way, and these proved to be accurate.

Then, in 1980, Mattera *et al.* [142] (MAT) presented a new representation of potential energy curves for diatomic systems using a function Dunham-type:

$$V_{MAT}(R) = d_0 f^2(x)[1 + d_1 f(x) + d_2 f^2(x) + \cdots], \tag{3.354}$$

where $x = \frac{R-R_e}{R_e}$ and $f(x)$ as well as the Thakkar proposal, which contains a free parameter:

$$f(x) = 1 - \left(1 + \frac{\gamma x}{p}\right)^{-p} \tag{3.355}$$

with $p > 0$.

The coefficients d_i are given in terms of Dunham coefficients a_i, the first five being:

$$d_0 = \tfrac{a_0}{\gamma^2}$$

$$d_1 = \tfrac{a_1}{\gamma} + 1\tfrac{1}{p}$$

$$d_2 = \tfrac{a_2}{\gamma^2} + \tfrac{3}{2}\left(1 + \tfrac{1}{p}\right)\left[d_1 - \tfrac{1}{18}\left(\tfrac{11}{p} + 7\right)\right]$$

$$d_3 = \tfrac{a_3}{\gamma^3} + 2\left(1 + \tfrac{1}{p}\right)\left[d_2 - \tfrac{d_1}{8}\left(\tfrac{7}{p} + 5\right) + \tfrac{1}{24}\left(\tfrac{10}{p^2} + \tfrac{11}{p} + 3\right)\right]$$

$$d_4 = \tfrac{a_4}{\gamma^4} + \tfrac{5}{2}\left(1 + \tfrac{1}{p}\right)\left[d_3 - \tfrac{d_2}{15}\left(\tfrac{17}{p} + 13\right) + \tfrac{d_1}{20}\left(\tfrac{15}{p^2} + \tfrac{19}{p} + 6\right) - \tfrac{1}{900}\left(\tfrac{274}{p^3} + \tfrac{401}{p^2} + \tfrac{194}{p} + 31\right)\right]. \tag{3.356}$$

These coefficients can be determined since the Dunham coefficients are known, and if p and γ are properly chosen.

The main advantage of the present expansion is the high flexibility of its leading term:

$$V_0(R) = d_0 \left\{1 - \left[1 + \frac{\gamma}{pR_e}(R - R_e)\right]^{-p}\right\}^2, \tag{3.357}$$

and this function has a interesting property, because $V_0(R)$ becomes the Morse potential [8] for $p \to \pm\infty$, the Lennard-Jones (6,12) potential [51] for $p = 6$ and the Kratzer potential [16] for $p = 1$ [143].

Mattera *et al.* also obtained the νth vibrational level E_ν of a particle in the potential $V_0(R)$ [144]:

$$E\nu = d_0 - d_0 \left[\left(1 + \frac{\delta}{A^2} \right)^{-1/S} - \frac{\nu + \frac{1}{2}}{AS} \right], \tag{3.358}$$

where m is the mass of particle, $A = \frac{(2md_0)^{1/2} R_e}{2\hbar\gamma}$, $\delta = \frac{\left(1+\frac{1}{p}\right)}{32p}$, $\frac{1}{S} = \frac{1}{2} - \frac{3+\frac{1}{p}}{4p}$. The Eq. (3.358) is more accurate than the Dunham [24] expansion of E_{nu} evaluate for V_0 up to the cubic term in $\left(\nu + \frac{1}{2}\right)$.

To get a proper $V_0(R)$ for a given diatomic system, Mattera *et al.* proposed two ways:

(i) p and γ are obtained from Dunham coefficients a_i by setting $d_1 = d_2 = 0$ in Eq. (3.356), producing:

$$p = \frac{12a_2 - 11a_1^2}{12a_2 - 7a_1^2}, \qquad \gamma = -\frac{a_1}{\left(1 + \frac{1}{p}\right)}, \qquad d_0 = \frac{a_0}{\gamma^2}; \tag{3.359}$$

(ii) d_0, $\frac{\gamma}{R_e}$ and p are determined by a direct fit of the vibrational spectrum with Eq. (3.358).

The procedure (ii) with the correct choice of R_e proved to be more suitable, leading to a term V_0 that accurately reproduces the RKR curves [9–11]. The procedure (i) showed to be less satisfactory in most cases, depending on quite accurate knowledge of the Dunham coefficients. The V_0 term was calculated using both procedures for HHg and CO, whereas for Ar_2, V_0 was obtained from the procedure (ii) only. Here, all diatomic systems considered are in their ground electronic states.

Mattera *et al.* obtained that for CO both procedures yield accurate results and for HHg the procedure (ii) was more adequate. Furthermore, the p values obtained in both ways, (i) or (ii), differed significantly from those obtained by Thakkar [22]. They also showed that large p values are more suitable in describing molecular interactions, indicating that the Morse potential was still a good representation of diatomic potentials.

In 1994, Camacho *et al.* [134] presented a comparative study of the eight most important power-series expansions, including Dunham [24], SPF [129], Thakkar [22], Huffaker [133], Ogilvie [141], Mattera [142] and Šurkus *et al.* [145](see the next section), as fitting functions for approximating rotationless RKR potentials [9–11]. The eight potentials given by truncated power series expansions were analyzed for CO ($X^1\Sigma^+$), H_2 ($X^1\Sigma_g^+$) and LiH ($X^1\Sigma^+$ and $A^1\Sigma^+$) diatomic system and for CO ($X^1\Sigma^+$) was analyzed also the behaviour of V_0 term.

Camacho *et al.* showed that the worst fit for CO corresponded to Ogilvie function due to the convergence of this potential, which is very slow and its limits give a finite small number when $R \to 0$. On the other hand, the Mattera potential presented the smallest standard and mean deviations for this diatomic system. For the ground electronic state of LiH, the best fitting was obtained by Thakkar potential, and in this case, the Dunham potential presented the worst fit, followed by the Ogilvie potential, which also showed greater deviations than the others. For LiH ($A^1\Sigma^+$) and H_2 ($X^1\Sigma_g^+$), the Mattera potential presented, in both cases, lower deviations than Thakkar, SPF, Huffaker, Ogilvie, and Dunham. Moreover, a good fit with only V_0 term of a power series expansion was obtained more accurately from functions with two nonlinear parameters, such as the Mattera or Šurkus potential.

However, Camacho *et al.* observed that for fitting power series expansions with an intermediate number of fundamental basis functions it was better to use a type of function with only one non-linear parameter, such as the Thakkar or Huffaker potential, because the effort in calculating the second optimum non-linear parameter of the Mattera function, for instance, was not the precision of the fits.

3.1.31 The Dmitrieva-Zenevich function

In 1983, Dmitrieva and Zenevich [146] (DZ) proposed a four-parameter potential energy function also inspired by the Dunham expansion, following the trend of the proposals at the time. Inspired by Simons, Parr, and Filan [129], the potential was proposed using the power series on $\xi(R) = \frac{R-R_e}{R_e}$, and they presented the function as a closed-form.

The potential proposed is given by:

$$\begin{aligned} V_{DZ_I}(\xi) &= \frac{a_0\xi^2}{(1-\frac{1}{3}a_1\xi)^3}, \qquad \xi \leq \xi_m \\ V_{DZ_{II}}(\xi) &= D_e - \frac{C}{R_e^6(1+\xi)^6}, \qquad \xi > \xi_m, \end{aligned} \tag{3.360}$$

where a_0 and a_1 are Dunham's coefficients [24]

$$a_0 = \frac{\omega_e^2}{4B_e} \tag{3.361}$$

and

$$a_1 = -1 - \frac{\alpha_e\omega_e}{6B_e^2} \tag{3.362}$$

where α_e, ω_e and B_e have their usual meanings.

The constants C and ξ_m are obtained by relations:

$$V_{DZ_I}(\xi_m) = V_{DZ_{II}}(\xi_m) \tag{3.363}$$

ensuring also the continuity of the function in ξ_m and

$$\left.\frac{dV_{DZ_I}}{d\xi}\right|_{\xi=\xi_m} = \left.\frac{dV_{DZ_{II}}}{d\xi}\right|_{\xi=\xi_m}. \tag{3.364}$$

These conditions result in the quartic equation:

$$\frac{\xi_m\left[-\frac{5}{3}a_1\xi_m^2+\left(8+\frac{1}{3}a_1\right)\xi_m+2\right]}{6\left(1-\frac{1}{3}a_1\xi_m\right)^4}=\frac{D_e}{a_0} \tag{3.365}$$

and the smaller positive root of this equation gives the desired ξ_m. Then, the C parameter can be obtained from:

$$C=\frac{a_0\xi_m\left(2+\frac{1}{3}a_1\xi_m\right)(1+\xi_m)^7R_e^6}{6\left(1-\frac{1}{3}a_1\xi_m\right)^4}. \tag{3.366}$$

Note that Eqn (3.360) fulfills:

(i) As $\xi\to\infty$, the potential converges asymptotically to a finite value, and in this case, we have, $V_{DZ_{II}}\to D_e$;

(ii) The potential has a minimum (in the region $\xi\le\xi_m$) at $R=R_e$, *i. e.*, $\left.\frac{V_{DZ_I}}{dR}\right|_{R=R_e}=0$;

(iii) $V_{DZ_{II}}\to\infty$ at $\xi=-1$(or equivalently at $R=0$).

Dmitrieva and Zenevich [146] analyzed their potential for H_2, I_2, N_2, O_2, CO, NO, OH and HF diatomic systems in their ground electronic states, and compared them with RKR [9–11] experimental curves [15]. Their potential presented the mean error from 0.52% for HF and O_2 to 1.8% for NO and 1.9% for I_2.

To calculate the anharmonicity $\omega_e x_e$, they suggested to use the expression:

$$\omega_e x_e=\frac{7}{8}B_e\left(1+\frac{\alpha_e\omega_e}{6B_e^2}\right)^2 \tag{3.367}$$

and tested for the eight diatomic systems mentioned above, giving an average error of 7.9%, much lower than those produced with the potentials: Morse [8], Rosen-Morse [29], Rydberg [9], Pöschl-Teller [30], Linnett [61], Frost-Musulin [114], Lippincott [43] and Varandas [147].

3.1.32 The Šurkus function

We have seen several potential energy functions represented as a power series, all based on Dunham's expansion,

$$V_{DUN}=a_0\xi^2\left(1+\sum_{i=1}^{\infty}a_i\xi^i\right) \tag{3.368}$$

with different proposals for ξ, being:

(i) $\xi = \frac{(R-R_e)}{R_e}$ by Dunham [24];

(ii) $\xi = \frac{(R-R_e)}{R}$ by SPF [129];

(iii) $\xi = s(p)\left[1 - \left(\frac{R_e}{R}\right)^p\right]$ by Thakkar [22];

(iv) $\xi = 2\frac{(R-R_e)}{R+R_e}$ by Ogilvie [141].

Then, in 1984, Šurkus, Rakauskas and Bolotin [145] showed that actually, all these potentials (i)-(iv) could be obtained from a generalized form for ξ, given by:

$$\xi_{SUR} = s(p)\frac{(R^p - R_e^p)}{(R^p + nR_e^p)} \tag{3.369}$$

where n and p are real numbers with the conditions that $p \neq 0$ and $n \neq -1$, and $s(p) = 1$ if $p > 0$ and $s(p) = -1$ if $p < 0$, like defined by Thakkar [22] (see Section 3.1.27).

Here ξ is a parameter in the Šurkus (SUR) potential, given by:

$$V_{SUR}(R) = g_0\xi^2\left(1 + \sum_{i=1}^{n} g_i\xi^i\right). \tag{3.370}$$

Šurkus observed that:

(a) if $n = 0$ and $p = -1$ in (3.369), we have (i);

(b) if $n = 0$ and $p = 1$ in (3.369), we have (ii);

(c) if $n = 0$ in (3.369), we have (iii);

(d) if $n = 1$ and $p = 1$ in (3.369), we have (iv).

Note that the parameter ξ_{SUR} remains finite for any value of R, ensuring that the Šurkus generalized potential may produce a qualitative approximation of the potential curve for all parts of the internuclear separation.

The Dunham's formulas to coefficients a_i are defined by the derivatives of the potential energy function at the minimum, in this case, given by:

$$a_0 = \frac{1}{2}R_e^2\left(\frac{d^2V_{SUR}}{dR^2}\right)_{R=R_e} \tag{3.371}$$

and

$$a_i = \frac{R_e^{i+2}}{[a_0(i+2)!]}\left(\frac{d^{i+2}V_{SUR}}{dR^{i+2}}\right)_{R=R_e}. \tag{3.372}$$

Šurkus *et al.* [148] considering the case when $p > 0$, he obtained the parameters g_i relating them to the Dunham parameters a_i by equations:

$$g_0 = a_0\xi_1^{-2}$$

$$g_1 = a_1\xi_1^{-1} - \xi_2\xi_1^{-2}$$

$$g_2 = a_2\xi_1^{-2} - \tfrac{1}{4}\xi_2^2\xi_1^{-4} - \tfrac{1}{3}\xi_3\xi_1^{-3} - \tfrac{3}{2}g_1\xi_2\xi_1^{-2}$$

$$g_3 = a_3\xi_1^{-3} - \tfrac{1}{6}\xi_2\xi_3\xi_1^{-5} - \tfrac{1}{12}\xi_4\xi_1^{-4} - \tfrac{3}{4}g_1\xi_2^2\xi_1^{-4} - \tfrac{1}{2}g_1\xi_3\xi_1^{-3} - 2g_2\xi_2\xi_1^{-2}$$

$$g_4 = a_4\xi_1^{-4} - \tfrac{1}{36}\xi_3^2\xi_1^{-6} - \tfrac{1}{24}\xi_2\xi_4\xi_1^{-6} - \tfrac{1}{60}\xi_5\xi_1^{-5} - \tfrac{1}{8}g_1\xi_2^3\xi_1^{-6} - \tfrac{1}{2}g_1\xi_2\xi_3\xi_1^{-5} - \tfrac{1}{8}g_1\xi_4\xi_1^{-4}$$

$$-\tfrac{3}{2}g_2\xi_2^2\xi_1^{-4} - \tfrac{2}{3}g_2\xi_3\xi_1^{-3} - \tfrac{5}{2}g_3\xi_2\xi_1^{-2}$$

$$g_5 = a_5\xi_1^{-5} - \tfrac{1}{72}\xi_3\xi_4\xi_1^{-7} - \tfrac{1}{120}\xi_2\xi_5\xi_1^{-7} - \tfrac{1}{360}\xi_6\xi_1^{-6} - \tfrac{1}{8}g_1\xi_2^2\xi_3\xi_1^{-7} - \tfrac{1}{12}g_1\xi_3^2\xi_1^{-6}\xi_1^{-6} - \tfrac{1}{8}g_1\xi_2\xi_4\xi_1^{-6}$$

$$-\tfrac{1}{40}g_1\xi_5\xi_1^{-5} - \tfrac{1}{2}g_2\xi_2^3\xi_1^{-6} - g_2\xi_2\xi_3\xi_1^{-5} - \tfrac{1}{6}g_2\xi_4\xi_1^{-4} - \tfrac{5}{2}g_3\xi_2^2\xi_1^{-4} - \tfrac{5}{6}g_3\xi_3\xi_1^{-3} - 3g_4\xi_2\xi_1^{-2} \tag{3.373}$$

where

$$\xi_1 \equiv R_e \frac{d\xi}{d_R}\bigg|_{R=R_e} = \frac{p}{(n+1)},$$

$$\xi_2 \equiv R_e^2 \frac{d^2\xi}{d_R^2}\bigg|_{R=R_e} = \xi_1(p-1) - 2\xi_1^2,$$

$$\xi_3 \equiv R_e^3 \frac{d^3\xi}{d_R^3}\bigg|_{R=R_e} = \xi_1(p-1)(p-2) - 6\xi_1^2(p-1) + 6\xi_1^3,$$

$$\xi_4 \equiv R_e^4 \frac{d^4\xi}{d_R^4}\bigg|_{R=R_e} = \xi_1(p-1)(p-2)(p-3) - 2\xi_1^2(p-1)(7p-11) + 36\xi_1^3(p-1) - 24\xi_1^4,$$

$$\xi_5 \equiv R_e^5 \frac{d^5\xi}{d_R^5}\bigg|_{R=R_e} = \xi_1(p-1)(p-2)\cdots(p-4) - 10\xi_1^2(p-1)(p-2)(3p-5)$$

$$+30\xi_1^3(p-1)(5p-7) - 240\xi_1^4(p-1) + 120\xi_1^5,$$

$$\xi_6 \equiv R_e^6 \frac{d^6\xi}{d_R^6}\bigg|_{R=R_e} = \xi_1(p-1)(p-2)\cdots(p-5) - 2\xi_1^2(p-1)(p-2)(31p^2 - 132p + 137)$$

$$+90\xi_1^3(p-1)(6p^2 - 19p + 15) - 40\xi_1^4(p-1)(39p-51) + 1800\xi_1^5(p-1)$$

$$-720\xi_1^6,$$

$$\xi_7 \equiv R_e^7 \frac{d^7\xi}{d_R^7}\bigg|_{R=R_e} = \xi_1(p-1)(p-2)\cdots(p-6) - 14\xi_1^2(p-1)(p-2)(p-3)(9p^2 - 39p + 42)$$

$$+42\xi_1^3(p-1)(p-2)(43p^2 - 141p + 116) - 840\xi_1^4(p-1)(10p^2 - 29p + 21)$$

$$+4200\xi_1^5(p-1)(4p-5) - 15120\xi_1^6(p-1) + 5040\xi_1^7. \tag{3.374}$$

In the case that $p < 0$, relationships can be obtained from (3.373) by substituting $-g_1$, $-g_3$, $-g_5$ for g_1, g_3 and g_5 respectively. Thus, if the spectroscopic constants $F_{\nu J}$ are known, the coefficients a_i can be calculated with Dunham's formulas [24], and substituting a_i into (3.373) and (3.374) the parameters g_i of the potential (3.370) can be obtained.

Šurkus *et al.* [145] also obtained relations between the dissociation energy D and the coefficients g_i. If $p > 0$ and $R \to \infty$, then $\xi \to 1$, and thus we have:

$$D = g_0 \left(1 + \sum_{i=1}^{N} g_i\right). \tag{3.375}$$

On the other hand, if $p < 0$ and $R \to \infty$, then $\xi \to \frac{1}{n}$, and thus we have:

$$D = \frac{g_0}{n^2} \left(1 + \sum_{i=1}^{N} \frac{g_i}{n_i}\right). \tag{3.376}$$

Since the dissociation energy is known, relations (3.375) and (3.376) can be used to estimate the following coefficient g_i on the basis of the coefficients determined.

Firstly, Šurkus *et al.* [145] applied their potential for ($X^1\Sigma_g^+$) H_2 diatomic system. In order to obtain coefficients g_i of the $V_{SUR}(R)$ from Eq. (3.373), the values of p and n were estimated using the relationships:

$$n = \left[\frac{2p}{(p - a_1 - 1)}\right] - 1 \tag{3.377}$$

and

$$p^2 - \frac{9}{2}a_1^2 + 6a_2 - 1 = 0. \tag{3.378}$$

The roots of Eq. (3.378) provide two potentials [148], being:

(i) V_{SUR_I}: $p = 1.1634$, $n = 0.3170$, $g_0 = 0.465369$ (a.u.), $g_1 = g_2 = 0$;

(ii) $V_{SUR_{II}}$: $p = 1$, $n = 0.5$, $g_0 = 0.817083$ (a.u.); $g_1 = -0.4050$, $g_2 = -0.0096$.

To evaluate their potential to ($X^1\Sigma_g^+$) H_2, Šurkus *et al.* [145] compared it with the Kolos-Wolniewicz potential (V_{KW}) using the expression $\Delta_i = (|V_{KW}(R_i) - V(R_i)|/D) \times 100\%$, where D is the dissociation energy of the ground state of H_2. The mean error for V_{SUR_I} and $V_{SUR_{II}}$ potentials was 5.3%, whereas for SPF it was 5.9%, for Thakkar it was 6.2% and for Ogilvie it was 7.5%.

The Šurkus potential showed to be accurate mainly for diatomic systems containing cations in their ground electronic states. In 1991, he applied his generalized potential to SiF^+ [149] and obtained better results than SPF, Thakkar, Ogilvie, and Huffaker. In 1992, he obtained the potential energy function of PO^+ [150], and in 1994, he obtained the potential energy function of KrH^+ [151], standing out for the correct long-range behavior for both.

In 1994, the good result of the Šurkus potential for ($X^1\Sigma_g^+$) H_2 was confirmed by Camacho *et al.* [134] which showed that the Šurkus potential was better and more accurate than Mattera [142], Huffaker [133], SPF [129], Thakkar [22], Ogilvie [141], Engelke [140] and Dunham [24] potentials.

3.1.33 The Pseudogaussian function

Still in 1984, Sage [152] introduces a new potential with three parameters, and as well as Morse [8], it can be used for discussing large-amplitude stretching vibrations. Sage called his potential a Pseudogaussian (PG), and energy levels and wavefunctions can be found for the three-dimensional rotating system using the same methods as for the one-dimensional oscillator for this potential, in contrast with the Morse oscillator.

The Pseudogaussian potential proposed by Sage is given by:

$$V_{PG}(R) = D_e \left\{ 1 - \left[1 + \frac{\beta}{2}\left(1 - \frac{R_e^2}{R^2}\right)\right] \exp\left[\frac{\beta}{2}\left(1 - \frac{R^2}{R_e^2}\right)\right]\right\} \tag{3.379}$$

where $\beta = -2 + (4+2\Delta)^{1/2}$ with R_e and D_e having their usual meanings and $\Delta = \frac{k_e R_e^2}{2D_e}$ the Sutherland parameter.

This function is similar to the three parameter Varshni III potential (3.252) (presented in Section 3.1.21) in some aspects. Note that $V_{PG}(R)$ satisfies:

(i) $V_{PG}(R)$ come asymptotically to a finite value, in this case D_e, as $R \to \infty$;

(ii) $V_{PG}(R)$ has a minimum at $R = R_e$, *i. e.*, $\left.\frac{dV_{PG}}{dR}\right|_{R=R_e} = 0$ and $\left.\frac{d^2V_{PG}}{dR^2}\right|_{R=R_e} = k_e$;

(iii) $V_{PG} \to \infty$ at $R = 0$.

We obtained the expressions for the spectroscopic parameters α_e and $\omega_e x_e$, from Dunham's relations (2.57) and (2.58):

$$\alpha_e = \left\{ \frac{8 + 3\Delta - (4+2\Delta)(4+2\Delta)^{1/2}}{3\Delta} + 1 \right\} \frac{6B_e^2}{\omega_e} \tag{3.380}$$

and

$$\omega_e x_e = \left\{ \frac{64(10+9\Delta) - 4(20+3\Delta)(4+2\Delta)(4+2\Delta)^{1/2}}{\Delta^2} + 22(6+\Delta) \right\} \frac{2.1078 \times 10^{-16}}{3R_e^2\mu}, \tag{3.381}$$

where, for $\omega_e x_e$ we use the approximation suggested by Varshni (see Eq. (7) in Ref. [14]).

For comparison only, if we use the equations (3.380) and (3.381) to calculate α_e and $\omega_e x_e$ with the same experimental value Δ used by Varshni (see table VIII in Ref.[14]) and with R_e, μ and ω_e collected by Herzberg [96] for OH diatomic system, the errors correspond to -23.15% and -15.1% respectively. However, for the Morse potential the errors are only 0% and $+13.9\%$ for α_e and $\omega_e x_e$, respectively. The results for $V_{PG}(R)$ potential also are less accurate than the Varshni potentials V_{VAR_I} and $V_{VAR_{III}}$, both with three parameters.

As well as the Morse potential, the PG function yields a soluble Schrödinger equation [153], but in many aspects, the PG potential is easier than the Morse function. This can be seen when dealing with a non-rotating molecule, for example.

To obtain the PG eigenfunctions, Sage suggested an expansion of the Schrödinger equation in terms of a complete set of three-dimensional pseudoharmonic (PH) oscillator functions given by [152]:

$$V_{PH} = \frac{1}{8} k_e R_e^2 \left(\frac{R}{R_e} - \frac{R_e}{R} \right)^2 . \tag{3.382}$$

The PH basis set corresponds to functions with the same equilibrium force constant k_e and bond length R_e as the PG oscillator. Furthermore, these functions have reasonable behavior at $R = 0$, near the equilibrium bond length R_e and at ∞ [154], and for small amplitude motion they correspond to the rotating and harmonically vibrating diatomic molecule. As well as the PG potential, the PH oscillator provides exactly the energy levels and wavefunctions for any angular momentum using the polynomial method, as demonstrated by Sage and Goodisman [155].

Sage analyzed the PG potential to the electronic ground state of the non-rotating OH system, and he compared his results with the Morse [8] potential. The RKR [9–11] experimental curve was used as a reference to calculate the deviations from these potentials.

The vibrational energy levels related to the PG potential were obtained from a linear variational calculating using a PH basis set with a maximum of fifty basis functions. Sage observed that with 25 functions the lowest 8 energy levels were determined to 0.1 cm^{-1}, but all states $\nu \geq 10$ had errors larger than 100 cm^{-1}, and even for 50 functions accurate energy were found for $\nu \leq 11$. Thus, if there is interest in states near the dissociation limit, the PH functions should be modified using smaller values of k_e or larger values of R_e. For example, using the force constant equal to $0.6k_e$ and equilibrium bond length equal to $1.2R_e$, Sage showed that only 25 PH functions gave comparable results to the original calculations with 40 PH functions, a considerable improvement.

Sage observed that to OH system, the PG potential coincides with the Morse potential if $R \to R_e$ and when $R \to \infty$, but in other regions, the PG potential lies above the Morse. Although the potential PG itself has not promoted major improvements over the potential of Morse, a modified version of this was able to accurately represent the true internuclear potential. This modified version called MODPG is the sum of one PG potential with force constant $0.6k_e$ and dissociation $0.4D$ and one with $0.4k_e$ and $0.6D$, respectively [152].

In 1985, Sage and Goodisman [155] showed the advantages that the pseudoharmonic function possess over the harmonic, such as the pseudoharmonic potential has a lager force constant inside the equilibrium distance than outside and becomes infinite for

$R = 0$; its eigenfunctions and eigenvalues may be obtained in closed form, including when a centrifugal force is present. Thus, pseudoharmonic functions are one of the best for building potential energy curves.

Royappa *et. al* [42], in a comparative study already cited before, compared for 14 diatomic systems in their ground electronic state the Pseudogaussian potential with the potentials: Morse [8], Rydberg [9], Lippincott [43], Varshni III [14] and Deng-Fan [41], all with three parameters, and also with others potentials with 2, 4, 5 and 8 parameters (as can be seen in before sections). In relation to the functions with three parameters, the Pseudogaussian potential energy curve, on average, presented a lower error than Lippincott and Deng-Fan, but it proved to be less accurate than Varshni, Rydberg and mainly in relation to Morse, with almost twice the average error. Particularly for OH diatomic system, the same results were observed.

3.1.34 The Varandas function

The construction of Varandas potential [156] was inspired a method known as many-body-expansion (MBE). The many-body expansion was proposed by Sorbie and Murrell [157], in 1975, when they presented the method for constructing analytical potential energy surfaces for stable triatomic system from spectroscopic data. The analytical potential for triatomic system are an extension of Extended Rydberg function [131]. They chose as variables, for the potential of the ABC system, the three internuclear distances $R_1(R_{AB})$, $R_2(R_{BC})$ and $R_3(R_{CA})$. The three bond lengths are independent coordinates but they must accomplish the triangulation restriction $R_i \leq R_j + R_k$. The complete potential is written as a sum of two and three-body terms as follows:

$$V(R_1, R_2, R_3) = V_{AB}(R_1) + V_{BC}(R_2) + V_{AC}(R_3) + V_I(R_1, R_2, R_3), \tag{3.383}$$

where the two-body potentials $V_{AB}(R_1)$, $V_{BC}(R_2)$ and $V_{AC}(R_3)$ are given by Murrell-Sorbie potential (3.314):

$$V_{XY} = -D_e(1 + a_1 R + a_2 R^2 + a_3 R^3)e^{-a_1 R} \tag{3.384}$$

and the three-body potential has the form:

$$V_I(R_l, R_2, R_3) = P(s_1, s_2, s_3) \prod_{i=1}^{3} (1 - anh\gamma_i s_i/2) \tag{3.385}$$

being P a polynomial up to quartic terms and s_i the internuclear distance relative to the triatomic equilibrium configuration. V_I becomes zero at all dissociation limits, *i. e.*, when any two of the three coordinates becoming infinite.

The essential feature of the model is to take the potential as a many-body expansion the individual terms of which are determined by the potential functions for the dissociation fragments. The MBE was first applied to H_2O system by Sorbie and Murrell [157]. In 1976, Murrell, Sorbie, and Varandas [158] applied the same potential to O_3, making the first application to a system in which there is more than one stable minimum in the triatomic surface.

Then, in 1977, Varandas and Murrell [159] extended the Sorbie and Murrell potential (3.383) to deal with larger polyatomic systems. This extension is based upon a many-body expansion of the total potential energy and has the objective of reproducing both the equilibrium properties of any stable molecule on the surface and the asymptotic dissociation limits. In this work, they presented a general N-body potential which consists of expressing the total molecular potential energy as a many-body expansion in the energy of all the fragments. According to this approach, the potential of a polyatomic molecule is written as:

$$V_{ABC\cdots N}(\mathbf{R}) = \sum V_{AB}^{(2)}(R_1) + \sum V_{ABC}^{(3)}(R_1, R_2, R_3) + \cdots + \sum V_{ABC\cdots N}^{(n)}(\mathbf{R}) \quad (3.386)$$

where the summations extend to all distinct interactions of a given type, and the energy of the separated atoms, in the states which are produced by adiabatically removing them from the polyatomic, is taken as the zero of energy. The coordinate $\mathbf{R}$ denotes the set of all interatomic separations and is assumed that only one atomic state is produced upon dissociation. Analogously, $V_{AB}^{(2)}(R_1)$ represents the two-body interaction potential for atoms A and B separated by R_1, and $V_{AB}^{(2)}(R_1) \to 0$ asymptotically, when $R_1 \to \infty$. Still, $V_{ABC}^{(3)}(R_1, R_2, R_3)$ represents a three-body term that must become zero as any of the three atoms is infinitely separated from the other two, and so on for the higher-order N-body energy terms.

In the same year, Varandas and Murrell [160] presented an MBE type function which covered a limited region of the ground state surface of ammonia. This region contains the two minima and the inversion barrier. They concluded that the surface, in general, was in fair agreement with the experimental data. However, the barrier to inversion however was more than twice as great as the experimental value. In 1983, Špirko [161] showed that several approximations to the ammonia potential function were introduced and this potential function was, unfortunately, of very limited accuracy. At the time, Špirko presented a significantly better description of the genuine ammonia potential function by using a modified Pliva potential function (see more details in Ref. [162]).

In 1982, Varandas and Brandão [163] expressed the interaction diatomic potential in terms of the Hartree-Fock (HF) interaction energy, $V_{HF}(R)$, and the interatomic correlation energy as approximated semi-empirically from the second-order dispersion energy calculated including the effect of charge overlap between the electron clouds of the two interacting species, $V_{inter/disp}(R)$. The total interaction energy by the sum of the Hartree-Fock interaction energy and the interatomic correlation energy that goes asymptotically to the dispersion energy:

$$V(R) = V_{HF}(R) + V_{inter/disp}(R) \tag{3.387}$$

The dispersion energy calculated, including the effect of charge overlap, is given by:

$$V_{inter/disp}(R) = -\sum_{l_A,l_B} C_{l_A,l_B}\chi_{l_A,l_B}(R)R^{-2L} \tag{3.388}$$

with χ_{l_A,l_B} being R-dependent dispersion damping functions which account for the charge overlap effects. These functions are given by general form [163]:

$$\chi_{l_A,l_B}(R) = \{1 - \exp\Big\{[-d_1{}^{(2L)}x(1 + d_2{}^{(2L)}x)]\Big\}\}^{2L} \tag{3.389}$$

with

$$x = \frac{R}{\rho}, \tag{3.390}$$

$$\rho = \frac{(R_e + \gamma R_0)}{2}, \tag{3.391}$$

$$R_0 = 2(\langle r_A{}^2\rangle^{1/2} + \langle r_B{}^2\rangle^{1/2}), \tag{3.392}$$

where R_e is the equilibrium diatomic geometry, is to be self-consistently determined, R_0 is the Le Roy [164] distance at which the undamped dispersion energy, and $d_i^{(2L)}(i = 1, 2; L = 3, 4, \cdots)$ are universal numerical constants which are obtained from existing ab initio data on the $^3\Sigma_u^+$ state of H_2. Still, $\langle r_A{}^2\rangle$ is the expectation value of the square of the radius of the outermost electrons in the interacting species A.

As the dispersion damping functions corresponding to a given value of L have the same R-dependence irrespective of the specific pair (l_A, l_B) involved, $V_{inter/disp}(R)$ assumes the approximate form to:

$$V_{inter/disp}(R) = -\sum_{L=3} C_{2L}\{1 - \exp\Big\{[-d_1{}^{(2L)}x(1 + d_2{}^{(2L)}x)]\Big\}\}^{2L}R^{-2L} \tag{3.393}$$

with

$$\rho = \frac{(R_e + 2.5R_0)}{2}, \tag{3.394}$$

The short range repulsive region of the potential can be approximately described by Hartree-Fock theory. In many cases the potential shows, in this region, an inverse exponential dependence in R which is commonly approximated by a Born-Mayer [33] type function:

$$V_{HF}(R) = A\exp\left\{\left(-\sum_{i=1}^{N} b_i R^i\right)\right\} \tag{3.395}$$

being N usually 1 or 2. Varandas and Brandão [163] obtained an equally good functional form given by:

$$V_{HF}(R) = AR^{-1}\exp\left\{\left(-\sum_{i=1}^{N} b_i R^i\right)\right\}. \tag{3.396}$$

They showed that by combining the asymptotic power series expansion of the dispersion energy suitably damped to account for charge overlap effects at a small R with the generalized Hartree-Fock repulsion good agreement was obtained with the available information on the lowest triplet state potential of the alkali dimers. In all other applications made including rare gas-rare gas, H-rare gas, and alkali-rare gas interactions as well as $Mg_2(^1\Sigma_g^+)$, and the isotropic components of the H-H_2, He-H_2 and H_2-H_2 potential energy surfaces, the model presented in (3.387) produced results in excellent agreement with ab initio and experimental data. Thus, the model provides a physically correct description of the interaction potential particularly at the intermediate regions close to the van der Waals minimum [163]. This success indicated that a general potential for N-body systems was about to be born which would be widely used worldwide.

Then, in 1984, Varandas [165] suggested using a double many-body expansion (DMBE) of potential energy surfaces which, being an extension of the previous approach (3.386) leading to a reliable description of the potential surface from short to large interatomic separations. He used for this a well-known approach making a further partition of the molecular potential energy by splitting each N-body energy term into Hartree-Fock and correlation energy type components.

In the DMBE approach the two-body energy terms is given by:

$$V_{AB}^{(2)}(R_1) = V_{AB,\ HF}^{(2)}(R_1) + V_{AB,\ corr}^{(2)}(R_1) \tag{3.397}$$

and analogously, the three-body energy terms is given by:

$$V_{ABC}^{(3)}(R_1, R_2, R_3) = V_{ABC,\ HF}^{(3)}(R_1, R_2, R_3) + V_{ABC,\ corr}^{(3)}(R_1, R_2, R_3). \tag{3.398}$$

As the two-body energy terms are written as a sum of the near Hartree-Fock energy, which is purely repulsive in the case of interactions involving neutral closed-shell atoms, and approximate representation of the correlation energy which is generally an attractive contribution, Varandas referred to this model by HFACE, *i. e.*, Hartree-Fock-approximate correlation energy [165]. From this moment, the long-range term $V_{inter/disp}(R)$ is referred as $V_{corr}(R)$.

This model was applied to the triatomic system HeH_2, and the results were in good agreement with available accurate ab initio calculations. Varandas [165] highlighted some advantages of using the DMBE approach:

Firstly, one expects different rates of convergence of the many-body ex-

> pansion at short distances where the Hartree-Fock energy is the dominant component, and at large distances where the interatomic correlation energy dominates. Secondly, there are practical advantages in treating the Hartree-Fock and correlation energy components separately due to their different functional forms. The third reason is related to our main goal which is to interpolate the potential energy surface at intermediate distances, where a fully correlated ab initio electronic structure calculation is prohibitively expensive, from its asymptotic energy components at short and large distances which are much easier to compute. Finally, one should refer to the advantages of following current quantum chemical ideas on the partitioning of the total interaction energy, thus conveying the model a sound full basis lying on physically meaningful energy components (VARANDAS, 1984).

In 1986, Varandas and da Silva [166] showed how to obtain diatomic potential energy surfaces, in special, using the Hartree-Fock Approximate Correlation Energy (HFACE) model. As before, the total potential is given by:

$$V(R) = V_{HF}(R) + V_{corr}(R) \tag{3.399}$$

where $V_{HF}(R)$ stands for the (extend) Hartree-Fock energy including the amount of correlation energy which is necessary to guarantee the proper behavior on dissociation, and $V_{corr}(R)$ is the interatomic correlation energy which is semiempirically represented by the dispersion energy damped.

The global short-range energy was chose as

$$V_{HF}(R) = -DR^{\alpha}\left(1 + \sum_{i=1}^{3} a_i r^i\right)\exp(-\gamma r), \tag{3.400}$$

being $r = R - R_e$, D the dissociation energy and α can be zero, and in this case, it represents the Hartree-Fock energy by the Extended-Rydberg potential, as suggested by Murrell and Sorbie [60]; or $\alpha = -1$, which was imposed the proper Coulombic behaviour at small values of R [166].

The γ value can be obtained using the similar method (3.315) proposed by Murrell and Sorbie in the section 3.1.26, from the quartic equation:

$$U^{(4)} + 4\gamma U^{(3)} + 6\gamma^2 U^{(2)} + 4\gamma^3 U^{(1)} + \gamma^4 D = 0, \tag{3.401}$$

and then, the coefficients a_i, $i = 1, 2, 3$, by the relations:

$$a_1 = \frac{U^{(1)}}{D} + \gamma \tag{3.402}$$

$$a_2 = \frac{1}{2}\left[\frac{U^{(2)}}{D} + 2\gamma\frac{aU^{(1)}}{D} + \gamma^2\right] \tag{3.403}$$

$$a_3 = \frac{1}{6}\left[\frac{U^{(3)}}{D} + 3\gamma\frac{U^{(2)}}{D} + 3\gamma^2\frac{U^{(1)}}{D} + \gamma^3\right] \tag{3.404}$$

being

$$U^{(i)} = \frac{d^i U(R)}{dR^i} \tag{3.405}$$

the ith derivative of $U(R) = -R^{-\alpha}[V(R) - V_{corr}(R)]$ with respect to R. The largest γ-root gives the best potential in general.

To represent V_{corr}, they used:

$$V_{corr} = -\sum_{n=6,8,10,\cdots} C_n^{AB}\chi_n(R)R^{-n} \tag{3.406}$$

where now, the damping functions are defined as:

$$\chi_n(R) = [1 - \exp\{(-Ax - Bx^2\})]^n \tag{3.407a}$$

$$x = 2R/(R_e + 2.5R_0) \tag{3.407b}$$

$$A_n = \alpha_0 n^{-\alpha_1} \tag{3.407c}$$

$$B_n = \beta_0 \exp\{(-\beta_1 n)\} \tag{3.407d}$$

where $\alpha_0 = 16.36606$, $\alpha_1 = 0.70172$, $\beta_0 = 17.19338$ and $\beta_1 = 0.09574$ are universal parameters dimensionless for all isotropic interactions, and R_0 is given by Eq.(3.392).

Varandas and da Silva [166] suggested the universal relationship:

$$\frac{C_n^{AB}}{C_6^{AB}} = k_n R_0^{[a(n-6)/2]}, \quad n = 8, 10 \tag{3.408}$$

where $\alpha = 1.57$, $k_8 = 1$ and $k_{10} = 1.13$, and the coefficient C_6^{AB} is known (see Ref. [167]). From this correlation, they obtained:

$$\frac{C_6 C_{10}}{C_8^2} = k_{10}, \tag{3.409}$$

and in particular, for homonuclear interactions:

$$\begin{aligned} \frac{C_8^{AA}}{C_6^{AA}} &= 8.82(\langle r^2\rangle^{1/2})^{1.57} \\ \frac{C_{10}^{AA}}{C_6^{AA}} &= 88.59(\langle r^2\rangle^{1/2})^{3.14}. \end{aligned} \tag{3.410a}$$

They analyzed the behavior of the HFACE model for 77 diatomic systems in their ground electronic state. For bound-state interactions, if $\alpha = 0$ in Eq.(3.400), in general, in the valence region their potential and the Extended-Rydberg [60] showed similar accuracy and, in the long-range region, the HFACE potential proved to be superior with correct behavior at $R \to \infty$. Still, if $\alpha = -1$, the results proved to be slightly less accurate than V_{HF} with $\alpha = 0$, when both are compared to RKR data [31]. The HFACE model proved to be a real general analytic representation of the potential energy curves for diatomic interactions. This potential was considered the most realistic and accurate to represent bound-state and van der Waals diatomics systems, which is still widely used today. This model is known as EHFACE2 (extended Hartree-Fock approximate correlation energy to diatomic systems).

Then, in 1992, Varandas and da Silva [168], following previous work, presented the best version of the general potential for diatomic systems, called EHFACE2U then given by:

$$V_{EHFACE2U} = V_{EHF} + V_{dc} \tag{3.411}$$

where now, the first term represents the extended-Hartree-Fock type energy and the second term provides the dynamical correlation energy. Here, V_{dc} corresponds exactly to V_{corr} in Eq.(3.406), with the same characteristics of the damping functions in Eq.(3.407).

One of the changes in relation to the potential previously proposed was the definition of the parameter γ, which is now given as:

$$\gamma = \gamma_0[1 + \gamma_1 anh(\gamma_2 R)] \tag{3.412}$$

adding two new parameters to potential proposed in Ref. [166]. However, these parameters provide the correct asymptotic behavior at $R \to \infty$.

To obtain the a_i and γ_i parameters, three fit methods were proposed by Varandas and da Silva. We discussed one of these here, and the others can be seen in Ref. [168].

The a_i and γ_i parameters were determined from a least-squares fit. The second essential difference between the EHFACE2 and EHFACE2U is that, now, to make this least-squares fit, the total kinetic field of the total potential must be normalized to give the correct description of the potential energy at $R \to 0$, *i. e.* [168],

$$\int_0^\infty [T(R) - T(\infty)]dR = Z_A Z_B \tag{3.413}$$

where the electronic kinetic energy is given by:

$$T = -V_{EHFACE2U}(R) - R\frac{dV_{EHFACE2U}(R)}{dR} \tag{3.414}$$

and Z_A and Z_B are the nuclear charges of the atoms A and B. This expression together with the expression for the potential energy,

$$U = 2V_{EHFACE2U}(R) + R\frac{dV_{EHFACE2U}(R)}{dR} \tag{3.415}$$

provides the well known virial theorem relating the electronic kinetic energy T, the potential energy U and the total Born-Oppenheimer energy $V(R) = T(R) + U(R)$. Furthermore, $T(0) = -W(0)$ is the energy of the united-atom (this condition is represented by U in EHFACE2U).

From Eqs.(3.413) and (3.1.34), the integral form of the virial theorem is obtained:

$$V = \frac{1}{R}\left\{Z_A Z_B - \int_0^{\infty}[T(R') - T(\infty)]dR'\right\} \tag{3.416}$$

and thus, the normalization condition ensures also the correct Coulomb potential [168]:

$$\lim_{R\to 0} V_{EHFACE2U}(R) = \frac{Z_A Z_B}{R}. \tag{3.417}$$

Varandas and da Silva also observed that, if $T(\infty) = -V_{EHFACE2U}(\infty) = 0$, the normalization condition for V_{EHF} with $\alpha = -1$, corresponds to impose:

$$D\left[1 + \sum_{n=1}^{3} a_i(-R_e)^i\right] \exp\{\{\gamma_0[1 - \gamma_1 anh(\gamma_2 R_e)]\}\} = Z_A Z_B. \tag{3.418}$$

The EHFACE2U potential energy function proved to be quite accurate to describe the 13 chemical stable diatomic systems, which were evaluated: H_2, Li_2, Na_2, K_2, Rb_2, Cs_2, Cl_2, N_2 and O_2, HF, CO, OH and NO, all in their ground electronic state. In addition, Varandas and da Silva presented a case study of Ar_2 van der Waals molecule and obtained the most accurate potential energy curve reported at the time (see the details in Ref. [168]).

The EHFACE2U potential energy curve is considered one of the best and more accurate functions to describe diatomic interactions, it is still widely used in recent researches [169–171]. In a recent work presented by da Silva and Ballester [172] the diatomic potential energy curves for triplet electronic states, $X^3\Sigma^-$ and $B^3\Sigma^-$ of SO has been described using the approach proposed by Varandas and da Silva [168]. Another recent application this potential can be seen in Ref. [173]. In a detailed investigation about the vibronic transition parameters as Franck-Condon factors, r-centroids, Einstein coefficients, and radiative lifettimes for some bands of the second positive ($C^3\Pi_u - B^3\Pi_g$) and Herman infrared ($C''^5\Pi_u - A'^5\Sigma_g^+$) band systems of N_2. Again, the diatomic potential energy curves for all electronic states studied have been modeled using the approach proposed by Varandas and da Silva [168].

3.1.35 The Schiöberg function

We have seen that the Morse potential [8] is still, in relation to some potentials, more accurate. However, as mentioned in Section 3.1.3, the Morse potential presents some problems, such as not warranting proper asymptotic limits, *i. e.*, if $R \to 0$,

$V_{MOR}(R)$ assumes a finite value. Although this should not affect the properties of the bound state, it will give a rise to some difficulties in solving the collision problems considered. The Morse function also is inaccurate for large R, due to the replacement of the Van der Waals term by an exponential.

In an attempt to obtain a potential that could improve the accuracy of the Morse potential, Schiöberg [174] (SCH) proposed in 1986, a hyperbolic potential function with three parameters given by:

$$V_{SCH}(R) = D[1 - \sigma \coth{(aR)}]^2 \tag{3.419}$$

where D, a and σ are adjustable positive parameters. Using the relation $\coth{(aR)} = \frac{e^{aR}+e^{-aR}}{e^{aR}-e^{-aR}}$, the function (3.419) can be rewrite as:

$$V_{SCH}(R) = D\left[1 - \sigma - \frac{2\sigma}{(e^{2aR}-1)}\right]^2. \tag{3.420}$$

The Schiöberg potential must satisfy:

(i) $\left.\frac{dV_{SCH}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{SCH}(\infty) - V_{SCH}(R_e) = D_e$, where D_e is the depth of the well;

(iii) $\left.\frac{d^2V_{SCH}}{dR^2}\right|_{R=R_e} = k_e;$

(iv) $V_{SCH} \to \infty$ at $R = 0$.

Wang *et al.* [81] observed that to satisfy the condition (i), we must have:

$$\sigma = \frac{e^{2aR_e}-1}{e^{2aR_e}+1}. \tag{3.421}$$

Now, by using the condition (ii), we obtain:

$$D(1-\sigma)^2 - D\left[1 - \sigma - \frac{2\sigma}{(e^{2aR_e}-1)}\right]^2 = D_e, \tag{3.422}$$

and using the relation (3.421), we can obtain a relation to parameter D given by:

$$D = \frac{D_e}{4}(e^{2aR_e}+1)^2. \tag{3.423}$$

Substituting the expressions (3.421) and (3.423) into the potential (3.420), we have a new expression to Schiöberg potential:

$$V_{SCH}(R) = D_e \left(1 - \frac{e^{2aR_e} - 1}{e^{2aR} - 1}\right)^2 . \tag{3.424}$$

where $2a = b$, being b a parameter in the Tietz-Hua potential(3.292).

Wang *et al.* [81] used this expression to compare the Schiöberg potential with the Manning-Rosen potential [79] and with the Deng-Fan potential [41], and they concluded that these three functions correspond to the same potential, actually.

The expressions for the vibrational rotational coupling parameter α_e and anharmonicity parameter $\omega_e x_e$, can be obtained from Dunham's relations (2.57) and (2.58):

$$\alpha_e = \left\{ \frac{8a^3 R_e^3}{\Delta} \left[\frac{e^{4aR_e}(e^{2aR_e} + 1)}{(e^{2aR_e} - 1)^3} \right] + 1 \right\} \frac{6B_e^2}{\omega_e} \tag{3.425}$$

and

$$\omega_e x_e = \left\{ \frac{120a^3 R_e^4}{\Delta^2} \left[\frac{e^{4aR_e}(e^{4aR_e} + 1)^2}{(e^{2aR_e} - 1)^3} \right] - \frac{16a^4 R_e^2}{\Delta} \left[\frac{e^{4aR_e}(7e^{4aR_e} + 22e^{2aR_e} + 7)}{(e^{2aR_e} - 1)^4} \right] \right\} \times W, \tag{3.426}$$

where $W = \frac{2.1078 \times 10^{-16}}{\mu}$, and B_e and ω_e have their usual meanings, and Δ is the Sutherland parameter.

Schiöberg [174] claimed that his potential was a better description for the potential energy of a molecular vibration than the Morse function, and he showed it for H_2 in its ground electronic state. In special, in the region of large R, the Schiöberg potential is closer to reality than the Morse potential for some diatomic molecules [175]. However, in 2012, Wang *et al.* [81] showed that the Schiöberg potential is not better than the traditional Morse potential in simulating the atomic interaction for diatomic molecules.

3.1.36 The Reduced function

In this moment of history, the problem of obtaining reliable diatomic potentials is considered solved, especially after the EHFACE potential described earlier (Section 3.1.34). However, in 1989, according to Tellinghuisen *et. al* [176], there was still a search for the "magic potential" which he called the *Holy Grail of Spectroscopy.*

The *Holy Grail of Spectroscopy* would be a universal analytical function that would describe the potential energy curve accurately and without prior knowledge of the potential. Some researchers claimed that this function must also satisfy the Lippincott criterion [15], which the average absolute deviation of less than 1% of D between experimental energies and those calculated by the function at the distances of the spectroscopic potentials, *i. e.*:

$$\sigma_{av} = 100 \sum (|V_{expt} - V_{calc}|)/(N_p D), \tag{3.427}$$

where N_p is the number of points on the spectroscopically derived potentials.

The Reduced Potential Curves (RPC) method would produce such a universal potential with ideal characteristics. The idea of the reduced state equation of gases in thermodynamics introduced by Puppi [177], in 1946, is analogous to the reduced potential. Frost and Musulin [114] were the pioneers to use this method (see Section 3.1.20), proposing, in 1954, the first Reduced Potential Curve:

$$V_{RPC_I}(\rho) = \frac{V(\rho)}{D_e} \qquad \text{with} \qquad \rho(R) = (R - R_{ij})/(R_e - R_{ij}) \tag{3.428}$$

with

$$R_{ij} = R_e - A \tag{3.429}$$

being $A = (KD_e/k_e)^{1/2}$.

Later, in 1963, Jenč and Plíva [178] observing the reduced Frost-Musulin model, they tested to obtain reduced potential curves from experimental potential curves calculated by the RKRV method. The RKRV method was proposed by Vanderslice and coauthors (see the references 7-16 in Ref. [178]) and was a modification of the Rydberg-Klein-Rees [9–11] analytical method, being applied to calculate the potential functions of a series of diatoms.

By analyzing the diatomic systems H_2, H_2^+, LiH, BeH^+, OH and OF in their ground electronic states, they concluded that the mean value K in Eq. (3.223) should be $K = 3.96$ instead $K = 4.00$ used by Frost and Musulin, yielding better coincidence of the reduced curves. In addition, the coincidence of the reduced curves for O_2, N_2, CO, and NO, all in their ground electronic states, were also analyzed, and for these a pronounced discrepancy using the Frost-Musulin potential was observed, even using $K = 3.96$. This suggested some modifications to FM potential.

They observed that, for $R = 0$, the value ρ is negative and assumes different values for different diatomic systems. Then, they proposed the reduced internuclear distance given by:

$$\rho = [R-(1-e^{-R/\rho_{ij}})\cdot\rho_{ij}]/[R_e-(1-e^{-R/\rho_{ij}})\cdot\rho_{ij}] = (\xi+e^{-\xi}-1)/(\xi_e+e^{-\xi_e}-1) \tag{3.430}$$

where ρ_{ij} was introduced instead R_{ij}, $\xi = R/\rho_{ij}$ and $\xi_e = R_e/\rho_{ij}$. This new definition for the parameter ρ satisfies the conditions:

(i) $\rho \geq 0$;

(ii) if $R \to 0$, then $\rho \to 0$;

(iii) if $R = R_e$, then $\rho = 1$.

The parameter ρ_{ij} is determined, assuming the universal value $K = 3.96$, as:

$$\rho_{ij} = (R_e - A)/(1 - e^{-R_e/\rho_{ij}}), \tag{3.431}$$

where A has been defined before.

For the modified Frost-Musulin potential the hydrides coincided remarkably, similarly, the curves of the other molecules also showed a close coincidence. However, the two groups of molecules do not quite coincide. Then, Jenč and Plíva concluded that Frost-Musulin curves exist for groups of closely related diatomic molecules, but not universally. They also compared the reduced RKRV potential for LiH, BeH^+, and HF with the Morse [8], Rydberg [9], Varshni I and VI [14] and Lippincott [43] potentials and concluded that the approximations afforded by the individual functions are different for different diatomic systems.

Then, in 1989, Tellinghuisen *et. al* [176] suggested that even where the reduced potentials presented poor agreement, their repulsive branches were often in good agreement, and this behavior could be until in approximating unknown potentials.

Tellinghuisen *et. al* to use a similar potential proposed by Frost and Musulin [114]:

$$V_{RPC_{II}} \equiv \frac{V(R)}{D_e} = x^2 \tag{3.432}$$

with

$$x \equiv (2\pi^2 c\mu/D_e\hbar)^{1/2}\omega_e(R - R_e). \tag{3.433}$$

They evaluated the behavior of their potential for 35 molecular states. The reduced potential curves for alkali-metal diatomic systems in their ground electronic states were represented practically by a unique curve, coinciding in the attractive region and slightly different in the repulsive region. For the ground electronic states of halogens, a good description of the repulsive and spectroscopic region was obtained, but not so good in the attractive branch. In turn, for the electronically excited states of halogens, the curves in the attractive region perform poorly in contrast with the repulsive branch.

Tellinghuisen *et. al* also obtained the reduced potential for homonuclear diatomic systems Cl_2, N_2, O_2, P_2, S_2, Se_2 and Te_2 in their ground electronic states, and in addition, for N_2(A) and ICl(X). The reduced potentials for all diatomic systems coincided quite well in both branches.

The same alkali-metal diatomic systems were analyzed by Tellinghuisen *et. al* [176] using the Jenč and Plíva [178] reduced potential (described above). For this group of the molecules, the Jenč and Plíva model showed considerably less agreement in the attractive branch than the Tellinghuisen *et. al* approach.

Thus, it is possible to observe that obtaining a universal function to represent "all diatomics" in a unique reduced potential curve is not a simple task.

3.1.37 The Aguado and Paniagua function

One of the simplest and generally successful methods of obtaining potential energy curves for diatomic systems directly from spectroscopic data is through the RKR methods [9–11], as already mentioned in previous sections, and used in the vast majority of cases as a parameter for comparing whether the potential is well fitted. However, the results obtained by the RKR method are presented in the form of tables containing, in general, the numbers ν, $G(\nu)$, B_ν, R_+ and R_-, not being very convenient for a rapid interpretation of the potential behavior.

Aiming at producing accurate and well-behaved potential energy curves in 1992, Aguado, Camacho, and Paniagua [179] (ACP) presented a simple functional form, similar to the perturbed-Morse-oscillator (PMO) potential, with better results mainly for the long-range region. ACP presented analytical potential energy curves for the CO and LiH systems, both in $X^1\Sigma^+$ electronic state, obtained by fitting the RKR values in the Chebyshev sense [179].

For a tabulated function $y_i = f(x_i)$ $(i = 1, 2, \cdots, n)$, where y_i are the observed $G(\nu) + Y_{00}$ and x_i are the turning points rotation-less potential curve, they suggested a approximated potential function $V_{ACP}(R)$ written as a linear combination of functions ϕ that will be conveniently chosen,

$$V_{ACP}(R) = \sum_{k=0}^{m} c_k \phi_k(x) \tag{3.434}$$

where $\phi_k(x)$ belongs to the basis of functions $\{\phi_k\}$, $k = 0, 1, \cdots, m$.

To calculate error vector Q, with components q_i given by $q_i = V(x_i) - y_i$, related RKR data, the method the maximum norm that uses the Chebyshev technique was chosen. Such a methodology was selected because of the interest in getting an error vector Q with a limited value point by point [179].

The chosen basis function was one that contains functions similar to PMO

$$\phi_k(x) = [1 - e^{\beta x}]^k, \quad k = 0, 1, \cdots, m. \tag{3.435}$$

where β is a nonlinear parameter independently set to obtain the best approximation and $x = R - R_e$, with R and R_e as already defined in this work.

The procedure proposed by ACP [179] to obtain the energies and consequently of the potential energy curves for the systems of interest, starts with the use of $V_{ACP}(R)$ (3.434) and the functions ϕ_k(3.435) in the radial equation of Schrödinger for $J = 0$:

$$\left(\frac{-\hbar}{4\pi\mu c} \frac{d^2}{dR^2} + V(R) \right) \psi_\nu = E_\nu \psi \nu \tag{3.436}$$

Its resolution is carried out through the diagonalization of the Hamiltonian matrix, in order to obtain the eigenvalues E_ν. For this is used as a basis the orthogonal functions of Hermite given by:

$$\chi_n(x) = e^{-\alpha x^2/2} H_n(\alpha^{1/2} x), \quad n = 0, 1, 2 \cdots \tag{3.437}$$

where H_n are the Hermite polynomials and $\alpha \approx 2\pi\nu_e\mu/\hbar$.

The Hamiltonian matrix obtained through of the integrals $V_{nm} =< \chi_n|e^{-\beta jx}|\chi_m >$, which can be calculated using the recurrence relation,

$$V_{nm} = -\frac{\beta j}{\alpha^{1/2}} V_{n-1m} + 2mV_{n-1m-1} \tag{3.438}$$

where the first column ($m = 0$), provides $V_{00} = \left(\frac{\pi}{\alpha}\right)^{1/2} e^{\beta^2 j^2/4\alpha}$.

ACP [179] showed that for the systems CO and LiH, both in the $X^1\Sigma^+$ electronic state, the optimal numbers of fundamental functions were 15 and 8 respectively. This already represents the first advantage of the method, because it is a finite and relatively small set of parameters facilitating further calculations.

In general, the ACP [179] method provided an optimum fit for the potential energy curves of the tested systems. It also presents an excellent degree of self-consistency for all evaluated parameters E_ν, B_ν and for the potential curves themselves CO and LiH, both in the state $X^1\Sigma^+$.

However, still in 1992, Aguado and Paniagua [180] (AP) proposed a functional form to obtain analytical potentials of triatomic molecules ABC, in which the full potential was written as an many-body-expansion (MBE) [56]:

$$\mathrm{V_{ABC}} = \sum_{\mathrm{A}} \mathrm{V_A}^{(1)} + \mathrm{V_{AB}}^{(2)}(\mathrm{R_{AB}}) + \mathrm{V_{ABC}}^{(3)}(\mathrm{R_{AB}}, \mathrm{R_{AC}}, \mathrm{R_{BC}}) \tag{3.439}$$

where $\mathrm{R_{AB}}$,$R_{AC}$and $\mathrm{R_{BC}}$ are the internuclear distances and the sums are over all the terms of a given type and where $\mathrm{V_A}^{(1)}$ is the energy of atom A in its appropriate electronic state; $\mathrm{V_{AB}}^{(2)}$ is the two-body energy that corresponds to the diatomic potential energy curve which vanishes asymptotically when $\mathrm{R_{AB}} \to \infty$ and goes to infinity when $\mathrm{R_{AB}} \to 0$; $\mathrm{V_{ABC}}^{(3)}$ is the three-body energy.

The diatomic terms $\mathrm{V_{AB}}^{(2)}$ of the potential (3.439) are expressed as a sum of two terms corresponding to the short- and long-range potentials, and will be called $\mathrm{V_{AP}}$ [180]:

$$\mathrm{V_{AP}}^{(2)}(\mathrm{R_{AB}}) = \mathrm{V_{short}}^{(2)} + \mathrm{V_{long}}^{(2)} \tag{3.440}$$

where

$$\mathrm{V_{short}}^{(2)} = \frac{\mathrm{c_0 e}^{-\alpha_{\mathrm{AB}}\mathrm{R_{AB}}}}{\mathrm{R_{AB}}} \tag{3.441}$$

and

$$\mathrm{V_{long}}^{(2)} = \sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{c_i} \rho^{\mathrm{i}}{}_{\mathrm{AB}} \tag{3.442}$$

where (3.441), with the restriction $\mathrm{c_0} > 0$, ensures that the diatomic potential goes to infinity when $\mathrm{R_{AB}} \to 0$. Aguado-Paniagua [181] showed that a modified form of the functions, introduced by Rydberg [9], in the polynomial variables ρ, given by (3.440)

$$\rho_{\mathrm{AB}} = \mathrm{R_{AB}} e^{-\beta_{\mathrm{AB}}{}^{(2)}\mathrm{R_{AB}}}, \quad \beta_{\mathrm{AB}}{}^{(2)} > 0. \tag{3.443}$$

The linear parameters $\mathrm{c_i}$, $\mathrm{i} = 0, 1, \cdots, \mathrm{N}$ and the nonlinear parameters α_{AB}, both in the Eq.(3.440) and β_{AB} (Eq. (3.443)) are determined by fitting the *ab initio* energies for the diatomic fragments computed at the same level of theory than the used in the triatomic system [180].

Although it is a proposition for a triatomic potential, the two-body term $\mathrm{V_{AP}(R_{AB})}$ in Eq. (3.440) was known as a new diatomic potential of Aguado-Paniagua, being very used today due to its high precision for several systems, in excited states including (see for example Ref. [182]).

In 2019, a recent work by Araujo *et. al* [23] has compared four potential energy functions: Rydberg [9], Hulburt-Hirschfelder [7], Murrell-Sorbie [60] and Aguado-Paniagua [181] to N_2, O_2 and SO diatomic systems in their ground electronic states. Based on PECs obtained by fit ab initio points, the spectroscopic parameters R_e, D_e, ω_e and $\omega_e x_e$ of the molecules have been computed. Although, in overall potential the Aguado-Paniagua function proved to be the most accurate for all diatomic analyzed, the same did not happen with the spectroscopic parameters. Surprisingly, the Rydberg potential, the oldest of the functions considered, showed less deviation in the calculation of the parameter R_e for N_2 and SO diatomic systems. In addition, the Rydberg function proved to be the second most accurate, behind AP, in relation to the overall potential of the SO. More details are presented in Chapter 5.

3.1.38 The Williams-Poulios function

Potential energy functions that are exact solutions to the Schrodinger equation are extremely desirable, as we have already seen throughout this article. Thinking about that,in 1993, Williams and Poulios [183] proposed a simple method for generating exactly solvable quantum mechanical potentials. This method was applied to Gegenbauer polynomials (see Ref. [184]) to generate the attractive radial Williams-Poulios (WP) potential, given by:

$$V_{WP}(R) = \frac{a^2}{4}\left[\frac{e^{-4\alpha R} + (A-8)e^{-2\alpha R} + (4-A)}{(1-e^{-2\alpha R})^2}\right] \tag{3.444}$$

where A is a real constant and $\alpha > \frac{1}{2}$ is given by:

$$\alpha = \frac{A - 2 - 4\nu^2}{8\nu + 4} \tag{3.445}$$

being ν the quantum number.

The energy for this solvable potential is obtained from:

$$E = \frac{a^2}{4}\left\{1 - 4\left[\frac{\nu^2 + \nu + (A-2)/4}{2\nu + 1}\right]^2\right\}. \tag{3.446}$$

Ovando *et. al* [185] observed that the standard potential V_{WP} was not a minimum. Then, they proposed to use the negative of the Williams-Poulios potential, given by:

$$V_{WP}^{-}(R) = \frac{b^2}{4}\left[Af(R) + 3f^2(R) + (A-4)\right] \tag{3.447}$$

where

$$f(R) = \frac{e^{-2\alpha R}}{1 - e^{-2\alpha R}}. \tag{3.448}$$

The potential (3.447) has a minimum provided that [185]:

$$-2D_e(e^{2\alpha R_e} - 1) = \frac{Ab^2}{4} \tag{3.449}$$

and

$$D_e(e^{2\alpha R_e} - 1)^2 = \frac{3b^2}{4} \tag{3.450}$$

leading to

$$D_e = \frac{b^2}{48}A^2 \tag{3.451}$$

and

$$f(R_e) = \frac{-A}{6}, \tag{3.452}$$

for which

$$R_e = \frac{1}{2\alpha}\ln 1 - \frac{6}{A}. \tag{3.453}$$

Ovando *et. al* obtained the relationships for parameters b and A, given by:

$$b = \frac{2\sqrt{3D_e}}{3f(R_e)} \tag{3.454}$$

and

$$A = -6f(R_e) \tag{3.455}$$

using the expression (3.448).

They also showed that the multiparameter exponential-type potentials by Manning-Rosen [79], Deng-Fan [41], Schiöberg [174], Tietz [120], Tietz-Hua [123], Modified Extended Rydberg [186] and the negative Williams-Poulos potential are equivalent. In this equivalence, the potential (3.447) can be rewrite as:

$$V_{WP}^{-}(R) = D_e\left(1 - \frac{e^{2\alpha R_e} - 1}{e^{2\alpha R} - 1}\right)^2. \tag{3.456}$$

Note that it is now easy to see that this potential meets the conditions:

(i) $\left.\frac{dV^{-}_{WP}}{dR}\right|_{R=R_e} = 0;$

(ii) $V^{-}_{WP}(\infty) - V^{-}_{WP}(R_e) = D_e.$

The vibrational rotational coupling parameter α_e and the anharmonicity $\omega_e x_e$ can be obtained from Dunham relations (2.57) and (2.58), and are equivalent to the potentials mentioned above. In Section 3.1.49 we will detail the multiparameter exponential-type potentials.

3.1.39 The Fayyazudin function

In 1995, Fayyazudin and Rafi [187] (FR) proposed an empirical potential function to describe the bound states of diatomic systems. The potential has four parameters, which can be related to spectroscopic parameters well known.

The potential is given by:

$$V_{FR}(R) = \frac{K}{R^n} + \lambda R e^{-aR} \tag{3.457}$$

where K, λ and a can be determined from D_e, k_e and R_e, and n is a free parameter greater than one.

This potential satisfies the desirable features, *i. e.*, $V_{FR} \to \infty$ at $R = 0$, and $V_{FR} \to 0$ at $R \to \infty$. In addition, this potential must satisfy:

(i) $\left.\frac{dV_{FR}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{FR}(\infty) - V_{FR}(R_e) = D_e$, *i. e.*, $V_{FR}(R_e) = -D_e$;

(iii) $\left.\frac{d^2V_{FR}}{dR^2}\right|_{R=R_e} = k_e = 4\pi^2 c^2 \mu \omega_e^2.$

From this conditions, Fayyazudin and Rafi obtained the relationships:

$$\lambda e^{-aR_e} = \frac{nK}{R_e^{n+1}(1 - aR_e)}, \tag{3.458}$$

$$K R_e^{-n} = -\frac{D_e(1 - aR_e)}{n + 1 - aR_e} \tag{3.459}$$

and

$$aR_e = \frac{(n^2 + 3n + 2\Delta) \pm \sqrt{(n^4 + 2n^3 + 5n^2) - 4\Delta n(n-1) + 4\Delta^2}}{2n} \tag{3.460}$$

where $\Delta = \frac{k_e R_e^2}{2D_e}$ is the Sutherland parameter. Only the negative sign in this equation is relevant.

The vibrational rotational coupling parameter α_e and the anharmonicity $\omega_e x_e$ were obtained from Dunham relations (2.57) and (2.58), but using the Varshni [14] method given by:

$$\alpha_e = \frac{6B_e^2}{\omega_e} F \tag{3.461}$$

and the anharmonicity $\omega_e x_e$, is given by:

$$\omega_e x_e = \frac{1}{8} B_e G \tag{3.462}$$

where

$$F = -\left[\frac{1}{3} X R_e + 1\right] \tag{3.463}$$

and

$$G = \frac{5}{3}\left(X R_e\right)^2 - Y R_e^2 \tag{3.464}$$

Here,

$$X = \frac{f_3}{f_2} \tag{3.465}$$

and

$$Y = \frac{f_4}{f_2} \tag{3.466}$$

being $f_2 = \left(\frac{d^2 V}{d_R^2}\right)_{R=R_e}$, $f_3 = \left(\frac{d^3 V}{d_R^3}\right)_{R=R_e}$ and $f_4 = \left(\frac{d^4 V}{d_R^4}\right)_{R=R_e}$. We can write X and Y in terms of $\omega_e x_e$ and α_e:

$$X = \frac{-3}{R_e}\left[\frac{\omega_e \alpha_e}{2B_e} + 1\right] \tag{3.467}$$

and

$$Y = \frac{5}{3} X^2 - \frac{8\omega_e x_e}{B_e R_e^2}. \tag{3.468}$$

The expressions to $R_e X$ and $R_e^2 Y$ obtained for the potential (3.457) can be seen in Ref, [187].

To evaluate the accuracy of their potential, Fayyazudin and Rafi calculated the values of α_e and $\omega_e x_e$ for eight diatomic systems in different electronic states: H_2 ($X^1\Sigma_g^+$), I_2 ($X^1\Sigma_g^+$), HF ($X^1\Sigma^+$), N_2 ($X^1\Sigma_g^+$), N_2 ($A^3\Sigma_u^+$) N_2 ($a^1\Pi_g$), N_2 ($B^3\Pi_g$), O_2 ($X^3\Sigma_g^-$), O_2 ($B^3\Sigma_u^-$), O_2 ($A^3\Sigma_u^+$), OH ($X^2\Pi_i$), OH ($A^2\Sigma^+$), NO ($X^2\Pi$), NO ($B^2\Pi$), CO ($X^1\Sigma^+$), CO ($a^3\Delta$), CO ($a'^3\Sigma^+$), CO ($A^1\Pi$) and CO ($e^3\Sigma^-$). Then, they compared their results with other potentials already treated here: Morse [8], Rosen-Morse [29], Rydberg [9], Pöschl-Teller [30], Linnett [61], Frost-Musulin [74], Varshni [14] III and Lippincott [43]. The average error for both spectroscopic parameters using the FR potential was less than for all other potentials.

In addition, they analyzed the deviation of their potential from the RKR curve to

H_2 ($X^1\Sigma_g^+$) diatomic system, and then, they compared with the same potentials. The FR potential provides good accuracy, being inferior only to the potentials of Hulburt-Hirschfelder, Rydberg, and Pöschl-Teller.

Then, in 1996, Fayyzudin *et. al* [188] extended the FR potential to five-parameters (FAY_I) given by:

$$V_{FAY_I}(R) = e^{-t\xi}\left[\frac{K}{\xi} - a - b\xi - c\xi^2\right] \tag{3.469}$$

where $\xi = R/R_e$, K, a, b, c ans t are parameters which can be obtained from known spectroscopic parameters.

They also considered the three-parameters potential function (FAY_{II}), doing $a = c = 0$ in Eq. (3.469):

$$V_{FAY_{II}}(R) = e^{-t\xi}\left[\frac{K}{\xi} - b\xi\right] \tag{3.470}$$

These potentials must satisfy the equations (i), (ii) and (iii) above, so that their parameters can be obtained. Fayyzudin *et. al* [188] showed that for V_{FAY_I} the parameters K, a, b and c can be expressed in terms of parameter t determined from polynomial:

$$t^4 + 4t^3 - 12\Delta t^2 + 24\Delta t - 6\Delta\left[(1+F)(5F+1) - \frac{G}{3}\right] = 0 \tag{3.471}$$

where F and G are defined in Eqs.(3.463) and (3.464). Only the root real positive is considered.

For $V_{FAY_{II}}$, the parameters can be obtained, using the relationships (i)-(iii), and are given by:

$$Ke^{-t} = \frac{D_e(t-1)}{2}, \tag{3.472}$$

$$be^{-t} = \frac{D_e(t+1)}{2} \tag{3.473}$$

and

$$t^2 + t - (1 + 2\Delta) = 0, \tag{3.474}$$

choosing the positive root again.

To evaluate the accuracy of their potentials V_{FAY_I} and $V_{FAY_{II}}$, seven diatomic systems in different electronic states were chosen (practically the same used by Fayyazudin and Rafi described above, see Ref. [188]) and compared with the Morse [8], Rosen-Morse [29], Rydberg [9], Pöschl-Teller [30], Linnett [61], Hulburt-Hirschfelder [7], Frost-Musulin [74], Varshni [14] III and Lippincott [43] potentials. They used the deviations from the RKR curve to check the behavior of the potentials, using Lippincott's criterion [15].

The five-parameters V_{FAY_I} was most accurate than all the others, except for the Hulburt-Hirschfelder potential which the average error was almost equal. The three-parameters $V_{FAY_{II}}$ perform slightly worse, but still showed more accuracy than Morse, Rosen-MOrse, Pöschl-Teller, Linnett, and Frost-Musullin.

In 2006, Lim [189] showed that the parameters of the Fayyazudin potential $V_{FAY_{II}}$ can be related to the parameters of the Extended-Rydberg potential proposed by Murrell and Sorbie [60]. From conversion matrices that convert the former's parameters into the latter and vice versa, they obtained a list of 71 sets of Fayyazuddin diatomic parameters applying one of the conversion matrices on the Huxley–Murrell [131] data. Potential energy curves of the OSi, FO, BeS, and HH diatomic parameters exhibit very good agreement between the two potential functions considered, confirming the conversion matrices validity. Based on the Huxley–Murrell parameters, the Fayyazuddin parameters were calculated for a total of 71 combinations of diatomic systems (see table 1 in Ref. [189]).

3.1.40 The Modified Extended Rydberg function

In 1997, Sun [190] by analyzing the Extended Rydberg potential [60], observed that it is still necessary to obtain a better theoretical method to easy calculate vibrational potential for stable diatomic systems, and for this, he suggested a Modified Extended Rydberg potential (MER) as a alternative to calculate potential energy curves:

$$V_{MER}(R) = -D_e\beta\left(\beta^{-1} + \sum_{n=1}^{m} a_n(R-R_e)^n\right)e^{-\beta a_1(R-R_e)} \qquad (3.475)$$

where β is an adjustable width parameter, and the potential width can be changed by varying the value of β.

The coefficients a_n can be obtained using the same equations (3.312) and (3.313) proposed by Murrell and Sorbie [60], and derived from:

$$Da_1^n - \sum_{k=2}^{n}\frac{1}{2}\frac{n!}{(n-k)!}a_1^{n-k}F_k = 0, \qquad (3.476)$$

and

$$a_n = -\frac{F_n}{2D} + (-1)^n\frac{(n-1)}{n!}a_1^n + \sum_{k=2}^{n-1}(-1)^{n-k+1}\frac{a_1^{n-k}a_k}{(n-k)!} \qquad (n \geq 2). \qquad (3.477)$$

The general expression for coefficients F_k can be obtained as:

$$F_n = (-1)^n\frac{2(n-1)}{n!}F_2^{n/2}D^{-\left(\frac{n}{2}-1\right)} \qquad (n \geq 3). \qquad (3.478)$$

Here D is a quantity related with D_e:

$$D = \beta D_e. \qquad (3.479)$$

Sun [190] considered the series to be truncated at fifth power and obtained the potential energy curve for N_2 and ClF in their ground electronic states. He compared his results with the Morse [8] potential and the main difference for N_2 occurred in the asymptotic region, precisely where the Morse potential fails.

In 2006, Royappa [42] showed that on average the Modified Extended Rydberg potential by Sun [190] provides the best accuracy among all 21 potential energy functions analyzed, including the Murrell-Sorbie potential [60].

Although the MER potential has better qualities than MS potential, it did not show satisfactory results in molecular asymptotic region for diatomic molecular electronic excited states. Then, in 1999, Sun and Feng [186] tried to find a physically better potential. For this, they proposed an energy-consistent method (ECM) which uses a new analytical potential to calculate numerical vibrational potentials. They built a new analytical potential by adding a potential correction $\Lambda(R)\delta V(R)$ to the Extended Rydberg potential (3.316):

$$V_{SF}(R) = V_{ER}(R) + \Lambda(R)\delta V(R) \tag{3.480}$$

where the potential correction $\Lambda(R)\delta V(R)$ remedies the $V_{ER}(R)$ potential such that the new potential V_{SF} behaves well enough not only in the equilibrium internuclear distance region, but also in the molecular asymptotic region. For $\delta V(R)$, they suggested:

$$\delta V(R) = V_{ER}(R) - V_{MOR}(R) \tag{3.481}$$

where $V_{MOR}(R) = D_e[e^{-2a(R-R_e)} - 2e^{-a(R-R_e)}]$ is the Morse [8] potential.

$\Lambda(R)$ is Eq. (3.480) is a force-field function and was chosen as:

$$\Lambda(R) = \lambda\frac{(R-R_e)}{R}[1 - e^{-\lambda^2(R-R_e)/R_e}]. \tag{3.482}$$

where λ is an adjustable parameter. This function should play two roles:

(i) It scales the potential changes $\delta V(R)$ in Eq. (3.481) properly to ensure the potential correction $\Lambda(R)\delta V(R)$ behaves correctly;

(ii) It ensures that the new potential satisfies the physical property that its nth-order derivative equals the nth force constant, f_n, at equilibrium.

Thus, the new potential proposed by Sun and Feng [186] is given by:

$$V_{SF} = [\Lambda + 1]V_{ER}(R) - \Lambda V_{MOR}(R) \tag{3.483}$$

which is physically well defined potential.

The numerical values of this new potential agree much better with the known exact diatomic potential than other analytical empirical functions, in particular for electronically excited states of diatomic systems as H_2 and O_2. Therefore, for Sun and Feng [186] the ECM generates much more accurate theoretical vibrational eigenvalues and eigenfunctions for the corresponding stable molecular states than other analytical potentials.

In 2006, Royappa [42] showed that on average the Modified Extended Rydberg potential by Sun [190] provides the best accuracy among all 21 potential energy functions analyzed, including the Extended Rydberg potential [60].Then, although the potential has eight parameters,

3.1.41 The Rafi function

In 2000, Rafi *et. al* [191] (RAF_I) proposed a four-parameter potential energy function to describe stable diatomic systems. This function is a modification of the Morse [8] potential, and is given by:

$$V_{RAF_I}(R) = D_e[1 - e^{-a(R-R_e)}]^2[1 + c anh(R - R_e)] \tag{3.484}$$

or

$$V_{RAF_I}(R) = D_e[1 - e^{-a(R-R_e)}]^2 \left[1 + c\frac{e^{a(R-R_e)} - e^{-a(R-R_e)}}{e^{a(R-R_e)} + e^{-a(R-R_e)}}\right] \tag{3.485}$$

where a is the Morse parameter given by $a = \sqrt{\frac{k_e}{2D_e}}$ and c can be determined from known spectroscopic parameters.

This potential satisfies the conditions:

(i) $\left.\frac{dV_{RAF_I}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{RAF_I}(\infty) - V_{RAF_I}(R_e) = D_e;$

(iii) $\left.\frac{d^2V_{RAF_I}}{dR^2}\right|_{R=R_e} = k_e = 4\pi^2c^2\mu\omega_e^2.$

(iV) $\left.\frac{d^3V_{RAF_I}}{d\xi^3}\right|_{R=R_e} = Xk_e$, where X is the cubic force constant.

(v) $\left.\frac{d^4V_{RAF_I}}{d\xi^4}\right|_{R=R_e} = Yk_e$, where Y is the cubic force constant.

Here, X and Y are the relationships defined by Varshni [14] given in Eqs. (3.465) and (3.466). See Eqs. (3.467) and (3.468) to remember how these parameters are related with $\omega_e x_e$ and α_e.

In 2005, Birajdar *et. al* [192] derived the vibrational rotational coupling parameter α_e from Dunham relation (2.57):

$$\alpha_e = -\left[\frac{-3R_e(a-c)}{3} + 1\right]\frac{6B_e^2}{\omega_e} \tag{3.486}$$

where they obtained the relationship for parameter c:

$$c = \left[\Delta^{1/2} - 1 - \left(\frac{\alpha_e\omega_e}{6B_e^2}\right)\right]\frac{1}{R_e} \tag{3.487}$$

where $\Delta^{1/2} = aR_e$ is the Sutherland parameter.

Using this expression for c, the anharmonicity $\omega_e x_e$, is given by:

$$\omega_e x_e = [8\Delta - 18\Delta^{1/2} + 15(cR_e)^2]\frac{2.1078\times 10^{-16}}{R_e^2\mu}. \tag{3.488}$$

Birajdar *et. al* [192] obtained the potential curves for I_2 and CO diatomic systems in their ground electronic states using the Rafi potential V_{RAF_I}, with the c parameter given by Eq. (3.487) and their results presented large deviations from the experimental RKR curves.

Then, in 2007, Rafi *et. al* [193] (RAF_{II}) proposed a new four-parameter empirical potential function to describe diatomic systems, given by:

$$V_{RAF_{II}}(R) = D_e[e^{-2a(R-R_e)}f(x) - 2e^{-a(R-R_e)}] \tag{3.489}$$

where

$$f(x) = \frac{1}{2}\{anh[b(R-R_e)] + e^{-b(R-R_e)} + \text{sech}\ [b(R-R_e)]\}. \tag{3.490}$$

The potential (3.489) can be rewrite as:

$$\begin{aligned} V_{RAF_{II}}(R) = D_e \Big[1 &- 2e^{-a(R-R_e)} + \tfrac{1}{2}e^{-a2(R-R_e)} \\ &\times \left(\tfrac{e^{b(R-R_e)} - e^{-b(R-R_e)}}{e^{b(R-R_e)} + e^{-b(R-R_e)}} + e^{-b(R-R_e)} + \tfrac{2}{e^{b(R-R_e)} + e^{-b(R-R_e)}}\right)\Big] \end{aligned} \tag{3.491}$$

being $b = \beta a$, where a is the Morse parameter $a = \sqrt{\frac{k_e}{2D_e}}$, and β can be obtained since the potential $V_{RAF_{II}}$ satisfies the conditions (i)-(iv) above. In this case, *beta* is given by:

$$XR_e = -3\Delta^{1/2}\left[1 + \frac{1}{4}\beta^3\right] \tag{3.492}$$

where XR_e is $XR_e = -3\left[\frac{\omega_e\alpha_e}{6B_e^2} + 1\right]$, with ω_e, α_e and B_e with their usual meanings.

To evaluate the accuracy of the potential $V_{RAF_{II}}$, Rafi *et. al* [193] using the Lippincott criterion [15], compared their results with RKR experimental data, for 15 diatomic systems: H_2, LiH, NaH, KH, CsH, K_2, Na_2, Rb_2, CO, ICl, XeO, I_2, Cs_2 and RbH, in their ground electronic states and for ($A^3\Pi$) state of ICl.

In addition, they compared their result with the Morse [8] potential, Fayyazudin-Rafi [188] potential and with the first proposal of the Rafi [191]. The average error of the potential $V_{RAF_{II}}$ was only 1.86% of D, whereas, Morse was 5.01% of D, Fayyazudin-Rafi was 3.30% of D and V_{RAF_I} was 4.06% of D.

3.1.42 The Noorizadeh-Pourshams function

In 2004, Noorizadeh and Pourshams [125] (NP) presented a new empirical potential energy function with four variational parameters. The purpose was to propose a mathematically simple and comprehensive potential, which can be applied to different diatomic systems in fundamental and excited states.

The potential is given by:

$$V_{NP}(R) = \frac{aR^b + m}{1 - e^{nR}} \tag{3.493}$$

where a, b, m and n are adjustable parameters.

This potential satisfies the basics conditions, *i. e.*, $V_{NP} \to \infty$ at $R = 0$, and $V_{NP} \to 0$ at $R \to \infty$. In addition, this potential must satisfy:

(i) $\left.\frac{dV_{NP}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{NP}(\infty) - V_{NP}(R_e) = D_e;$

(iii) $\left.\frac{d^2V_{NP}}{dR^2}\right|_{R=R_e} = k_e = 4\pi^2c^2\mu\omega_e^2.$

To evaluate the accuracy of the potential (3.493), Noorizadeh and Pourshams calculated the spectroscopic parameters R_e, D_e, B_e, k_e, ω_e, $\omega_e x_e$ and α_e for eight diatomic states in different electronic states, and then, they compared their results with experimental data. The diatomic systems chosen were: H_2 ($X^1\Sigma_g^+$), I_2 ($X^1\Sigma_g^+$), HF ($X^1\Sigma^+$), N_2 ($X^1\Sigma_g^+$), N_2 ($A^3\Sigma_u^+$) N_2 ($a^1\Pi_g$), N_2 ($B^3\Pi_g$), O_2 ($X^3\Sigma_g^-$), O_2 ($B^3\Sigma_u^-$), O_2 ($A^3\Sigma_u^+$), OH ($X^2\Pi_i$), OH ($A^2\Sigma^+$), NO ($X^2\Pi$), NO ($B^2\Pi$), CO ($X^1\Sigma^+$), CO ($a^3\Delta$), CO ($a'^3\Sigma^+$) and CO ($e^3\Sigma^-$). The average error for the calculated quantities were: R_e (0.43), D_e (1.87), B_e (0.82), k_e (3.68), ω_e (2.08), $\omega_e x_e$ (9.42) and α_e (10.78), showing good accuracy of the potential.

In addition, Noorizadeh and Pourshams [125] obtained the expressions for the vibrational rotational coupling parameter α_e and anharmonicity parameter $\omega_e x_e$, can be obtained from Dunham's relations (2.57) and (2.58). They compared their results with nine potential energy functions already presented above: Morse [8], Rosen-Morse [29], Rydberg [9], Pöschl-Teller [30], Linnett [61], Frost-Musulin [74], Varshini [14] III, Lippincott [109] and Fayyazudin [188]. The NP potential provided the most accurate result for $\omega_e x_e$, and for α_e only the Fayyazudin potential showed better accuracy than the NP potential.

The general behavior of the DN potential was also satisfactory for other diatomic systems. In the comparative study by Royappa *et. al* [42], previously described, they showed that the Noorizadeh-Pourshams potential in average, provide best accuracy than the potentials: Kratzer [16], Morse [8], Rosen-Morse [29], Rydberg [9], Pöschl-Teller [30], Linnett [61], Frost-Musulin [74], Varshini [14] III, Lippincott [43] Deng-Fan [41], Pseudogaussian [152], Levine [124], Tietz [122] II and Fayyazudin [188].

3.1.43 The Extended Lennard-Jones function

In 2000, considering the Lennard-Jones (2n,n) potential, Hajigeorgiou and Le Roy [194] proposed a modified version of the function which is given by:

$$V_{LJ}(R) = D_e \left[1 - \left(\frac{R_e}{R}\right)^n\right]^2. \tag{3.494}$$

Hajigeorgiou and Le Roy observed that although this function was considered to be a correct model to describe diatomic systems, there was not the flexibility required to represent accurately extensive experimental information. However, this function with the appropriate choice of the power n it has the correct theoretically predicted limiting long-range functional behavior.

The Modified Lennard-Jones (MLJ) proposed has the generalized form:

$$V_{MLJ}(R) = D_e \left[1 - \left(\frac{R_e}{R}\right)^n \phi(R)\right]^2. \tag{3.495}$$

where $\phi(R)$ is a empirical function given by:

$$\phi(R) = e^{-\beta_{MLJ}(z)z} \tag{3.496}$$

being $z = \frac{(R-R_e)}{(R+R_e)}$ one-half of the Ogilvie-Tipping expansion parameter [141].

This function has the form at $R \to \infty$ [194]:

$$V_{MLJ}(R) = D_e - 2D_e e^{\beta_\infty} \left(\frac{R_e}{R}\right)^n = D_e - \frac{C_n}{R^n}, \tag{3.497}$$

where $\beta_\infty \equiv \lim_{R\to\infty} \beta_{MLJ}(z)$, and

$$C_n = 2D_e(R_e)^n e^{-\beta_\infty} \tag{3.498}$$

or

$$\beta_\infty = \ln [2D_e(R_e)^n/C_n. \tag{3.499}$$

The function $\beta_{MJL}(z)$ is expressed as a power series in z, given by:

$$\beta_{MJL}(z) = \sum_{m=0}^{M} \beta_m z^m \tag{3.500}$$

so that

$$\beta_\infty = \lim_{z\to 1}(z) = \sum_{m=0}^{M} \beta_m, \tag{3.501}$$

with the last term expressed by:

$$\beta_M = \ln [2D_e(R_e)^n/C_n] - \sum_{m=0}^{M-1} \beta_m. \tag{3.502}$$

Although this modified version of the Lennard-Jones potential is quite accurate, the function $\phi(R)$ is complicated to obtain.

Then, in 2010, Hajigeorgiou [195] proposed an Extended Lennard-Jones (ELJ) given by:

$$V_{ELJ}(R) = D_e \left[1 - \left(\frac{R_e}{R}\right)^{n(R)}\right]^2, \tag{3.503}$$

where the function $n(R)$ is the simplest function:

$$n(R) = \beta_0 + \beta_1\zeta + \beta_2\zeta^2 + \beta_3\zeta^3 \tag{3.504}$$

being

$$\zeta = \frac{R - R_e}{z^q R + R_e} \tag{3.505}$$

with $z = (R - R_e)/(R + R_e)$ and q a even integer.

Note that the function $n(R)$ is well-behaved in the limit $R \to \infty$, because in this case $\zeta \to +1$.

The potential (3.503) satisfies:

(i) $V_{ELJ}(R)\Big|_{R=R_e} = 0;$

(ii) $V_{ELJ}(\infty) - V_{MRM}(R_e) = D_e.$

Hajigeorgiou [195] concluded that for $R < R_e$ the best results were obtained with $q = 6$, and for $R > R_e$, with $q = 4$. To determine the coefficients β_i, $i = 1, 2, 3$ in

Eq. (3.504), he related them with the Dunham coefficients [24], obtaining:

$$\beta_0 = \sqrt{\frac{a_0}{D_e}}, \tag{3.506}$$

$$\beta_1 = \frac{a_0 a_1}{2\beta_0 D_e} + \frac{\beta_0}{2} + \frac{\beta_0^2}{2}, \tag{3.507}$$

$$\beta_2 = \frac{a_0 a_2}{2\beta_0 D_e} - \frac{f_2}{24\beta_0}, \tag{3.508}$$

where

$$f_2 = 7\beta_0^4 - 36\beta_1\beta_0^2 + 18\beta_0^3 + 12\beta_1^2 - 24\beta_0\beta_1 + 11\beta_0^2, \tag{3.509}$$

and

$$\beta_3 = \frac{a_0 a_3}{2\beta_0 D_e} + \frac{f_3}{24\beta_0}, \tag{3.510}$$

where

$$f_3 = -28\beta_1\beta_0^3 + 14\beta_0^4 - 54\beta_1\beta_0^2 + 36\beta_2\beta_0^2 + 21\beta_0^3 + 12\beta_1^2 - 24\beta_1\beta_2 - 22\beta_0\beta_1 + 24\beta_0\beta_2 + 10\beta_0^2 + 36\beta_0\beta_1^2 + 3\beta_0^5. \tag{3.511}$$

Hajigeorgiou [195] tested his potential V_{ELJ} for sixteen diatomic systems in their ground electronic states: AgH, Cl_2, CO, Cs_2, DF, HCl, HF, KLi, Li_2, LiH, MgH, Na_2, NaH, NaK, O_2 and RbCs. To evaluate the accuracy of these results he used the Lippincott criterion [15] given by Eq. (3.427), where the experimental data were obtained from the RKR method. Besides, Hajigeorgiou compared the ELJ potential with the Hulburt-Hirschfelder [7] and Murrell-Sorbie [60] potentials and the average deviation of the V_{ELJ} was about four times less than the of ER and five times less than that of HH.

The potential V_{ELJ} was analyzed ignoring the cubic term in $n(R)$, but it presented an inferior result.

3.1.44 The Modified Rosen-Morse function

In 2012, Zhang *et. al* [196], proposed a modification for the Rosen-Morse potential [29]. Inspired by the reduced potential curves suggested by Frost and Musulin [114] (see sections 3.1.20 and 3.1.36) they considered the effect of inner-shell radii R_{ij} of two atoms for diatomic molecules given by:

$$R_{ij} = R_e - \sqrt{\frac{KD_e}{k_e}} \tag{3.512}$$

where K is defined by Eq. (3.223).

By introducing the parameter R_{ij}, the Modified Rosen-Morse (MRM) potential is given by [29]:

$$V_{MRM}(R) = D_e \left(1 - \frac{e^{\frac{2(R_e - R_{ij})}{d}} + 1}{e^{\frac{2(R - R_{ij})}{d}} + 1}\right)^2. \quad (3.513)$$

This potential satisfies the three basics conditions:

(i) $\left.\frac{dV_{MRM}}{dR}\right|_{R=R_e} = 0$;

(ii) $V_{MRM}(\infty) - V_{MRM}(R_e) = D_e$;

(iii) $\left.\frac{d^2V_{MRM}}{dR^2}\right|_{R=R_e} = k_e = \mu\omega_e^2$,

where R_e, D_e have their usual meanings, and k_e is approximated with a slight correction being omitted [24].

Using the (iii) condition, Zhang *et. al* [196] obtained the value of the d parameter:

$$d = 2\left[\sqrt{\frac{k_e}{2D_e}} + \frac{1}{R_e - R_{ij}} W\left((R_e - R_{ij})\sqrt{\frac{k_e}{2D_e}} e^{-(R_e - R_{ij})\sqrt{\frac{k_e}{2D_e}}}\right)\right]^{-1}, \quad (3.514)$$

where W is the Lambert W function, which satisfies $z = W(z)e^{W(z)}$ (see mathematical details of this function on p.331 in Ref. [197]).

Zhang *et. al* also obtained expressions for the Morse [8] parameter a and for the original Rosen-Morse [29] parameter d. Then, they compared their Modified Rosen-Morse potential with the Morse and Rosen-Morse potentials for six diatomic systems: ICl (A'$^3\Pi_2$) , I_2 (XO_g^+), Cs_2 ($X^1\Sigma_g^+$), MgH ($X^2\Sigma^+$), $^6Li_2$ ($X^1\Sigma_g^+$) and $^7Li_2$ ($X^1\Sigma_g^+$).

To evaluate the accuracy of these functions, Zhang *et. al* used the experimental RKR [9–11] data, and obtained the average deviation from Lippincott criterion [15] given by Eq. (3.427). The Modified Rosen-Morse provided to be more accurate for the six systems analyzed, with an average error between the evaluated systems of only 2.94% of D, while the Morse potential is given an average error of 8.68% of D and the standard Rosen-Morse of 6.90% of D.

In 2014, Tang *et. al* [198] presented a study about the vibrational energy levels calculated using the Modified Rosen-Morse potential for $^7Li_2$ ($6^1\Pi_u$) and SiC ($X^3\Pi$), and both were in good agreement with the experimental RKR data. For these diatomic systems, Tang *et. al* also compared the Modified Rosen-Morse potential with the Morse [8], Frost-Musulin [114], Varshni [14] III and Lippicott [199] potentials. For $^7Li_2$ ($6^1\Pi_u$), the Modified Rosen-Morse potential is the most accurate, and for SiC ($X^3\Pi$) this potential is superior to the Morse, Frost-Musulin, and Lippincott potentials.

3.1.45 The Uddin function

Still in 2012, Uddin *et. al* [200] (UDD) proposed a five-parameter potential energy to describe stable diatomic systems. This potential is given by:

$$V_{UDD}(\xi) = \frac{K}{\xi^3} - e^{-t\xi}(a + b\xi + c\xi^2) \tag{3.515}$$

where $\xi(R) = \frac{R}{R_e}$, K, t, a, b and c are parameters which can be obtained by spectroscopic parameters D_e, R_e, k_e,$\omega_e x_e$, α_e and B_e, all previously defined throughout the text.

The first term of the potential corresponds to repulsive energy and the second term is analogous to the Extended-Rydberg potential proposed by Murrell and Sorbie [60], but with a coefficient of cubic term equal to zero.

To determine the five parameters, Uddin *et. al* claimed that the potential (3.515) must satisfy two extra conditions, in addition to the usual ones. They are:

(i) $V_{UDD}(\xi)\Big|_{\xi=1} = -D_e$;

(ii) $V_{UDD}(\xi)$ has a minimum at $R = R_e$, *i. e.*, $\frac{dV_{UDD}}{d\xi}\Big|_{\xi=1} = 0$;

(iii) $\frac{d^2V_{UDD}}{d\xi^2}\Big|_{\xi=1} = k_eR_e^2$;

(iV) $\frac{d^3V_{UDD}}{d\xi^3}\Big|_{\xi=1} = k_eR_e^3X$, where $XR_e = -3\left(\frac{\omega_e\alpha_e}{6B_e^2} + 1\right)$ is a anharmonic force constant;

(V) $\frac{d^4V_{UDD}}{d\xi^4}\Big|_{\xi=1} = k_eR_e^4Y$, where $YR_e^2 = \frac{5}{3}X^2R_e^2 - 8\frac{\omega_e x_e}{B_e}$ is a anharmonic force constant.

Here, X and Y are the relationships defined by Varshni [14] given in Eqs. (3.465) and (3.466).

These conditions applied to the potential (3.515) yields a six order polynomial [200]:

$$t^6 - 3t^5\left(4 + \frac{2\Delta}{3}\right) + 3t^4\left(\frac{-2\Delta XR_e^2}{3} + 4\Delta + 20\right) + t^3\left(16\Delta XR_e - \frac{2\Delta YR_e^2}{3} - 120\right)$$
$$+6\Delta^2(-8XR_e + YR_e^2 - 40) + 24\Delta(-YR_e^2 + 30) + 40\Delta(6XR_e + YR_e^2) = 0 \tag{3.516}$$

where Δ is the Sutherland parameter. This polynomial has six roots. They analyzed the behaviour of the potential V_{UDD} for 14 different states of the seven diatomic systems, and only one of the six roots was workable for all states.

Uddin *et. al* [200] suggested rewrite the potential (3.515) in the form:

$$V_{UDD}(\xi) = D_e \left[\left(1 + \frac{K/D_e}{\xi^3} \right) - \left(\frac{1 + K/D_e}{a+b+c} \right) e^{-t(\xi-1)}(a + b\xi + c\xi^2) \right], \tag{3.517}$$

where the depth of the well D_e was included, so that $V_{UDD}(R = R_e) = 0$ and $V_{UDD}(\infty) \to D_e$.

Uddin *et. al* analyzed the diatomic systems: H_2 ($X^1\Sigma_g^+$), N_2 ($X^1\Sigma_g^+$), N_2 ($a^1\Pi_g$), N_2 ($B^3\Pi_g$), O_2 ($X^3\Sigma_g^-$), OH ($X^2\Pi_i$), OH ($A^2\Sigma^+$), HF ($X^1\Sigma^+$), NO ($X^2\Pi_{1/2}$), NO ($B^2\Pi$), CO ($X^1\Sigma^+$), CO ($A^1\Pi$), CO ($e^3\Sigma^-$) and CO ($a'^3\Sigma^+$), and compared them with experimental RKR [9–11] curves. With the exception of the OH $A^2\Sigma^+$ state of OH and $A^1\Pi$ state of CO, the potential provide excellent agreement with the RKR curves.

3.1.46 The New Deformed Schiöberg-type function

In 2015, Mustafa [201] proposed a new deformed Schiöberg-type [174] (NDS) potential given by:

$$V_{NDS}(R) = A(B + anh_q(\alpha R))^2, \tag{3.518}$$

where $A > 0$, B, q and α are four adjustable parameters and the q deformation of the usual functions is defined by relationships:

$$\begin{aligned} anh_q(x) &= \tfrac{\mathrm{senh}_q(x)}{\cosh_q(x)}; \quad \mathrm{senh}_q(x) = \tfrac{e^x - qe^{-x}}{2} \\ \cosh_q(x) &= \tfrac{e^x + qe^{-x}}{2}. \end{aligned} \tag{3.519}$$

The potential (3.518) must satisfy:

(i) $\left. \frac{dV_{NDS}}{dR} \right|_{R=R_e} = 0;$

(ii) $V_{NDS}(\infty) - V_{NDS}(R_e) = D_e;$

(iii) $\left. \frac{d^2V_{NDS}}{dR^2} \right|_{R=R_e} = k_e = 4\pi^2c^2\mu\omega_e^2,$

where R_e, D_e and k_e have their usual meanings. Mustafa added the additional condition, $V_{NDS}(R_e) = 0$, which simply shift the zero of potential, without physically affecting its properties.

Using these conditions, the parameters A, B and q can be obtained by:

$$A = \frac{D_e}{4q^2}(e^{2\alpha R_e} + q)^2, \tag{3.520}$$

$$B = -\left(\frac{e^{2\alpha R_e} - q}{e^{2\alpha R_e} + q}\right), \tag{3.521}$$

and

$$q = -\left(1 - \frac{2\alpha}{\sqrt{\frac{k_e}{2D_e}}}\right) e^{2\alpha R_e}. \tag{3.522}$$

Mustafa [201] also showed that his New Deformed Schiöberg-type is equivalent to the Tietz-Hua [123] potential, considering the correspondences: $\left(1 - \frac{2\alpha}{\sqrt{\frac{k_e}{2D_e}}}\right) = c$ and $2\alpha = b$ in Eq. (3.292). Thus, the expressions to α_e and $\omega_e x_e$ can be obtained in the same way.

He obtained a closed-form analytical solution for the ro-vibrational energy levels using the supersymmetric quantization. The ro-vibrational energy values obtained for NO ($X^1\Pi_r$), O_2 ($X^3\Sigma_g^-$), O_2^+ ($X^2\Pi_g$) and the vibrational values obtained for N_2 ($X^1\Sigma_g^+$) presented high accuracy.

3.1.47 The Improved Pöschl-Teller function

The Pöschl-Teller potential [30] has been widely explored by several researchers ([42, 125, 202], many times in different versions. In this section, we present two of them.

In 1994, Şimęk and Yalçin [203] proposed a generalized Pöschl-Teller (GENPT) potential which was also an exact solution for the Schrödinger equation. This new potential as well as the original Pöschl-Teller potential has four parameters and is given by:

$$V_{GENPT}(R) = \frac{Ae^{-2aR}}{(1 + b^2e^{-2aR})^2} + \frac{Be^{-2aR}}{(1 - b^2e^{-2aR})^2} \tag{3.523}$$

where a, b, A and B are constants that can be obtained in terms of spectroscopic constants.

The function (3.523) must satisfy the following properties:

(i) $\left.\frac{dV_{GENPT}}{dR}\right|_{R=R_e} = 0$;

(ii) $V_{GENPT}(\infty) - V_{GENPT}(R_e) = D_e$;

(iii) $\left.\frac{d^2V_{GENPT}}{dR^2}\right|_{R=R_e} = k_e$,

where R_e, D_e and k_e have their usual meanings.

Using these conditions, Şimęk and Yalçin [203] obtained the constants a, b, A and

B in potential (3.523), given by:

$$a = \pm\tfrac{\sqrt{\Delta}}{eR_e}, \qquad b^2 = y_e e^{\pm\sqrt{\Delta}}$$
$$B = \tfrac{D_e b^2}{4}\tfrac{(1-y_e)^4}{y_e^2}, \qquad A = B\left(\tfrac{1+y_e}{1-y_e}\right)^4 \tag{3.524}$$

where y_e is given by:

$$y_e^2 = \frac{\pm\sqrt{\Gamma/\Delta}-1}{1\pm\sqrt{\Gamma/\Delta}}, \tag{3.525}$$

being $\Delta = k_e R_e^2/2D_e$ the Sutherland parameter and $\Gamma = \frac{1}{9}\left(\frac{f_3}{f_2}\right)^2 R_e^2$, with $f_2 = \left.\frac{d^2V_{GENPT}}{dR^2}\right|_{R=R_e}$ and $f_3 = \left.\frac{d^3V_{GENPT}}{dR^3}\right|_{R=R_e}$.

The vibrational rotational coupling parameter α_e can be obtained from Dunham relation (2.57):

$$\alpha_e = -\left[\frac{R_e f_3}{3f_2}+1\right]\frac{6B_e^2}{\omega_e} \tag{3.526}$$

and the anharmonicity $\omega_e x_e$, given by:

$$\omega_e x_e = 8\Delta\frac{2.1078\times 10^{-16}}{R_e^2\mu}. \tag{3.527}$$

This version of the Pöschl-Teller potential was not well accepted. The coefficients of the potential (3.523) are extremely difficult to obtain, requiring the solution of complicated algebraic equations. Besides, in 1996, Znojil [204] demonstrated that the "exact" solution to the Schrödinger equation presented by Şimęk and Yalçin was not correct.

Then, in 2017, Jia, Zhang and Peng [17] presented a improved version of the Pöschl-Teller potential [30]. They considered the potential (3.107):

$$V_{PT}(R) = \frac{A}{\operatorname{senh}^2\alpha(R-R_e)} - \frac{B}{\cosh^2\alpha(R-R_e)} \tag{3.528}$$

where, they assumed $A = \frac{\hbar^2\alpha^2}{8\pi^2\mu}\beta(\beta-1)$ and $B = \frac{\hbar^2\alpha^2}{8\pi^2\mu}\gamma(\gamma+1)$.

By using of the conditions (i), (ii) and (iii), applied to this potential, they obtained the following expressions to A and B:

$$A = D_e \operatorname{senh}^4\alpha(R_e-R_0), \tag{3.529}$$

$$B = D_e \cosh^4\alpha(R_e-R_0). \tag{3.530}$$

To obtain $V_{PT}(R_e)=0$, they added a uniform shift $-\frac{1}{\sqrt{AB}}(a-\sqrt{AB})(B-\sqrt{AB})$ to the right hand of expression (3.528).

Thus, the improved Pöschl-Teller (IMPT) potential proposed by Jia *et. al* [17] is given by:

$$V_{IMPT}(R) = D_e + D_e \left(\frac{\operatorname{senh}^4 \alpha(R_e - R_0)}{\operatorname{senh}^2 \alpha(R - R_0)} - \frac{\cosh^4 \alpha(R_e - R_0)}{\cosh^2 \alpha(R - R_0)} \right) \tag{3.531}$$

where now,

$$\alpha = \pi c \omega_e \sqrt{\frac{\mu}{2D_e}}. \tag{3.532}$$

Using the Dunham relation (2.57), they obtained α_e:

$$\alpha_e = -\left[1 + \frac{8D_e R_e \alpha^3}{k_e} \left(\frac{\operatorname{senh}^3 \alpha(R_e - R_0)}{\cosh \alpha(R_e - R_0)} - \frac{\cosh^3 \alpha(R_e - R_0)}{\operatorname{senh} \alpha(R_e - R_0)} \right)\right] \frac{6B_e^2}{\omega_e}. \tag{3.533}$$

From Eqs. (3.532) and (3.533), the parameter R_0 is given by [17]:

$$R_0 = \frac{1}{4\pi c \omega_e} \sqrt{\frac{2D_e}{\mu}} \ln \left[\frac{4\pi^2 c^2 \mu \omega_e^3 \alpha_e + \frac{3}{2}\frac{3\hbar^2\omega_e^2}{\mu R_e^4} + \frac{3\hbar^2 \pi c \omega_e^3}{R_e^3}\sqrt{\frac{1}{2\mu D_e}}}{4\pi^2 c^2 \mu \omega_e^3 \alpha_e + \frac{3}{2}\frac{3\hbar^2\omega_e^2}{\mu R_e^4} - \frac{3\hbar^2 \pi c \omega_e^3}{R_e^3}\sqrt{\frac{1}{2\mu D_e}}} \right] \tag{3.534}$$

Jia *et. al* [17] applied the improved Pöschl-Teller potential for H_2, LiH, LiD, HF, and CO in their electronic ground states. They compared their function with the Morse potential [8] and calculated the average absolute deviations of these potentials from experimental RKR curves. For all systems analyzed, for the overall potential, the improved Pöschl-Teller presented more accurate results than Morse. In the branch of $R < R_e$ the improved Pöschl-Teller performs better than Morse and in the branch $R > R_e$ they practically coincide.

3.1.48 The Fu-Wang-Jia function

In 2019, the interest in obtaining a closed-form representation of the interaction of two atoms for diatomic systems in chemistry and physics remained very high, despite the various models presented over the nearly one hundred years of research in the area.

Among the potentials presented, the Tietz potential has been evidenced as a typical potential energy model, widely used in several recent researchers (see for example Refs. [205, 206]). Considering this, in 2020, Fu, Wang, and Jia [18] has proposed an improved five-parameter exponential-type potential energy for diatomic systems, and they explored the relationship between their potential and the Tietz potential.

We are referring to an improved model, because, in 2001, the same researchers Fu, Wang, and Jia [207] (FWJ) presented a unified exponential-type molecule potential that contains special cases of most previously given exponential-type molecule potentials and their deformations, such as the Generalized Morse potential [41] (proposed by Deng-Fan), Tietz-Hua potential [123], improved Pöschl-Teller potential [17], and others.

The five-parameter exponential-type potential energy is given by [207]:

$$V_{FWJ}(R) = P_1 + \frac{P_2}{e^{2\alpha R} + q} + \frac{P_3}{(e^{2\alpha R} + q)^2} \tag{3.535}$$

where P_1, P_2, P_3, q and α are adjustable parameters, with $q \neq 0$.

This potential satisfies the following relationships:

(i) $\left.\frac{dV_{FWJ}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{FWJ}(\infty) - V_{FWJ}(R_e) = D_e;$

(iii) $\left.\frac{d^2V_{FWJ}}{dR^2}\right|_{R=R_e} = k_e,$

where R_e, D_e and k_e have their usual meanings.

By using these conditions, Fu *et. al* [18] obtained two expressions to parameters P_2 and P_3, given by:

$$P_2 = -2D_e(e^{2\alpha R_e} + q) \tag{3.536}$$

$$P_3 = D_e(e^{2\alpha R_e} + q)^2. \tag{3.537}$$

Substituting these expressions to P_2 and P_3 in Eq. (3.535), the potential is rewrite as:

$$V_{FWJ}(R) = P_1 + D_e\left(1 - \frac{e^{2\alpha R_e} + q}{e^{2\alpha R} + q}\right)^2 - D_e \tag{3.538}$$

or putting $V_{FWJ}(Re) = 0$, and replacing α by $\alpha/2$ for simplify, Fu *et. al* obtained:

$$V_{FWJ}(R) = D_e\left(1 - \frac{e^{\alpha R_e} + q}{e^{\alpha R} + q}\right)^2. \tag{3.539}$$

This potential corresponds exactly to the improved Tietz potential showed by same researchers in Ref. [126], and choosing $q = 0$, the improved five-parameter exponential-type potential corresponds to Morse potential [8]. Still, if $q \neq 0$, the parameter α is given by [18]:

$$\alpha = \pi c\mu\omega_e\sqrt{\frac{2\mu}{D_e}} + \frac{1}{R_e}W\left(\pi c\omega_e R_e q\sqrt{\frac{2\mu}{D_e}}e^{-\pi c\omega_e R_e\sqrt{2\mu/D_e}}\right), \tag{3.540}$$

where W represents the Lambert W function, which satisfies $z = W(z)e^{W(z)}$ [197].

Fu *et. al* [18] analyzed the behavior of their potential for the ground electronic state of CO and compared their results with RKR experimental curves, obtaining good agreement.

3.1.49 The Improved Multiparameter Exponential-type function

In 2012, García-Martinez *et. al* [208] proposed the solution to a spectral problem involving the Schrödinger equation for a particular class of multiparameter exponential-type potentials (MPETP), given by:

$$V_{MPETP}(R) = \frac{qAe^{-R/K}}{1-qe^{-R/K}} + \frac{qBe^{-R/K}}{(1-qe^{-R/K})^2} + \frac{q^2Ce^{-2R/K}}{(1-qe^{-R/K})^2} \tag{3.541}$$

where A, B, C, q and k are adjustable parameters.

Then, in 2020, Xie and Jia [209], observed that to represent the internuclear interaction of a diatomic systems, this potential must satisfy the conditions:

(i) $\left.\frac{dV_{MPETP}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{MPETP}(\infty) - V_{MPETP}(R_e) = D_e;$

(iii) $\left.\frac{d^2V_{MPETP}}{dR^2}\right|_{R=R_e} = k_e,$

where R_e, D_e and k_e have their usual meanings.

Using these conditions, they obtained the relationships:

$$A + B = -\frac{2D_e}{q}(e^{R_e/k} - q), \tag{3.542}$$

and

$$B + C = \frac{D_e}{q^2}(e^{R_e/k} - q)^2. \tag{3.543}$$

Thus, by substituting the Eqs. (3.542) and (3.543) into (3.541), Xie and Jia rewrite the MPETP potential as a improved multiparameter exponential-type potential (IMPETP), given by:

$$V_{IMPETP}(R) = D_e\left(1 - \frac{e^{R_e/k} - q}{e^{R/k} - q}\right)^2. \tag{3.544}$$

The IMPETP is equivalent to the Tietz [120] and Williams-Poulos [183] potentials (see Refs. [126, 185]).

In addition, Xie and Jia [209] obtained the expressions to parameters k and q as function of the known spectroscopic parameters:

$$k = \frac{1}{2\pi c\omega_e\sqrt{\frac{2\mu}{D_e}} - \frac{1}{R_e}} \tag{3.545}$$

and

$$q = -\left(\frac{1}{\pi c\omega_e k}\sqrt{\frac{D_e}{2\mu}} - 1\right) e^{R_e/k} \tag{3.546}$$

To evaluate the efficiency of the improved multiparameter exponential-type potential, Xie and Jia simulated the internuclear potential energy curve for $A^3\Pi_1$ state of CIF and compared their results with the Morse [8] potential. They used the Lippincott criterion to calculate the deviation of the IMPETP from RKR experimental curves. They obtained that the average absolute deviation of the IMPETP was 0.653% of D, whereas the Morse potential given 8.56% of D, showing that the Morse potential is not suitable for reproducing this molecular state of CIF. Furthermore, they obtained the potential curve for $X^2\Sigma^+$ state of CP. Again, the IMPETP was more accurate than Morse and showed an excellent agreement with the experimental RKR curve.

3.1.50 The New Modified Morse function

This is the last potential that we will discuss here. This is the most recent analytical representation of potential energy interaction for diatomic systems we found until the end of this work. The function is a New Modified Morse potential and has been proposed in 2020 by Desai, Mesquita, and Fernandes [6] to try to reduce the discrepancy between the experimental and calculated values. The new function contains one more parameter than the original Morse function, and this will be responsible for improving accuracy in the region where the potential extends to near the dissociation limit.

The New Modified Morse potential (NMM) is given by:

$$V_{NMM}(R) = D_e\{1 - \exp\{[-\alpha\,\mathrm{senh}\,(\beta(R - R_e))]\}\}^2 \tag{3.547}$$

where α is dimensionless constant, β is a parameter with units of cm^{-1}. These parameters are related to the Morse parameter a, by:

$$\alpha\beta = \sqrt{\frac{k_e}{2D_e}} = a \tag{3.548}$$

since $\frac{d^2V_{NMM}}{dR^2} = k_e$. In addition, as well as the Morse potential, V_{NMM} satisfies also the conditions:

(i) $\left.\frac{dV_{NMM}}{dR}\right|_{R=R_e} = 0;$

(ii) $V_{NMM}(\infty) - V_{NMM}(R_e) = D_e$, where D_e is the depth of the well.

By using the Dunham relation (2.58), Desai *et. al*, obtained the anharmonicity constant given by:

$$\omega_e x_e = \left(\alpha^2\beta^2 - \frac{\beta^2}{2}\right)\frac{2.1078\times10^{-16}}{\mu}. \tag{3.549}$$

In the same way, we can obtain the parameter α_e from Dunham relation (2.57):

$$\alpha_e = [\alpha\beta R_e - 1]\,\frac{6B_e^2}{\omega_e}. \tag{3.550}$$

To obtain the optimized value of α parameter in Eq. (3.547), Desai *et. al* developed a program to solve the Schrödinger equation for all values of α within a select range, from the observed value of $\omega_e x_e$. Then, the range was extended till they got the minimum value of the sum of the absolute difference between each calculated and observed vibrational energy eigenvalue. These were obtained by solving the time-dependent Schrödinger equation for their dimensionless reduced potential, which was calculated by applying the Matrix Numerov method (see all details in Ref. [6]).

Desai *et. al* analyzed the behavior of the New Modified Morse potential for the $X^1\Sigma_g^+$ state of the H_2 and N_2 systems and compared them with RKR experimental curves. Morse [8] and Hulburt-Hirschfelder [7] potentials were also used in the comparison.

They observed that in the region $R > R_e$, for the H_2, the average absolute deviation for V_{NMM} was almost half that produced by V_{HH} and V_M. For the N_2, the differences were even greater, with the average absolute deviation of the New Modified Morse potential corresponding to practically one-third of the deviation of the Hulburt-Hirschfelder and almost one-tenth of the deviation of the Morse.

The anharmonicity constant obtained using the New Modified Morse potential also proved to be quite accurate, with a deviation of about 1.2% from the observed value, while the original Morse function presents about 21% deviation.

Although this function has been verified only two diatomic systems, the results obtained by Desai *et. al* suggest a relatively simple new potential such as the original Morse function, but with far superior results.

4 A comparative analysis for N_2 ($X^1\Sigma_g^+$), CO ($X^1\Sigma^+$) and HeH^+ ($X^1\Sigma^+$) diatomic systems

A comparative analysis for the N_2, CO, and HeH^+ diatomics systems in their ground electronic states will be presented in this chapter.

We recognize that analyzing a few diatomic systems is not ideal, considering the particularities of each potential presented in this review. However, along with the text we have already highlighted which systems each potential offers the best accuracy. Thus, in this section, we want to give a compact view of the behavior of potentials for three different ranges of R: over the repulsive part of the potential, over the attractive part of the potential, and over the whole range.

4.1 Calculations

In this review, the potential energy functions that depends on adjustable parameters are: V_{RM}, V_{HYL}, V_{EM}, V_{TH}, V_{THA}, V_{OGI},V_{MAT}, V_{SUR}, $V_{EHFACE2U}$, V_{AP}, V_{MER}, V_{NP}, V_{IMPT}, V_{FWJ}, V_{IMPETP} and V_{NMM}. These functions were fitted to calculated *ab initio* energies. The electronic structure calculations for the homo-and heteronuclear systems were carried out using as reference complete active space self-consistent (CASSCF) [210] wave function. Dynamical correlation effects were included by means of internally contracted multireference configuration interaction (MRCI(Q)) [211]. The aug-cc-pV5Z basis set of Dunning was employed, and we have performed CASSCF followed by MRCI(Q) approach. All calculations were performed with the Molpro 2012 package of *ab initio* programs [212].

On the other hand, the potential energy curves from functions that do not depend on adjustable coefficients have been directly calculated using the experimental data given by Huber and Herzberg [96]. The spectroscopic constants used for calculating such non-adjustable potentials can be seen in table 1.

To have a precise measure of the accuracy of the various potentials, we have used the

Table 4.1: Molecular constants [96] used in the calculations of the potential energy curves for $N_2(X^1\Sigma_g^+)$, $CO(X^1\Sigma^+)$ and $HeH^+(X^1\Sigma^+)$.

	D_e (eV)	R_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	α_e (cm^{-1})	B_e (cm^{-1})
N_2	9.9056	1.09768	2358.57	14.324	0.017318	1.99824
CO	11.2265	1.12832	2169.81358	13.2883	0.01750	1.93128
HeH^+	2.0452	0.7743	3228.4	157.71	2.636	34.887

least-squares Z-test method proposed by Murrell and Sorbie [60], given by Eq. 3.321. RKR data used in the comparison for the diatomic systems N_2 [213] and CO [214] were obtained from the literature. For HeH^+ we have used the experimental Born-Oppenheimer energy values [215], because the conventional RKR method for obtaining experimental energy curves is intractable.

4.2 Results

The results of the Z-test for three ranges of R can be observed in tables 4.2, 4.3 and 4.4, for (N_2), (CO), and (HeH^+), respectively. The smallest Z value implies the most accurate potential energy function.

For the diatomic system N_2, in the repulsive part, the most accurate potential energy function was the Extended Rydberg (V_{ER}), which can be seen in Fig. 4.5. Then, the Levine (V_{LEV}) potential presented the second better result, as can be seen in Fig. 4.7. Both were obtained using the experimental data, without a fit. Next, the Extended Lennard-Jones (V_{ELJ}) and the Varandas and da Silva ($V_{EHFACE2U}$) performed the best results, both fitted, in this case. These results can be observed in Fig 4.4 and 4.2, respectively. On the other hand, in the attractive part, the best potential was the Varshni (VAR_{III}) potential, which does not depend on adjustable parameters and it can be observed in Fig. 4.1. Next, we have V_{ELJ}, the Simons-Parr-Filan (V_{SPF}), and the Modified Extended Rydberg (V_{MER}), which were all fitted and the graphics can be observed in Fig. 4.4, 4.6 and 4.3, respectively. V_{ELJ} is superior to all other potentials over the whole range of R. Next, V_{ER}, $V_{EHFACE2U}$, and V_{SPF} proved to be more accurate than the others.

On the other hand, for N_2 the Born-Mayer potential showed the greatest deviation from the RKR curve, as can be seen in Fig. 4.8. The same occurred for CO, as can be seen in Fig. 4.13. These results were already expected in view of the fact that the Born-Mayer potential is a repulsive potential, and therefore has no minimum.

Table 4.2: Results of the Z-test for $N_2(X^1\Sigma_g^+)$. Z values are given in $10^{-5}E_h{}^2\ a_0{}^{-1}$

RANGES	$\Delta R/a_0$	GENKRAT	LJ	MOR	RYD	BM
Repulsive branch (1.6544<R<2.0743)	0.420	824.586	1 184.116	157.207	194.764	1 044 946.6
Attractive branch (2.0743<R<3.0778)	1.004	95.528	585.683	53.693	37.075	40 068.184
Whole potential (1.6544<R<3.0778)	1.423	155.199	380.957	42.095	41.773	168 127.383

RM	DAV	PT	MR	NEW	HUG	HYL	EM	MS	HH
8.797	2 837.581	592.860	59.785	46.427	8.135	341.972	8.831	270.589	20.774
2.524	319.032	17.480	18.469	61.350	2.368	39.569	5.164	44.261	1.433
2.186	530.655	93.537	15.321	28.467	2.034	64.347	3.122	55.480	3.567

LIN	HEL	WY	LIP	FM	VAR_{III}	DF	TH	LEV	SPF	ER
13.396	-	33.298	821.181	8.829	3.182	10.522	17.722	0.241	1.627	0.096
2.000	-	715.661	59.024	3.536	0.119	29.575	1.381	1.012	0.229	0.500
2.679	-	257.164	141.830	2.548	0.511	11.975	3.099	0.392	0.320	0.189

THA	HUF	OGI	MAT	DZ	SUR	PG	EHFACE2U	SCH	RPC_{II}
4.095	3.782	3.730	4.031	1.794	3.764	14.929	0.319	2 755.523	1 707.831
0.810	0.806	0.778	0.777	7.505	0.785	1.282	0.717	25.613	1 396.130
0.898	0.842	0.771	0.858	2.910	0.838	2.646	0.302	415.137	743.462

AP	WP	FAY_{II}	MER	$RAFI_{II}$	NP	ELJ	MRM	UDD	NDS
4.528	2 757.500	47.059	4.937	225.219	10.435	0.272	369.333	3 108.995	17.726
1.148	26.547	11.712	0.380	37.306	0.710	0.271	18.984	24.910	1.382
1.072	415.339	11.064	0.861	46.342	1.788	0.135	61.124	466.984	3.099

IMPT	FWJ	IMPETP	NMM
116.404	17.722	17.730	4.960
55.806	1.381	1.383	7.959
37.292	3.099	3.101	3.536

Table 4.3: Results of the Z-test for CO($X^1\Sigma^+$). Z values are given in $10^{-5}E_h{}^2\ a_0{}^{-1}$

RANGES	$\Delta R/a_0$	GENKRAT	LJ	MOR	RYD	BM	RM
Repulsive branch (1.6890<R<2.1320)	0.443	469.897	469.967	1.019	3.727	548 267.785	3.097
Attractive branch (2.1320<R<3.1860)	1.054	284.017	283.840	1.776	6.424	7 241.027	2.468
Whole potential (1.6890<R<3.1860)	1.497	169.565	169.513	0.776	2.814	83 697.611	1.328

DAV	PT	MR	NEW	HUG	HYL	EM	MS	HH	LIN
2 108.226	3 946.702	33.847	6.745	0.660	1 666.928	30.511	19.829	0.515	2.141
169.032	274.522	15.599	0.148	0.097	60.933	13.313	7.968	0.009	0.069
371.558	680.814	10.503	1.051	0.132	268.175	9.204	5.741	0.079	0.341

HEL	WY	LIP	FM	VAR_{III}	DF	TH	LEV	SPF	ER	THA
-	28.366	624.046	9.125	20.477	346.128	6.470	12.206	22.719	0.498	24.394
-	3.588	100.822	1.029	10.009	13.247	0.436	5.664	2.230	0.028	2.468
-	5.462	127.868	1.713	6.556	55.895	1.111	3.801	4.148	0.084	4.479

HUF	OGI	MAT	DZ	SUR	PG	EHFACE2U	SCH	RPC_{II}	AP
29.796	23.088	24.742	1.543	27.268	41.437	30.706	11.130	1 044.960	5.872
1.897	2.554	2.459	2.644	0.246	21.308	1.880	9.261	2 293.515	0.875
5.078	4.316	4.528	1.159	4.122	13.637	5.215	4.909	962.326	1.177

WP	FAY_{II}	MER	$RAFI_{II}$	NP	ELJ	MRM	UDD	NDS	IMPT
11.130	363.925	10.812	10.065	157.127	0.522	51.204	18 438.152	6.469	8.545
9.261	3.326	58.142	0.928	9.467	0.011	21.377	340.065	0.437	1.142
4.909	55.035	367.106	1.816	11.789	0.081	15.107	2 848.737	1.111	1.667

FWJ	IMPETP	NMM
6.470	6.471	9.434
0.436	0.436	2.012
1.111	1.111	2.091

Table 4.4: Results of the Z-test for $HeH^+(X^1\Sigma^+)$. Z values are given in $10^{-5}E_h{}^2\ a_0{}^{-1}$

RANGES	$\Delta R/a_0$	GENKRAT	LJ	MOR	RYD	BM	RM
Repulsive branch (0.9000<R<1.4600)	0.563	139.000	139.885	2.763	9.514	-	23.617
Attractive branch (1.4600<R<10.0000)	0.737	2.616	1.356	0.012	0.082	-	1.311
Whole potential (0.9000<R<10.0000)	1.3	30.928	31.012	0.601	2.082	-	5.482

DAV	PT	MR	NEW	HUG	HYL	EM	MS	HH	LIN
-	12 357.302	24.283	0.708	3.762	39.357	1.640	61.430	0.191	29.062
-	963.975	0.155	0.879	0.002	0.858	0.415	42.719	0.011	0.114
-	2 947.164	5.299	0.402	0.815	8.760	0.472	25.395	0.044	6.321

HEL	WY	LIP	FM	VAR_{III}	DF	TH	LEV	SPF	ER
50.578	280.158	222.313	0.050	0.720	302.701	3.489	0.299	2.315	1.627
100.349	251.414	1.594	0.062	0.083	0.621	0.004	0.057	0.022	0.001
39.372	131.846	48.559	0.028	0.179	65.680	0.756	0.081	0.507	0.352

THA	HUF	OGI	MAT	DZ	SUR	PG	EHFACE2U	SCH	RPC_{II}
1.696	4.207	1.792	1.795	0.020	1.663	9.912	5.253	190.602	-
0.049	0.050	0.032	0.074	0.070	0.715	0.336	0.020	0.242	-
0.381	0.925	0.397	0.409	0.024	0.563	2.240	1.142	41.315	-

AP	WP	FAY_{II}	MER	$RAFI_{II}$	NP	ELJ	MRM	UDD
0.083	190.602	5 181.941	27 489.490	0.742	585.920	1.835	49.958	91.005
0.522	0.242	163.562	640.252	0.004	39.182	0.005	0.330	48.595
0.328	41.315	1 167.692	59 667.803	0.162	137.891	0.398	10.904	33.459

NDS	IMPT	FWJ	IMPETP	NMM
3.489	0.064	3.489	3.489	7.114
0.004	0.003	0.004	0.004	0.187
0.756	0.015	0.756	0.756	1.592

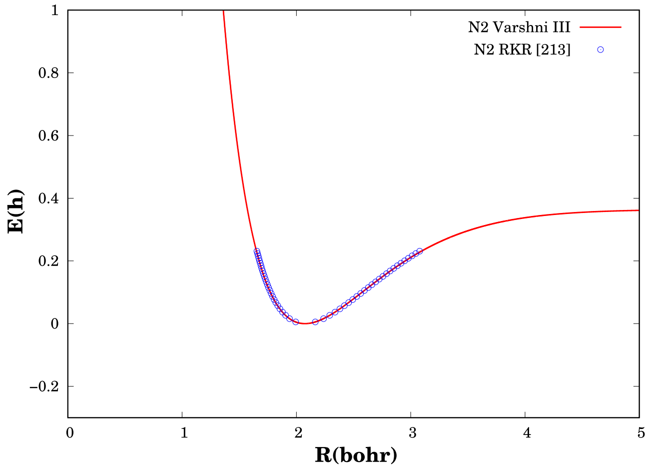


Figure 4.1: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Varshni III potential with the experimental RKR curve [213].

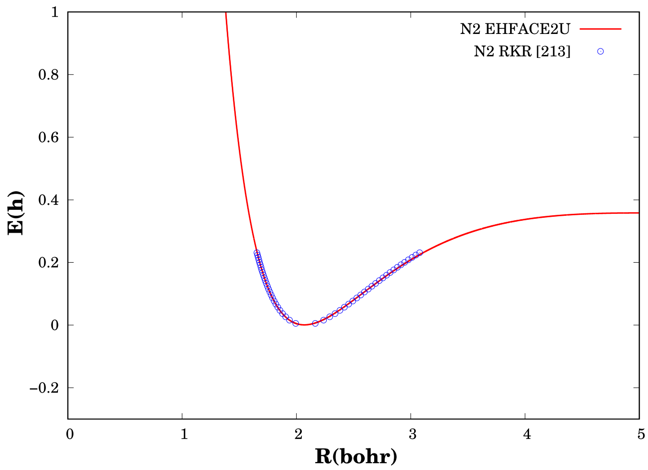


Figure 4.2: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the EHFACE2U potential with the experimental RKR curve [213].

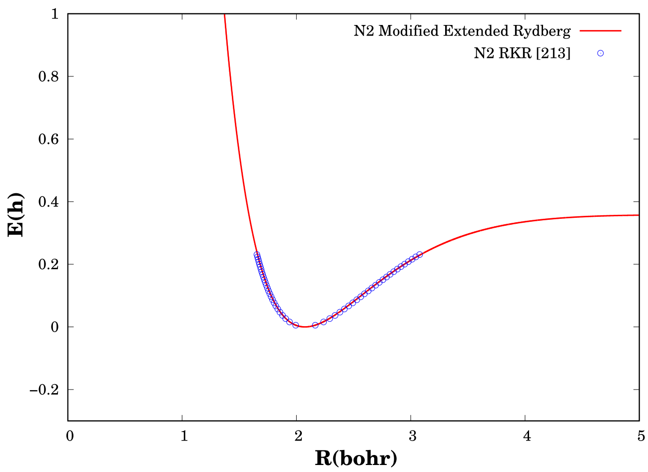


Figure 4.3: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Modified Extended Rydberg potential with the experimental RKR curve [213].

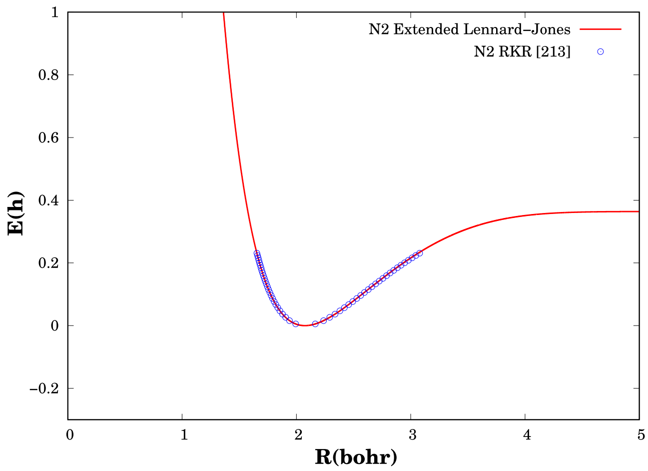


Figure 4.4: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Extended Lennard-Jones potential with the experimental RKR curve [213].

Thus, according to our comparative study, for the ground electronic state of N_2 the functions in order of decreasing accuracy, over the whole range of R, are: V_{ELJ}, V_{ER}, $V_{EHFACE2U}$, V_{SPF}, V_{LEV}, $V_{VAR_{III}}$, V_{OGI}, V_{SUR}, V_{HUF}, V_{MAT}, V_{MER}, V_{THA}, V_{AP}, V_{NP}, V_{HUG}, V_{RM}, V_{FM}, V_{PG}, V_{LIN}, V_{DZ}, $V_{TH} = V_{FWJ} = V_{NDS}$, V_{IMPETP}, V_{EM}, V_{NMM}, V_{HH}, $V_{FAY_{II}}$, V_{DF}, V_{MR}, V_{NEW}, V_{IMPT}, V_{RYD}, V_{MOR}, $V_{RAFI_{II}}$, V_{MS}, V_{MRM}, V_{HYL}, V_{PT}, V_{LIP}, $V_{GENKRAT}$, V_{WY}, V_{LJ}, V_{SCH}, V_{WP}, V_{UDD}, V_{DAV}, $V_{RPC_{II}}$ and V_{BM}.

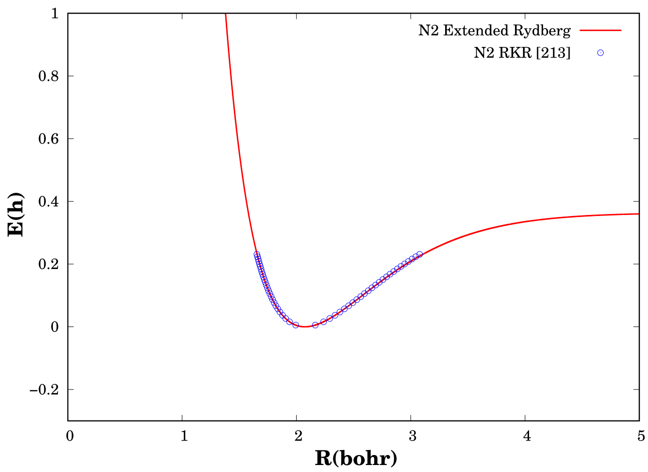


Figure 4.5: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Extended Rydberg potential with the experimental RKR curve [213].

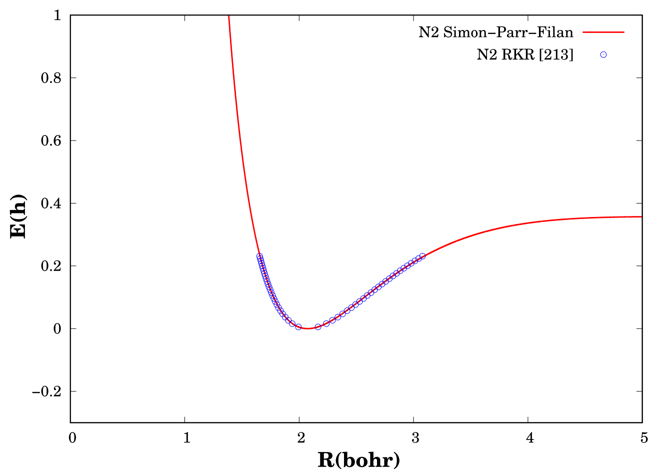


Figure 4.6: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Simons-Parr-Filan potential with the experimental RKR curve [213].

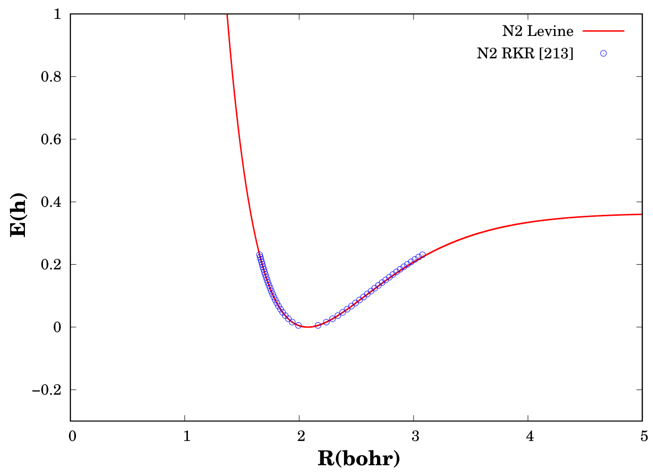


Figure 4.7: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Levine potential with the experimental RKR curve [213].

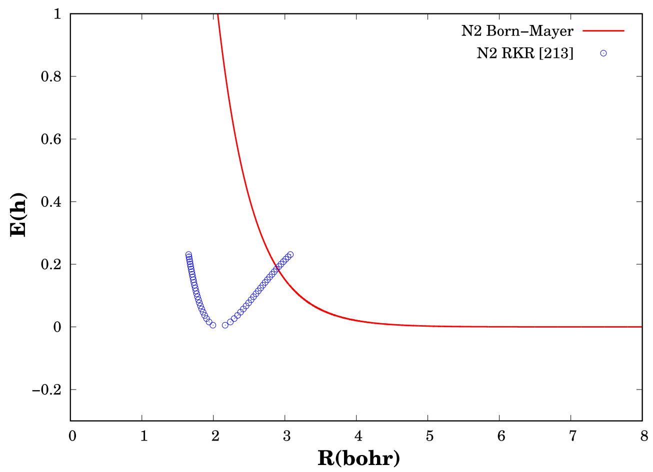


Figure 4.8: Comparison, for $\mathbf{N}_2$ $(X^1\Sigma_g^+)$, of the Born-Mayer potential with the experimental RKR curve [213].

For the diatomic system CO, as well as for N_2, the best potential in the repulsive part was the Extended Rydberg by Huxley and Murrell [131], as can be seen in Fig 4.12. Next, the Hulburt-Hirschfelder (V_{HH}), V_{ELJ} and the Huggins (V_{HUG}) were the most accurate, being all analytical functions which their parameters were obtained directly from experimental data, except V_{ELJ}. The accuracy of these potentials can be noted in Fig. 4.10, 4.11 and 4.9, respectively. In the attractive region, the results were similar to those in the repulsive region, being V_{HH}, V_{ELJ}, and V_{ER} those with the lowest Z value, respectively. The Hulburt-Hirschfelder potential proved to be the best among the 50 analyzed considering the whole potential.

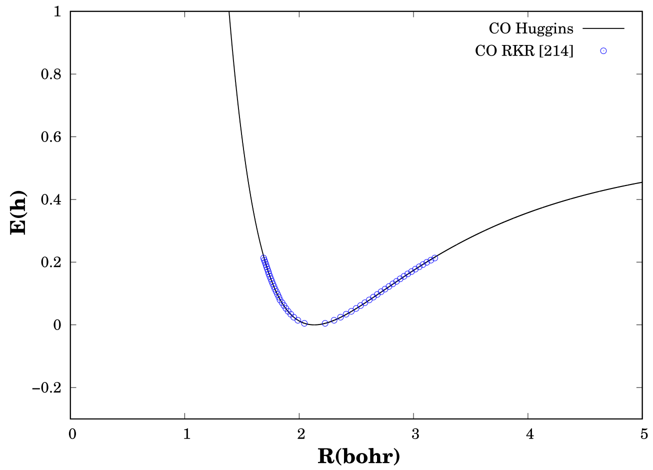


Figure 4.9: Comparison, for CO ($X^1\Sigma^+$), of the Huggings potential with the experimental RKR curve [214].

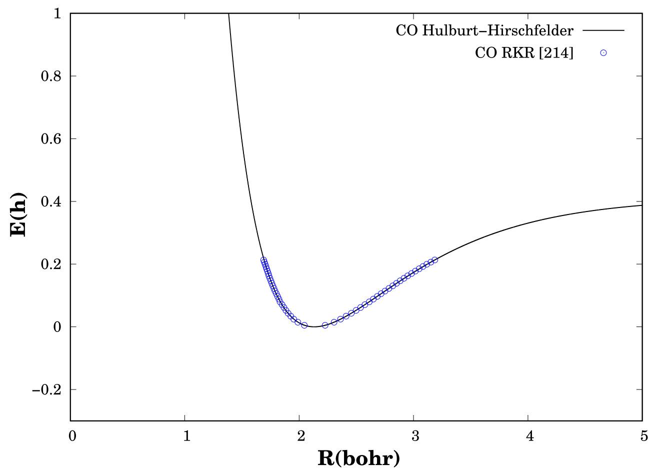


Figure 4.10: Comparison, for CO ($X^1\Sigma^+$), of the Hulburt-Hirschfelder potential with the experimental RKR curve [214].

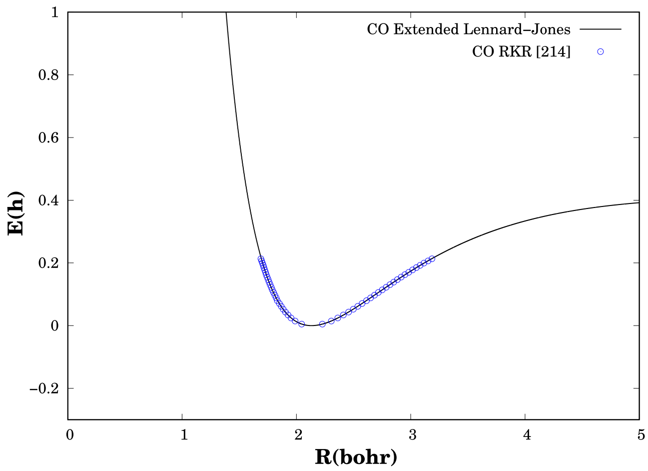


Figure 4.11: Comparison, for CO ($X^1\Sigma^+$), of the Extended Lennard-Jones potential with the experimental RKR curve [214].

For the ground electronic state of CO the functions in order of decreasing accuracy, over the whole range of R, are: V_{HH}, V_{ELJ}, V_{ER}, V_{HUG}, V_{LIN}, V_{MOR}, V_{NEW}, $V_{TH} = V_{FWJ} = V_{NDS} = V_{IMPETP}$, V_{DZ}, V_{AP}, V_{RM}, V_{IMPT}, V_{FM}, $V_{RAFI_{II}}$, V_{NMM}, V_{RYD}, V_{LEV}, V_{SUR}, V_{SPF}, V_{OGI}, V_{THA}, V_{MAT}, $V_{SCH} = V_{WP}$, V_{HUF}, $V_{EHFACE2U}$, V_{WY}, V_{MS}, $V_{VAR_{III}}$, V_{EM}, V_{MR}, V_{NP}, V_{PG}, V_{MRM}, $V_{FAY_{II}}$, V_{DF}, V_{LIP}, V_{LJ}, $V_{GENKRAT}$, V_{HYL}, V_{MER}, V_{DAV}, V_{PT}, $V_{RPC_{II}}$, V_{UDD}, and V_{BM}.

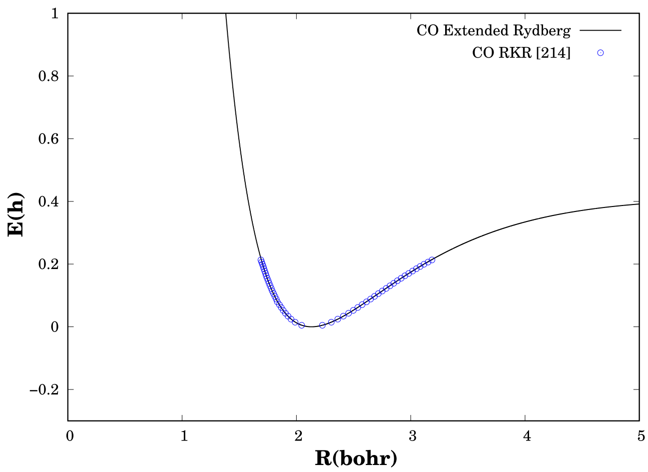


Figure 4.12: Comparison, for CO ($X^1\Sigma^+$), of the Extended Rydberg potential with the experimental RKR curve [214].

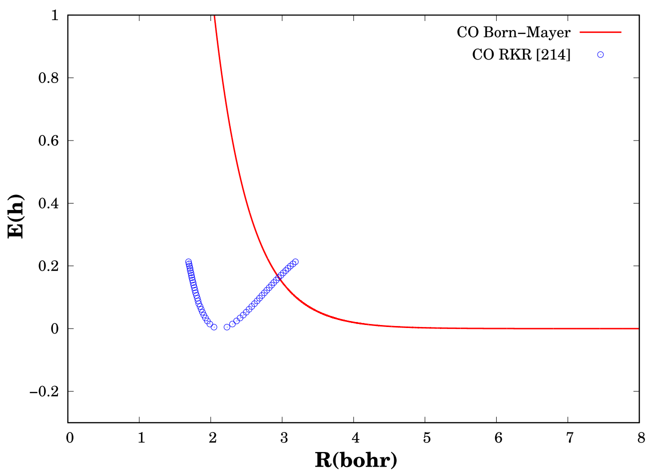


Figure 4.13: Comparison, for CO ($X^1\Sigma^+$), of the Born-Mayer potential with the experimental RKR curve [213].

Finally, for the diatomic system HeH^+ the results were slightly different from those obtained with N_2 and CO. The best function for the repulsive range was the Dmitrieva-Zenevich (V_{DZ}) potential without adjustable parameters as can be seen in Fig. 4.16. After, the fitted Frost-Musulin (V_{FM}) (see Fig. 4.18) and Improved Pöschl-Teller (V_{IMPT}) potential functions were the most accurate. In the attractive range, the function with the lowest Z value was V_{ER}, after V_{HUG} and V_{IMPT}, being the first a potential without fit and the second fitted. These results can be observed in Fig. 4.17, 4.14 and 4.15 respectively. Last, for the whole potential V_{IMPT} yielded the least deviation. Next, V_{DZ}, V_{FM}, and V_{HH} were the most accurate, respectively.

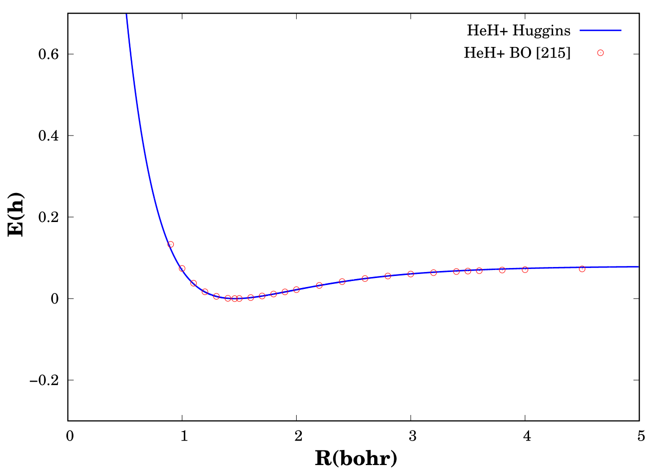


Figure 4.14: Comparison, for HeH^+ ($X^1\Sigma^+$), of the Huggings potential with the experimental Born-Oppenheimer curve [215].

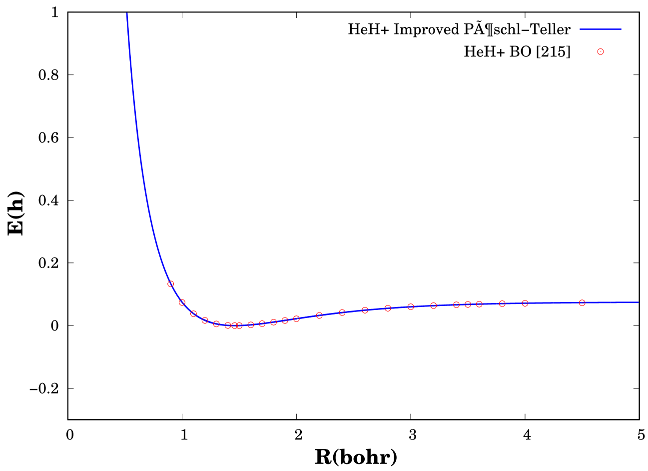


Figure 4.15: Comparison, for HeH^+ $(X^1\Sigma^+)$, of the Improved Pöschl-Teller potential with the experimental Born-Oppenheimer curve [215].

For the ground electronic state of HeH^+ the functions in order of decreasing accuracy, over the whole range of R, are: V_{IMPT}, V_{DZ}, V_{FM}, V_{HH}, V_{LEV}, $V_{RAFI_{II}}$, $V_{VAR_{III}}$, V_{AP}, V_{ER}, V_{THA}, V_{OGI}, V_{ELJ}, V_{NEW}, V_{MAT}, V_{EM}, V_{SPF}, V_{SUR}, V_{MOR}, $V_{TH} = V_{FWJ} = V_{NDS} = V_{IMPETP}$, V_{HUG}, V_{HUF}, $V_{EHFACE2U}$, V_{NMM}, V_{RYD}, V_{PG}, V_{MR}, V_{RM}, V_{LIN}, V_{HYL}, V_{MRM}, V_{MS}, $V_{GENKRAT}$, V_{LJ}, V_{UDD}, V_{HEL}, $V_{SCH} = V_{WP}$, V_{LIP}, V_{DF}, V_{WY}, V_{NP}, $V_{FAY_{II}}$, V_{PT} and V_{MER}.

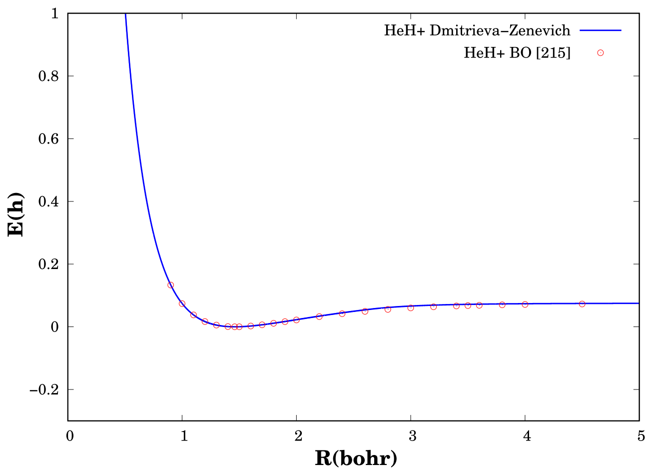


Figure 4.16: Comparison, for HeH^+ $(X^1\Sigma^+)$, of the Dmitrieva-Zenevich potential with the experimental Born-Oppenheimer curve [215].

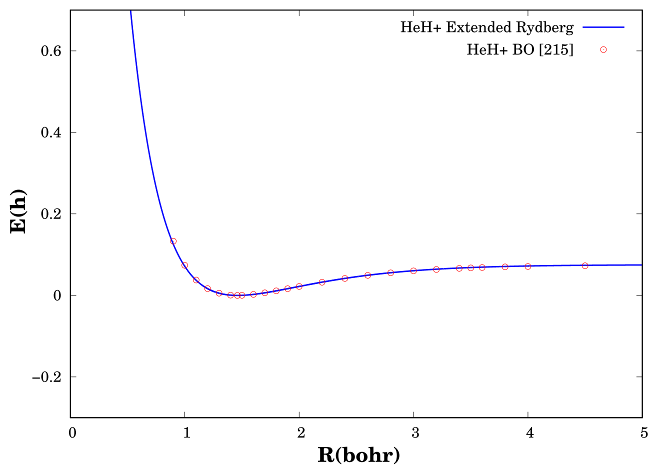


Figure 4.17: Comparison, for HeH^+ ($X^1\Sigma^+$), of the Extended-Rydberg potential with the experimental Born-Oppenheimer curve [215].

For the Heller function (V_{HEL}) was not possible to obtain potential energy curves for N_2 and CO. This is due to the fact that this potential describes well only van der Waals diatomics [21]. For HeH^+, the Born-Mayer (V_{BM}), the Davidson (V_{DAV}) and the Reduced ($V_{RPC_{II}}$) potentials did not provide correct PECs.

Note that, for the three diatomic systems considered here, the results for functions V_{TH}, V_{FWJ}, and V_{NDS} are identical, confirming the claims of Fu, Wang, and Jia [18] and Mustafa [201], respectively. For CO and HeH^+, V_{IMPETP} also proved to be equivalent to V_{TH}, V_{FWJ}, and V_{NDS}, and for N_2 their values for three regions analyzed yielded results approximately equivalents, confirming the statement of Xie and Jia [209].

For HeH^+, the Modified Extended Rydberg showed the greatest deviation from the Born-Oppenheimer experimental curve, demonstrating that such a function does not work well for this ion, as can be seen in Fig. 4.19.

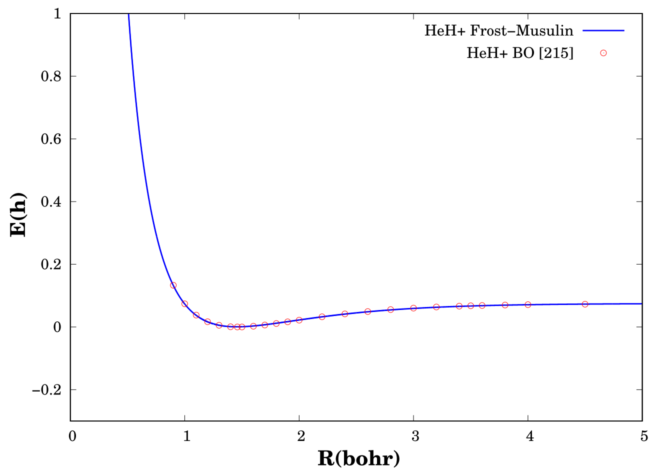


Figure 4.18: Comparison, for HeH^+ ($X^1\Sigma^+$), of the Frost-Musulin potential with the experimental Born-Oppenheimer curve [215].

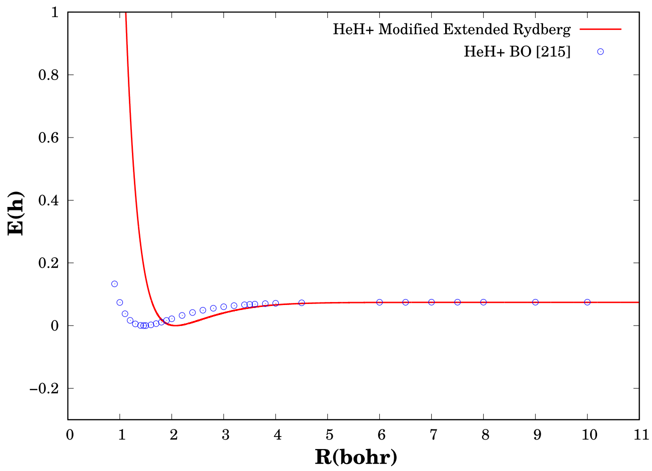


Figure 4.19: Comparison, for HeH^+ ($X^1\Sigma^+$), of the Modified Extended Rydberg potential with the experimental Born-Oppenheimer curve [215].

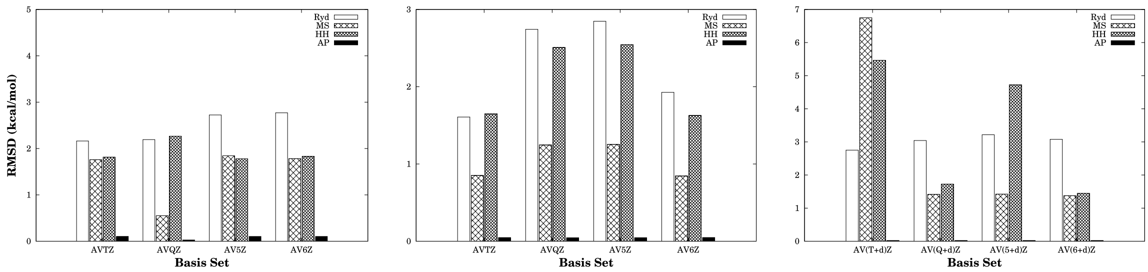
5 A comparative study of analytic representations of potential energy curves for O_2, N_2, and SO in their ground electronic states

In this chapter we will present some results of a work presented at the Quitel Congress in 2018 (see Ref. [23]). Here we will consider only the functions that were in fact adjusted, leaving out the historical review (which can be checked in chapter 3) and the functions of Thakkar and Hua (who not been adjusted). Here we refer to the Extended Rydberg potential as the Murrel-Sortbie potential.

Among the analytical representations available in the literature, four functions were chosen: Rydberg, Hulburt-Hirschfelder, Murrell-Sorbie and Aguado-Camacho-Paniagua. This selection was motivated considering that the first three were proposed a long time ago, and the curves were obtained theoretically or semi-empirically, in the case in which the functions were based on a compromise between results of empirical measures of experimental character and few reliable theoretical calculations available until the mid-1980s, except for very simple diatomic systems [216]. In counterpart, the latter potential Aguado-Paniagua, had been presented using *ab initio* calculation together with semi-empirical calculation techniques. Thus, the aim of this work is to apply *ab initio* calculation techniques to the earliest potentials and compare them with more recent ones, using O_2, N_2, and SO as case studies diatomic systems.

5.1 Electronic structure calculations

In order to obtain a sufficiently accurate potential energy curves, the electronic structure calculations for the homo-and heteronuclear systems were carried out using as reference complete active space self-consistent (CASSCF) [210] wave function. Dynamical correlation effects were included by means internally contracted multireference configuration interaction (MRCI) [211]. Such a strategy has been previously applied



(a) (b) (c)

Figure 5.1: Root-mean squared deviation of diatomic molecules: (a) $N_2(X^1\Sigma_g^+)$, (b) $O_2(X^3\Sigma_g^-)$, (c) $SO(X^3\Sigma^-)$ calculated in different basis set and potentials.

in several diatomic molecules [217–219]. Furthermore, the multireference Davidson correction (+Q) was included to compensate for the effects of higher-order correlation. The aug-cc-pVXZ (X = T,Q,5,6) basis sets of Dunning were employed. For each basis set, we have performed CASSCF followed by MRCI approach. It must be also highlighted that for the sulfur atom, we have used the Dunning correlation consistent basis set (aug-cc-pV(X+d)Z), which contain an additional d function for the purpose of partially ameliorating a known SCF-level deficiency in the AVXZ sets for second-row elements of periodic table [220].

All calculations were performed with the Molpro 2012 package of *ab initio* programs [212]. We must point out that Molpro only uses Abelian point group symmetry. Following this, we consider irreducible representations of the $D_{\infty h}$ point group for homonuclear molecules (N_2 and O_2) but due to limitations of the procedure, we adopted D_{2h} subgroup of $D_{\infty h}$ point group in the calculations; for SO, C_{2v} subgroup of $C_{\infty v}$ is used. In general, the mapping calculations of the PEC were made at intervals of 0.025 a_0 over the internuclear distance range from 1.0 to 15.0 a_0, where a_0 is the Bohr radius.

5.2 Results and discussion

5.2.1 Performance Analysis

We start this discussion showing the results obtained from the root-mean-square deviation (RMSD) for the different potentials, basis set and diatomic systems. From the statistical point of view, RMSD values are generally used to evaluate the error of the PEC in relation to the curve obtained via the points *ab initio* data. The root-mean-square deviation is calculated by:

$$\Delta E_{RMSD} = \left[\frac{1}{N} \sum_{i=1}^{N} \left(V_{ab\,initio} - V \right)^2 \right]^{1/2} \tag{5.1}$$

Table 5.1: Basis Set Dependence of the spectroscopic constants for the $N_2(X^1\Sigma_g^+)$

Potential	Basis set	R_e (a_0)	$\Delta R_e/R_e$[a] (%)	ω_e (cm^{-1})	$\Delta\omega_e/\omega_e$[b] (%)	D_e (eV)	$\Delta D_e/D_e$[c] (%)	$\omega_e x_e$ (cm^{-1})	$\Delta\omega_e x_e/\omega_e x_e$ (%)
Ryd.	AVTZ	2.07431	0.0	2394	1.52	9.41768	23.48	15.80	10.33
	AVQZ	2.07431	0.0	2391	1.39	9.63082	13.20	15.60	8.93
	AV5Z	2.07310	0.05	2395	1.56	9.73632	8.12	15.87	10.82
	AV6Z	2.07531	0.04	2396	1.61	9.76785	6.60	15.93	11.24
MS	AVTZ	2.06669	0.36	2449	3.85	9.54045	17.56	17.68	23.46
	AVQZ	2.08315	0.42	2399	1.73	9.76039	6.96	15.95	11.38
	AV5Z	2.05913	0.73	2474	4.91	9.88354	1.02	17.81	24.37
	AV6Z	2.05857	0.75	2476	5.00	9.91620	0.54	17.85	24.65
HH	AVTZ	2.06865	0.27	2418	2.54	9.46758	21.07	16.67	16.41
	AVQZ	2.06580	0.40	2434	3.22	9.61217	14.10	17.04	18.99
	AV5Z	2.06075	0.65	2443	3.60	9.81957	4.10	17.52	22.34
	AV6Z	2.06031	0.67	2445	3.68	9.86220	2.05	17.63	23.11
AP	AVTZ	2.09175	0.84	2326	1.35	9.44831	22.00	15.21	6.21
	AVQZ	2.08314	0.42	2349	0.38	9.69849	9.94	14.46	0.97
	AV5Z	2.08333	0.43	2345	0.55	9.77486	6.26	14.53	1.46
	AV6Z	2.08285	0.41	2346	0.50	9.80564	4.78	14.58	1.81

[a] The experimental values of ΔR_e can be seen in the Table 5.4
[b] The experimental values of $\Delta\omega_e$ can be seen in the Table 5.4
[c] The experimental values of ΔD_e can be seen in the Table 5.4

Table 5.2: Basis set dependence of the spectroscopic constants for the $O_2(X^3\Sigma_g^-)$

Potential	Basis set	R_e (a_0)	$\Delta R_e/R_e$ [a] (%)	ω_e (cm^{-1})	$\Delta\omega_e/\omega_e$ [b] (%)	D_e (eV)	$\Delta D_e/D_e$ [c] (%)	$\omega_e x_e$ (cm^{-1})	$\Delta\omega_e x_e/\omega_e x_e$ (%)
Ryd.	AVTZ	2.28969	0.42	1605	1.58	5.00247	8.55	13.21	10.26
	AVQZ	2.28970	0.42	1600	1.26	5.08499	4.93	13.18	10.01
	AV5Z	2.28970	0.42	1600	1.26	5.11076	3.80	13.17	9.93
	AV6Z	2.28970	0.42	1600	1.26	5.12831	3.03	13.15	9.76
MS	AVTZ	2.28889	0.39	1664	5.31	5.15345	1.93	13.72	14.52
	AVQZ	2.28115	0.05	1677	6.13	5.25710	2.61	13.78	15.02
	AV5Z	2.26425	0.69	1680	6.32	5.28918	4.02	13.82	15.35
	AV6Z	2.27939	0.02	1682	6.45	5.31066	4.96	13.85	15.60
HH	AVTZ	2.27876	0.05	1651	4.49	4.99806	8.74	13.64	13.85
	AVQZ	2.27106	0.39	1667	5.50	5.10291	4.14	13.70	14.35
	AV5Z	2.26937	0.46	1671	5.75	5.13348	2.80	13.72	14.52
	AV6Z	2.26898	0.48	1672	5.82	5.16390	1.47	13.77	14.94
AP	AVTZ	2.30267	0.99	1543	2.28	5.04119	6.85	12.80	6.84
	AVQZ	2.29298	0.56	1567	0.81	5.14910	2.12	12.45	3.92
	AV5Z	2.29152	0.50	1569	0.64	5.17947	0.79	12.39	3.42
	AV6Z	2.29166	0.51	1565	0.88	5.19745	0.001	12.42	3.67

[a] The experimental values of ΔR_e can be seen in the Table 5.5
[b] The experimental values of $\Delta\omega_e$ can be seen in the Table 5.5
[c] The experimental values of ΔD_e can be seen in the Table 5.5

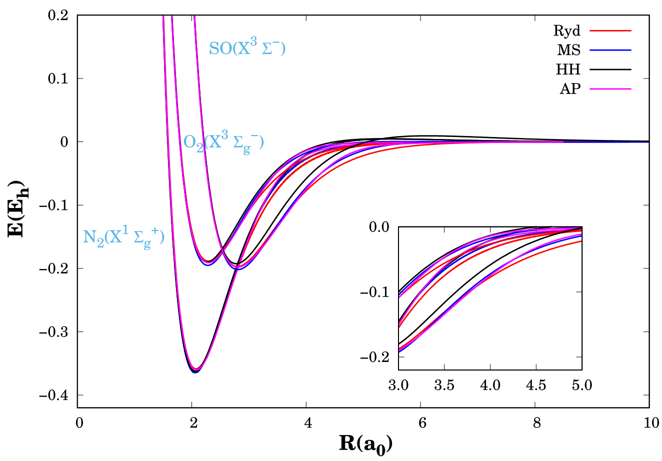


Figure 5.2: Potential energy curves for N_2, O_2, and SO calculated at the MRCI+Q/AV6Z level of theory.

where $V_{\text{ab initio}}$ represents the *ab initio* points and V is the potential energy given by four analytic forms selected among those previously presented.

To obtain the two-body energies, we have employed the functions of Rydberg (RYD), Murrell and Sorbie (MS), Hulburt-Hirschfelder (HH), and Aguado and Paniagua (AP). These potentials are very well documented in the literature being, accordingly, good models for this study [221–223]. We remember, of course, that the smaller RMSD values represents the better performance of the fit. To avoid long tables of coefficients, only the results calculated using these functions set are shown. The remaining data is gathered in Supplementary Material (see Ref. [23]).

To investigate in details the quality of the fits, graphics of the calculated RMSD values for N_2, O_2, and SO molecules can be seen in Figure 5.1. As expected, the best results are found when the AP function is used in combination with a higher basis set, so that for the three systems, differences in the order of 0.10, 0.04, and 0.02 kcal/mol were obtained from other data, respectively.

The ability of the other analyzed potentials, Ryd, MS and HH, to reproduce *ab initio* points [calculated mainly in the intermediate region] can be clearly seen in the Figure 5.2. The Ryd function is represented by a red solid line, while MS is in blue. In black are shown the results of the HH functions and those for AP are in magenta.

Comparing the RMSD test, in almost all cases the fits are above the threshold of chemical accuracy (1 kcal/mol) [224]. In particular, the AP function shows good performance with RMSD values below 0.25 kcal/mol. For sulfur monoxide Fig. 5.1 (c), note the very poor quality and the greater deviation of the fit in the AV(T+d)Z when the MS function is applied (RMSD value close to 7 kcal/mol). In such a Figure, the values of ΔE_{RMSD} for Rydberg function (2.75, 3.04, 3.21, 3.07 kcal/mol) are not significantly modified when changing the basis set. The same behaviour is observed for the MS potential (1.41, 1.42, 1.37 kcal/mol) in the basis sets AV(X+d)Z (X = Q,5,6).

In the case of nitrogen molecule (Fig. 5.1 (a)), when the Ryd potential is applied,

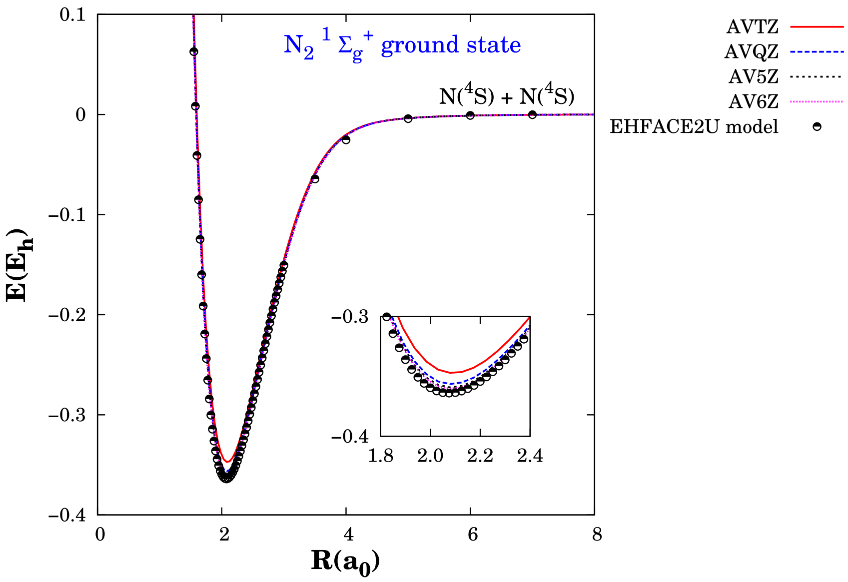


Figure 5.3: Potential energy curves for the ground electronic state of the N_2 molecule calculated with different basis sets. The circles represent energies calculated by EHFACE model from Ref. [226]. In addition, also plotted in the inset is a zoom of the minimum region of the curve.

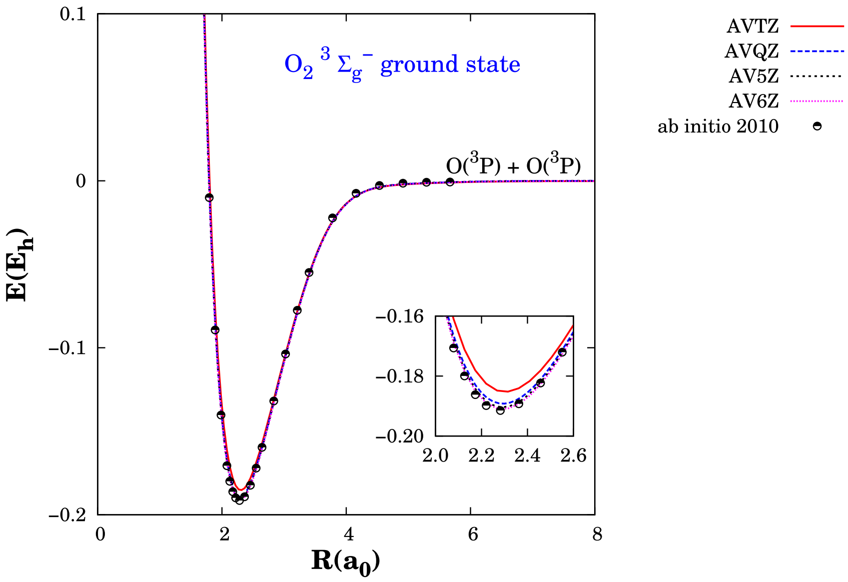


Figure 5.4: Potential energy curves for the ground electronic state of the O_2 molecule calculated with different basis sets. The circles represent *ab initio* points calculated in Ref. [227]. In addition, also plotted in the inset is a zoom of the minimum region of the curve.

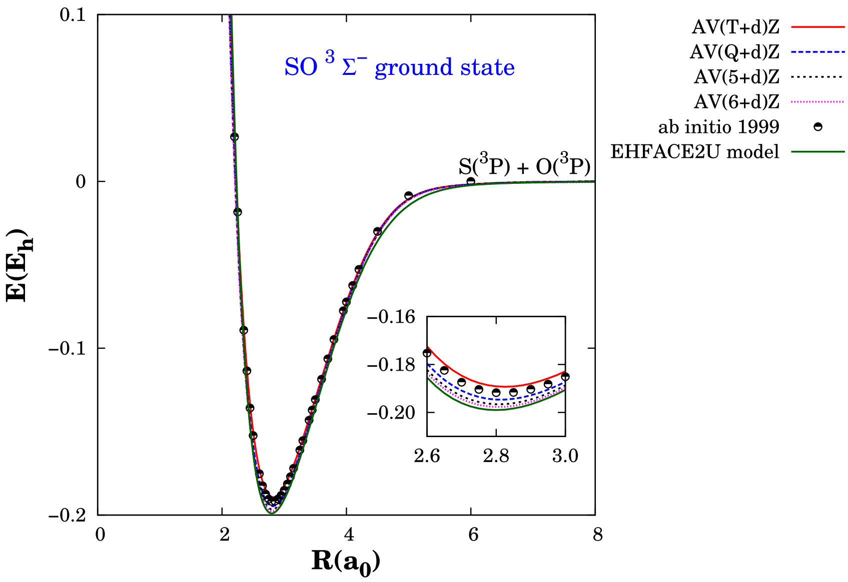


Figure 5.5: Potential energy curves for the ground electronic state of the SO calculated with different basis sets. The circles represent *ab initio* points calculated in Ref. [228]. Solid green line represents the analytical form (EHFACE model) obtained in Ref. [229]. In addition, also plotted in the inset is a zoom of the minimum region of the curve.

Table 5.3: Basis Set Dependence of the spectroscopic constants for the SO($X^3\Sigma^-$)

Potential	Basis set	R_e (a_0)	$\Delta R_e/R_e$ [a] (%)	ω_e (cm^{-1})	$\Delta\omega_e/\omega_e$ [b] (%)	D_e (eV)	$\Delta D_e/D_e$ [c] (%)	$\omega_e x_e$ (cm^{-1})	$\Delta\omega_e x_e/\omega_e x_e$ (%)
Ryd	AV(T+d)Z	2.79884	3.21(-4)	1204	4.87	5.17952	8.91	6.71	9.64
	AV(Q+d)Z	2.79884	3.21(-4)	1195	4.09	5.29416	4.81	6.68	9.15
	AV(5+d)Z	2.79884	3.21(-4)	1192	3.83	5.33319	3.42	6.66	8.82
	AV(6+d)Z	2.79884	3.21(-4)	1191	3.74	5.36028	2.45	6.63	8.33
MS	AV(T+d)Z	2.81980	0.74	1195	4.09	5.24626	6.52	6.68	9.15
	AV(Q+d)Z	2.81239	0.48	1211	5.48	5.40960	0.69	6.65	8.66
	AV(5+d)Z	2.80792	0.32	1216	5.92	5.46320	1.22	6.67	8.98
	AV(6+d)Z	2.80625	0.26	1218	6.09	5.49369	2.31	6.70	9.47
HH	AV(T+d)Z	2.82807	1.04	1103	3.91	4.66886	27.15	7.15	16.83
	AV(Q+d)Z	2.79948	0.02	1204	4.87	5.36251	2.37	6.40	4.57
	AV(5+d)Z	2.81032	0.41	1128	1.74	4.94807	17.18	6.73	9.96
	AV(6+d)Z	2.77639	0.80	1244	8.36	5.23775	6.83	7.05	15.19
AP	AV(T+d)Z	2.82532	0.94	1124	2.09	5.15158	9.91	6.41	4.73
	AV(Q+d)Z	2.81270	0.49	1134	1.21	5.29857	4.65	6.32	3.26
	AV(5+d)Z	2.80765	0.31	1139	0.78	5.35029	2.81	6.25	2.12
	AV(6+d)Z	2.80572	0.24	1141	0.60	5.38058	1.72	6.20	1.30

[a]The experimental values of ΔR_e can be seen in the Table 5.6
[b]The experimental values of $\Delta\omega_e$ can be seen in the Table 5.6.
[c]The experimental values of ΔD_e can be seen in the Table 5.6

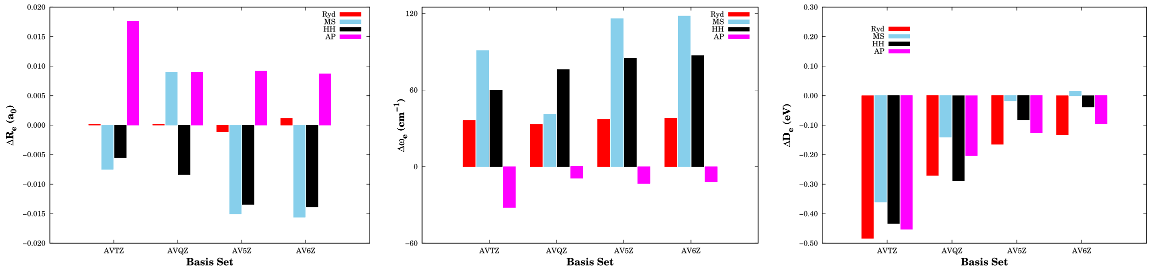
unexpectedly the values of ΔE_{RMSD} increases monotonically as the basis sets increases from AVTZ (2.16 kcal/mol) to AV6Z (2.77 kcal/mol). For the Hulburt-Hirschfelder function, the average value of the RMSD is around 2.0 kcal/mol. For MS function although 0.55 kcal/mol be the smaller value of RMSD found at AVQZ, the other basis sets present bigger values, near to 1.80 kcal/mol. The Aguado and Paniagua potential led to deviations of the magnitude of 0.10 kcal/mol these values being close to those found by Xiao-Niu *et al.* (0.09 kcal/mol) [225].

Finally, the plot of the oxygen molecule represented in Fig. 5.1 (b) demonstrated a Gaussian-like behaviour for the Ryd, MS, and HH functions with a peak at 2.80, 1.25, and 2.50 kcal/mol, respectively. Again, the lower RMSD values are found for the potential AP with a value of approximately 0.04 kcal/mol. As can be noted, the quality of the computed potentials critically depends upon the size of the basis set employed.

To conclude this section the potential energy curves for ground electronic states of N_2, O_2, and SO, are plotted in Figures 3 to 5. For convenience, in both cases, we used only the analytical representation proposed by Aguado and Paniagua (see Eq. (3.440)) together with basis set aug-cc-pVXZ where X is the cardinal number of the basis set (X = T, Q, 5, 6). For comparison, the theoretical data are available in Refs. [226] for N_2, [227] for O_2, and [228, 229] for SO are also included in this work. We justify the choice of these works mainly because their results reproduce well the experimental energies. Therefore, they are very close to spectroscopic accuracy.

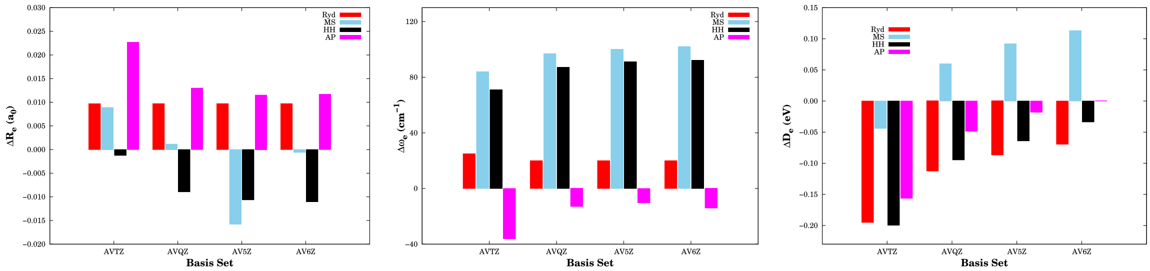
Figure 3 exhibits the curves for the ground electronic state of the N_2 molecule obtained in this work, along with the PEC extracted from the double many-body expansion (DMBE) potential energy surface for ground state HN_2 [226]. We highlight that the analytical form used by Poveda and Varandas to fit the *ab initio* points for nitrogen molecule is based on the EHFACE2U model [168]. It can be seen from this plot, the potential curves computed for AV5Z (dashed black line) and AV6Z (dashed magenta line) indicate excellent agreement for all points except in the region between $3.5 \leq R/a_0 \leq 5.0$, where the energies of the EHFACE model (circles) are lower than our potential curves. In addition, the major difference (around of 0.013 E_h or 0.35 eV) is observed in the zoom of this same figure if we compare the energies calculated at AVTZ (solid red line) basis set and the EHFACE model in the range of 1.8 a_0 to 2.4 a_0.

Figure 4 shows our potential energy curves now for the oxygen molecule, together with the *ab initio* energies reported by Bytautas *et al.* [227]. The electronic energies for $X^3\Sigma_g^-$ were calculated with the CBS limit, in addition, corrections such as the scalar relativity, spin-orbit coupling, and the core-electron correlation are included. The energies, namely, CBS+SR+SO+CV are listed in the last column of Table I from Ref. [227]. As before, our results at AVXZ (X = 5,6) basis set are in agreement with those previously reported in Ref. [227] within the range of internuclear distances considered here. When examining the inset of this same figure, we observe that there



(a) (b) (c)

Figure 5.6: Largest basis set used versus differences between our results obtained with the setup of table 5.1 and the experimental data: (a) ΔR_e, (b) $\Delta\omega_e$, (c) ΔD_e for N_2 molecule. The experimental values of 2.0743 a_0, 2358 cm^{-1}, and 9.9008 eV are from Ref. [231].

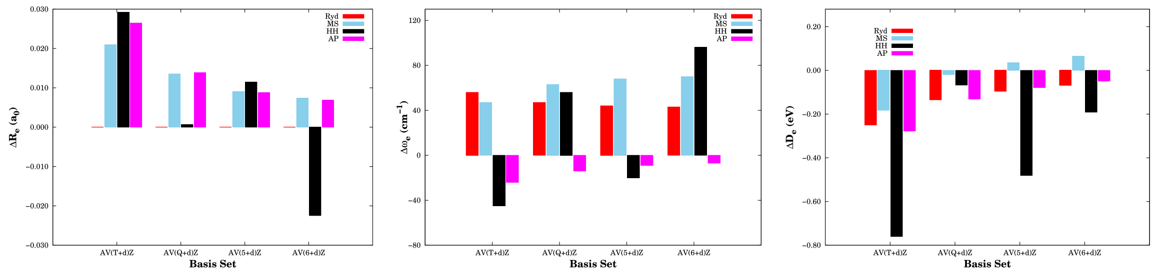


(a) (b) (c)

Figure 5.7: Largest basis set used versus differences between our results obtained with the setup of table 5.2 and the experimental data: (a) ΔR_e, (b) $\Delta\omega_e$, (c) ΔD_e for O_2 molecule. The experimental values of 2.280 a_0, 1580 cm^{-1}, and 5.197 eV are from Ref. [96].

are slight differences around the minimum between AVTZ basis set and the other ones.

Finally, in Figure 5 are represented potential energy curves for the sulfur monoxide molecule. The circles represent *ab initio* energies reported by Borin and Ornellas at internally contracted multireference configuration interaction (icMRCI) level of theory with the cc-pVQZ basis set [228]. For completeness, the solid green line illustrates the PEC for SO molecule extracted from the DMBE potential energy surface for ground state SO_2 [229, 230]. Again, the diatomic interactions are represented according to the EHFACE2U model. It can be noted that the electronic energies in function of internuclear distances listed in column 2 of Table 1 (Ref. [228]) are between our results obtained from the AV(T+d)Z (solid red line) and AV(Q+d)Z (dashed blue line) basis set (see zoom in the minimum region). There are small differences in all energies, in particular, in the energies calculated at AV(T+d)Z basis set are larger than EHFACE2U model (0.009 E_h or 0.24 eV).



(a) (b) (c)

Figure 5.8: Largest basis set used versus differences between our results obtained with the setup of table 5.3 and the experimental data: (a) ΔR_e, (b) $\Delta\omega_e$, (c) ΔD_e for SO molecule. The experimental values of 2.7986 a_0, 1148 cm^{-1}, and 5.429 eV are from Ref. [96].

5.2.2 Spectroscopic parameters

Based on PECs obtained by fit *ab initio* points, we computed the ground state spectroscopic parameters of the molecules analyzed here determined from the Eqs. (3.79), (3.181), (3.314), and (3.440). These results are presented in the Tables 5.1 to 5.3 and can be seen graphically in the Figures 5.6 to 5.8. The column one of all tables indicates the analytical form used in the fit, whereas the basis sets are given in column two. The third, fifth, and seventh columns of these tables show calculated values of the equilibrium bond distances R_e, harmonic vibrational frequencies ω_e, and the potential well depth D_e. The relative differences between the available experimental data and the results obtained by us given by $\Delta Y/Y$ ($Y = R_e$, ω_e, and D_e), are displayed in the fourth, sixth, and eighth columns, and are expressed in percentages. The experimental values adopted in this work were obtained from Refs. [231] for N_2 and [96] for O_2 and SO molecules. For completeness, the anharmonicity parameter ($\omega_e x_e$) from our curves and its comparison with the corresponding experimental values ($\Delta\omega_e x_e$) are also shown in last columns.

Although higher values of RMSD are found for the functional forms of RYD, MS and HH, it can be seen from these tables that in general, some spectroscopic parameters obtained by these analytical representations appear to be close to the experimental results. Note that in Figs. 5.6, 5.7, and 5.8 the red bars represent the Rydberg function, while in blue it refers to the Murrell-Sorbie potential. The black and magenta bars are used to refer to the potential HH and AP, respectively.

Notice now the results of the Table 5.1. Note that when we compare the bond lengths calculated by us with experimental values [231] for ground state N_2 molecule, we obtained a very good agreement with relative differences of $0 \leq \Delta R_e/R_e \leq 0.84$, in percentages. Surprisingly, the results for the Rydberg function (the earliest studied here) presents almost negligible ΔR_e since their root-mean-square deviation results overestimate the threshold of chemical accuracy by about 1.2 kcal/mol. Analyzing the fourth column, the consistently increasing quality with increasing base set size only

Table 5.4: Spectroscopic parameter from available results for $N_2(X^1\Sigma_g^+)$ molecule.

Method	R_e (a_0)	ω_e (cm^{-1})	D_e (eV)	Source
NOF-OIMP2/VTZ	2.0749	-	10.004	[232]
RHF	2.0862	2971	-	[233]
CCSD(T)/V6Z	2.0732	2370	-	[234]
RMR CCSD(T)/VQZ	2.0813	2343	9.893	[235]
Exp.	2.0743	2358	9.9008	[231]

for the potential AP is remarkable. However, the results of other functions exhibit inverse behaviour, *i. e.*, increasing the size of the basis set produces bond lengths less precise. This is the case, for example, of the MS function where we obtained DeltaR_e/R_e equal to 0.36% for AVTZ, 0.42% for AVQZ, 0.73% for AV5Z, and 0.75% for AV6Z. In contrast, the AP functions provide the following values for this relation: 0.84% for AVTZ, 0.42% for AVQZ, 0.43% for AV5Z and 0.41% for AV6Z. The Hulburt-Hirschfelder potential yields close values with experimental differences of: AVTZ $\sim 0.007a_0$, AVQZ $\sim 0.008a_0$, AV5Z $\sim 0.001a_0$, and AV6Z $\sim 0.001a_0$. Such information can be seen of form summarized in Fig. 5.6 (a).

In the sixth column of the Table 5.1, note that the vibrational frequencies present relative differences, with $\Delta\omega_e/\omega_e$ between 0.38 and 5.0%. Comparing the values obtained for ω_e for the four potentials in question, we conclude that the best result is obtained when the functional form proposed by Aguado and Paniagua is used at MRCI(Q)/AVXZ (X = T,Q,5,6) level of theory (see also Fig. 5.6 (b)).For this particular potential, our theoretical harmonic vibrational frequencies differ by less than 1.4% of the experimental values from Ref. [231]. Concerning to Rydberg function a similar results emerges from our analysis (around 1.6%), with deviations close to 38 cm^{-1} (in red), while for the MS potential are overestimated in $\sim$ 118 cm^{-1}. In addition, with respect to cardinal number X of the basis set, we obtained the values 2418, 2434, 2443, and 2445 cm^{-1}, corresponding to HH potential. In Fig. 5.6 (b), we identify that $\Delta\omega_e$ for these values (in black) slightly increases with the basis set as well as for Murrell-Sorbie potential (in blue), except in the case of aug-cc-pVQZ basis.

Further, in Table 5.1, the dissociation energies (D_e), obtained using all potentials are unexpectedly larger than the corresponding experimental values, relative differences are between 0.54 to 23.48 %. This large error can be partly attributed to the fit process, in particular for AVTZ basis. Energetically, the MS potential seems to represents reasonably well the experimental value of 9.9008 eV [231], however it may differ quantitatively in more than 7% when Dunning's augmented correlation consistent valence triple-ζ basis set (aug-cc-pVTZ) is used (see Fig. 5.6 (c)). From Fig. 5.2, one can see that the Murrell-Sorbie function has a larger depth in the well than the other functions described. This fact indicates consistency in our results. Moreover, according to Ref. [236] the reliable description of the dissociation profile of the ground state of the nitrogen molecule is a difficult problem for any *ab initio* method due to the presence of strong dynamical and nondynamical correlation effects.

Besides this study, a series of theoretical spectroscopic investigations have been performed about the N_2 system [232–235]. For the convenience of comparison, all these results are described in Table 5.4. In these investigations, probably the first calculations for this system, made by Fraga and Ransil [233], were made through the Hartree-Fock (RHF) restricted method. Their R_e and ω_e values are larger than the experimental results [231] by $0.01a_0$ and 613 cm^{-1}, respectively. Pawlowski et al. [234] computed the values of molecular properties by using the MP2/CCSD(T) level of theory in combination with a series of correlation-consistent basis sets. From what we know, the depth of the well was not calculated in their work. The bond length and harmonic frequency values calculated at CCSD(T)/V6Z differ of ours results with the AP function/AV6Z (and experimental) in $\sim$ 0.009 $(0.001)a_0$ and 24 (12) cm^{-1}. Subsequently, the treatments of the nitrogen molecule using the RMR CCSD and RMR CCSD(T) methods was verified by Li and Paldus [235]. As results, in both cases, the spectroscopic constants perform well when compared to the experimental ones. More recently, Piris using the formulation of the natural-orbital-functional second-order-Moller-Plesset (NOF-MP2) calculated binding energies and bond lengths for this system and others [232]. In general, the present spectroscopic parameters for the ground state of N_2 are in good agreement with the experimental [231] and previous theoretical data [232, 235].

Now, a complete discussion about the results from Table 5.2 and Fig. 5.7 for oxygen molecule is done. When equilibrium bond distances (R_e) are analyzed, the best value found corresponds to the relative difference of 0.02% for MS potential at MRCI(Q)/AV6Z level. In Fig. 5.7 (a), the Rydberg potential (in red) displays values almost constants around $0.01a_0$. On the other hand, the Table 5.2 shows that the deviations are in the range $0\% \leq \Delta R_e/R_e \leq 1.0\%$, which is in general agreement with Ref. [96]. An unusually large error in the AP representation leads to bond lengths with slightly overestimated (AVTZ basis), and they are more accurately predicted with the aug-cc-pV6Z basis. As one can see from Fig. 5.7 (a) or in the Table 5.2, Rydberg and HH predictions do not improve when larger basis are used for the bond lengths. However, the O2 bond lengths are very good with the AVXZ (X = Q, 6) basis sets, with small relative errors.

The relative errors in harmonic vibrational frequencies (ω_e) are represented in Fig. 5.7 (b). The MS function predictions show a typical error 80 to 100 cm^{-1} overestimate in most cases, whereas the AP frequencies are considerably improved, with most errors less than or equal to 1%. Obviously, the value 1569 cm^{-1} based on AV5Z is the best compared to the experimental value [96] of 1580 cm^{-1}, there is no significant deviation in this case. The values of ω_e for the Hulburt-Hirschfelder representation deviate from

Table 5.5: Spectroscopic parameter from available results for $O_2(X^3\Sigma_g^-)$ molecule.

Method	R_e (a_0)	ω_e (cm^{-1})	D_e (eV)	Source
B3P86/CC-PV5Z	2.2676	1645	5.22	[237]
DFT/ET-QZ3P-3Diffuse	2.2733	1621	-	[238]
CI	2.3054	1614	4.72	[239]
DFT/B3LYP	2.2790	1585	5.96	[240]
MRCI(Q)	2.2979	1522	5.09	[240]
CASPT2	2.2884	1536	5.17	[240]
Exp.	2.280	1580	5.19	[96]

the experiment results by 4.49%, 5.50%, 5.75%, and 5.82%, respectively for the basis AVXZ (X = T, Q, 5, 6). As before, the Rydberg interaction potential (in red) shows almost constant values for vibrational frequency (near to 1600 cm^{-1}). Note that this same behaviour was observed in Fig. 5.6 (b). From the information contained in this figure and those displayed of Table 5.2 (sixth column), we can easily find that the big errors of harmonic frequencies are obtained between the functional forms of MS (blue) and HH (black).

From the energetic point of view, we found the following results:

(i) relative differences of $0.01 \leq \Delta D_e/D_e \leq 8.0$, in percentage, were calculated being the depth of the well major described when the AP function in aug-cc-pV6Z basis set is used (5.19745 eV);

(ii) as well as for N_2, here the spectroscopic constant D_e tends to smaller differences from the experimental values at MRCI level of theory with Davidson correction if we increase cardinal numbers (X = T, Q,5, and 6) of basis, however, MS (blue) does not exhibit this behaviour see Fig. 5.7 (c);

(iii) our results with Rydberg are underestimated by 8.55%, 4.93 %, 3.80 %, and 3.03 %. compared to experimental values [96]. On the other hand, the AVXZ (X = Q, 5, 6) basis set for MS are overestimated by 2.61 %, 4.02 %, and 4.96 %. It can be clearly seen in Fig. 5.2 that the well for MS is deeper than Ryd potential.

For completeness, available theoretical results from the literature are summarized in Table 5.5. We are also including the experimental ones from Ref. [96]. Guan *et al.* calculate using time-dependent density functional theory (TDDFT) with Tamm-Dancoff approximation (TDA) spectroscopic properties and potential energy curves for the six lowest bound electronic states of the oxygen molecule. In Table IV, it can be seen that their theoretical values for the ground state at this level of theory provides: R_e near to experimental one and ω_e it is overestimated by $\sim 41 cm^{-1}$. Our values obtained from the AP function/AV5Z for the harmonic frequency (1569 cm^{-1}) and equilibrium bond distance (2.2915a_0) it seems to be better than of these, mainly ω_e. Dong-Lan *et al.* [237] proposed a potential energy surface for SO_2 in the ground

Table 5.6: Spectroscopic parameter from available results for $SO(X^3\Sigma^-)$ molecule.

Method	R_e (a_0)	ω_e (cm^{-1})	D_e (eV)	Source
icMRCI/VQZ	2.8213	1137	-	[228]
icMRCI(Q)/AV5Z	2.8090	1149	5.418	[241]
CI	2.8326	1200	-	[242]
DFT/B3LYP	2.8194	1129	5.72	[240]
MRCI(Q)	2.8289	1130	5.32	[240]
CASPT2	2.8043	1125	5.40	[240]
Exp.	2.7986	1148	5.429	[96]

electronic state using the many-body expansion theory. Table 2 and 3, from Ref. [237] contains features such as R_e, ω_e, and D_e removed of two-body terms not only for O_2 but also for SO molecule. There, the diatomics (O_2 and SO) are modeled by the MS potential function (Eq. (3.314)) minus a extra term (c_6/R^6). As results, the vibrational frequency is larger than the experimental one in at least 65 cm^{-1} and the depth of the well and equilibrium internuclear distance are in good agreement with your respective experimental values. However, the reported values of Schaefer obviously deviate from Ref. [96], see Table 5.5 for details. At last, comparing some of our results with those of Azizi *et al.* [240] slight differences are found. According to them, calculations at second-order multiconfigurational perturbation theory (CASPT2) and MRCI(Q) are of comparable accuracy for few-electron systems.

For the sulfur monoxide in the ground electronic state, the spectroscopic features of the functional forms used to fitting *ab initio* points of this molecule are displayed in Table 5.3 and Fig. 5.8. The triplet state considered here converge to the dissociation limit $S(^3P) + O(^3P)$. Looking at basis set effects, all binding energies calculated are lower than the experimental one. In opposition to this, the Murrell-Sorbie energies at AV5Z and AV6Z are above by $\sim$ 0.03 and 0.06 eV, respectively. These values are close to D_e (5.429 eV) reported in Ref. [96], however, the harmonic frequencies tend to increases in approximately 40 cm^{-1}. Again, the best results observed in Table 5.6 are for the Aguado and Paniagua function in combination with AV(6+d)Z basis ($R_e = 2.8057\,a_0$, $\omega_e = 1141\,cm^{-1}$, and $D_e = 5.3805\,eV$). The same tendency holds when analysing nitrogen and oxygen molecules (Tables 5.1 and 5.2). As can be seen from Table 5.3, the equilibrium bond lengths obtained for Rydberg functions reproduce the experimental value. On the other hand, this fact does not reflect better results of the other molecular features. For example, according to the present table, the frequencies for different basis sets are 1204, 1195, 1192, and 1191 cm^{-1}.

It is interesting to note that in Figs. 5.8 (a), (b), and (c), the Hulburt-Hirschfelder representation show higher deviation percentages in almost all spectroscopic constants chosen, see also Table 5.3 for complementary informations. So, one verified that for our purpose this function is inefficient compared the other ones. We infer that this fact can be directly connected with the values found in Fig. 5.1(c). In general, the bond lengths and harmonic frequencies estimate for the AP function are acceptable (less than 2.1 %).The main variations are predicted in the binding energy: 9.91%, 4.65%, 2.81%, and 1.72%, respectively for AV(T+d)Z, AV(Q+d)Z, AV(5+d)Z, and AV(6+d)Z.

Over the years many works have been done to SO system certainly due to its high reactivity. Historically, the sulfur monoxide has been detected in interstellar clouds and in the atmosphere of planets [243]. Its interest goes beyond the astrophysical studies being necessary in areas such as combustion [244] and photodissociation [245]. From an extensive literature, the spectroscopic properties of both experimental and theoretical were chosen from Refs. [228, 240–242] in order to comparison with our results. These values are conveniently listed in Table 5.6. As discussed, Borin and Ornellas calculated *ab initio* PECs at icMRCI/VQZ level of theory with the intention to study the singlet and triplet states of sulfur monoxide. As results, deviations from the experimental values for ground state (triplet state) were obtained by differences of $0.0227a_0$ for bond length and 11 cm^{-1} for vibrational frequency. These data show smaller variations of our best results: $0.0156a_0$ and 4 cm^{-1}. Unfortunately, an important constant, D_e, was not evaluated. In 2011, Yu and Bian performed the icMRCI calculations in combination with the aug-cc-pV5Z basis sets. The R_e, ω_e, and D_e values they provide for the $SO(X^3\Sigma^-)$ are $2.8090a_0$, 1149 cm^{-1}, and 5.418 eV, respectively. It is observed good accord between the present spectroscopic parameters and our results, and consequently, with experimental ones. Tabulated is also the data from Ref. [242]. There, a complete study for seven low-lying electronic states of sulfur monoxide is reported by Swope *et al.* carried out using configuration interaction (CI). They were found that ω_e it is overestimated around 52 cm^{-1}. Again, D_e was not evaluated for this work also. All other results are shown in table 5.6 one refer to Ref. [240] except the last line (Exp.) that contain values from Ref. [96]. It is interesting to note that all harmonic vibrational frequencies are smaller in relation to 1148 cm^{-1} [96]. In the contrary, There are a disagree for R_e, in a_0, by $\sim$ 0.0208 (DFT/B3LYP), 0.0303 (MRCI(Q)), and 0.0057 (CASPT2).

In general, our best spectroscopic constants predicted are in excellent agreement with theoretical and experimental results. Therefore, we can conclude that the AP function obtained at MRCI(Q)/ aug-cc-pV6Z level of theory can well describe the interaction potential of the sulfur monoxide molecule in the ground state. Furthermore, the same functional form presents similar results for other molecules investigated by us.

6 Methodology to obtain Accurate Potential Energy Functions for Diatomic Systems: A Mathematical point of view

As we saw in the previous chapters, there is no analytical representation of potential energy capable of accurately describing correct curves for all diatomic systems. Despite this, some of the potentials listed, describe satisfactorily the energy of interaction for a reasonable number of systems, mainly in their ground electronic state. In contrast, for excited states, there are few precise analytical models and, in general, these can be applied to a very small number of diatomics.

In this chapter our goal will be to suggest a mathematical step-by-step used to build potential models that well describe the energy of interaction of two bodies.

6.1 The choice of functions

In general, the more accurate and appropriate 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 $V(R)$ must satisfy 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)$\to \infty$.

Why choose such functions? Although we are talking about a function that describe a physical problem, we will find the answer first in mathematics. Let us begin our discussion with the Dunham potential, who can be considered "the father" of analytical potentials.

Dunham derived relationships to calculate the most important spectroscopic parameters (see Section 2.2). Note that, they depend on derivatives of potential. Then, the "ideal" potential energy function must satisfy some mathematical properties related with derivative 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.

6.2 Mathematical theory

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.

Note that the spectroscopic parameters in Eqs. (2.56), (2.57), (2.58) and (2.59) are obtained from derivatives of the potential at R_e, the equilibrium distance.

Definition 6.1. *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.* [246], p.52). The derivative of function V at point a is the limits

$$V'(a) = \lim_{x\to a} \frac{V(x) - V(a)}{x - a} = \lim_{h\to 0} \frac{V(a+h) - V(a)}{h}. \tag{6.1}$$

Theorem 6.1. *For the function $V : X \to \mathbb{R}$ to be derivable 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 6.1. *A function is continuous at points at which it is derivable.*

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 function is derivable (just remember the function $f(x) = |x|$).

Definition 6.2. *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 the derivatives $V', V'', \cdots, V^{(n)}$ exist and are continuous* [246].

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

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

Definition 6.3. *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 $|x - a| < \delta \Rightarrow |V(x) - V(a)| < \epsilon$* [246].

Theorem 6.2. *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 $V(x_n) = V(a)$* [246].

Corollary 6.2. *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. In addiction, if $U(a) \neq 0$, the function $V/U : X \to \mathbb{R}$ is continuous at a* [246].

This corollary is very important 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 results above, we can state:

Statement 6.1. *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 6.2. *All exponential function $e : \mathbb{R} \to \mathbb{R}^*$, where $\mathbb{R}^*$ denotes $\mathbb{R} - \{0\}$, is continuous and derivable 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 known that one of the characteristic of the BO potential energy function is that $V(R)$ should assumes 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 behaviour at infinity the potential will be useless for studying atomic collisions, or even for high-energy rotation-vibration states of the system [56].

This can be a problem when dealing with infinite expansions in 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 6.4. *A power series is a function given by [246]*

$$V(x) = \sum_{n=0}^{\infty} a_n (x - x_0)^n = a_0 + a_1(x - x_0) + \cdots + a_n(x - x_0)^n + \cdots . \tag{6.2}$$

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

Theorem 6.3. *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 a 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 6.4. *Suppose that r is the convergence radius of power series $\sum_{n=0}^{\infty} a_n(x - x_0)^n$. The function $V : (-r, r) \to \mathbb{R}$, defined by $V(x) = \sum_{n=0}^{\infty} a_n(x - x_0)^n$, is derivable, with $V'(x) = \sum_{n=0}^{\infty} n\, a_n(x - x_0)^{n-1}$, and the power series of $V'(x)$ still has a convergence radius equal to r.*

This theorem ensure that if the candidate function has a convergence radius r, then it will automatically derivable 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.

Statement 6.3. *The power series*

$$\sum_{n=0}^{\infty} \frac{x^n}{n!}, \tag{6.3}$$

converges for all $x \in \mathbb{R}$, then the function $V : \mathbb{R} \to \mathbb{R}$, defined by $V(x) = \sum_{n=0}^{\infty} \frac{x^n}{n!}$ 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 [246]

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots . \tag{6.4}$$

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

6.3 Discussion

Returning to the Dunham potential (2.44), where $\xi = (R - Re)/Re$, we have

$$V_D = a_0[(R - R_e)/R_e]^2 \left\{ 1 + \sum_{i=1}^{N} a_n[(R - R_e)/R_e]^n \right\} . \tag{6.5}$$

Note that this power series expansion is derivable and therefore continuous for all $R \in \mathbb{R}$. However, the convergence is not exactly what is required.

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 the well known Morse [8],

$$V_{MOR}(R) = D_e e^{-2a(R-R_e)} - 2D_e e^{-a(R-R_e)}. \tag{6.6}$$

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. In addiction, this function is derivable 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 behaviour, where the 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. In addition, they have the characteristics of potentials that we want to unite: one is composed only by exponentials and the other by a series of powers.

The history [247] and recent comparative studies [23] have shown that, in general, the most accurate analytical potential energy functions are obtained joining both functions. We can list the following functions as good examples of accurate analytical potentials:

(i) Extended Rydberg [60, 131]

$$V_{ER}(R) = D_e(1 + a_1(R - R_e) + a_2(R - R_e)^2 + a_3(R - R_e)^3)e^{-\gamma(R-R_e)}. \tag{6.7}$$

(ii) Varshni III [14]

$$V_{VAR_{III}}(R) = D_e\left\{1 - \frac{R_e}{R}\exp\{[-\beta(R^2 - R_e^2)]\}\right\}^2 \tag{6.8}$$

(iii) Levine [124]

$$V_{LEV}(R) = D_e\left\{1 - \frac{R_e}{R}\exp\{[-a(R^p - R_e^p)]\}\right\}^2. \tag{6.9}$$

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

The Hulburt-Hirschfelder [7] potential

$$V_{HH}(R) = D_e[(1 - e^{-x})^2 + (1 + bx)cx^3e^{-2x}] \tag{6.10}$$

does not appear in this list, although it apparently corresponds to the type of function we are search. 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 (described above) that are sums and/or product of exponential by polynomials, and in this case, they have adjustable parameters:

(i) EHFACE2U [168]

$$V_{EHFACE2U} = V_{EHF} + V_{dc} \tag{6.11}$$

where

$$V_{EHF}(R) = -DR^{\alpha}\left(1 + \sum_{i=1}^{3} a_i r^i\right)\exp(-\gamma r), \tag{6.12}$$

and

$$V_{dc} = -\sum_{n=6,8,10,\cdots} C_n^{AB}\chi_n(R)R^{-n} \tag{6.13}$$

(ii) Aguado and Paniagua [180]

$$\mathrm{V_{AP}}^{(2)}(\mathrm{R_{AB}}) = \mathrm{V_{short}}^{(2)} + \mathrm{V_{long}}^{(2)} \tag{6.14}$$

where

$$\mathrm{V_{short}}^{(2)} = \frac{\mathrm{c_0 e^{-\alpha_{AB} R_{AB}}}}{\mathrm{R_{AB}}} \tag{6.15}$$

and

$$\mathrm{V_{long}}^{(2)} = \sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{c_i}\rho^{\mathrm{i}}{}_{\mathrm{AB}} \tag{6.16}$$

Both potentials satisfy all the criteria described in chapter 4. 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 a large number of different diatomic systems in their fundamental and excited electronic states (see more details in Ref [247]).

6.4 Results

In this section, we will describe a methodology for how to build a potential, based on Dunham's potential.

1. First, two functions that satisfy all the criteria described in section 4 must be chosen, one being a polynomial expansion and the other an exponential one. (A tip: do not choose a function exactly like Dunham or Morse, as they already know that they do not meet all requirements);

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 $R \to \infty$;

3. The function can be given by:

$$V(R) = b_0 G^2(R) F^2(R) \left(1 + \sum_{i=1}^{N} b_n G^n(R) \right). \tag{6.17}$$

   where $F(R)$ is a exponential-type function, $G(R)$ 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 [9–11] potential derived from the energy levels of Eq. (2.48) (see Ref. [248]). 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:

$$\begin{aligned} & b_0 G^2(R) F^2(R) \left(1 + \textstyle\sum_{i=1}^{N} b_n G^n(R)\right) \\ & \quad = a_0[(R - R_e)/R_e]^2 \left\{1 + \textstyle\sum_{i=1}^{\infty} a_n[(R - R_e)/R_e]^n\right\} \end{aligned} \tag{6.18}$$

5. Now, a simple way to obtain coefficients b_n can be followed: taken the derivatives of both sides with respect 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 well used to obtain potential energy surfaces. One of the difficulties that may arise is in relation to obtaining 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. Thus, to use this method, the function must not have a degree greater than 8.

7 A New Generalized Potential Energy Function for Diatomic Systems

Despite the recent development of new and upgraded numerical approximations to solve the electronic problem, the state-of-the-art ab initio methodologies are not extensively used in systems with a large number of electrons [249, 250]. In turn, spectroscopic measurements, without the theoretical limitations, provide accurate data for such systems.

Therefore obtaining an accurate curve directly from experimental spectroscopic data is an interesting pathway.

Thus, in this chapter we introduce a new generalized potential for diatomic systems fine-tuned with spectroscopic information. Such a function is here tested for 22 diatomic systems comprising ground and excited electronic states. To quantify the accuracy of the analytical representations, we followed the least-squares Z-test method proposed by Murrell and Sorbie [60]. Spectroscopic parameters R_e, D_e and w_e, and the Morse [8] parameter α, are also calculated and compared with experimental data [96].

7.1 Potential Energy Function

The proposed generalized potential energy function for diatomic systems is given by:

$$V(R) = \begin{cases} \sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right) \left(\frac{R-R_e}{R}\right)\right]^n, \ R \leq R_e \\ \\ D_e \left[\frac{(1-e^{-2\alpha(R-R_e)})}{(1+e^{-\gamma\alpha(R-R_e)})}\right]^2, \ R > R_e \end{cases} \tag{7.1}$$

where $\beta = \frac{1}{3}\alpha$, being α the Morse [8] parameter, γ is a fine-tuning parameter $1 \leq \gamma \leq 3$, to be fixed by direct comparison with RKR data, R_e is the equilibrium distance and the c_n, $n = 2, \cdots, 8$ coefficients are related with the Dunham [24] coefficients.

The coefficients c_i has been obtained from relationships between derivatives of the new potential and derivatives of Dunham's potential. In last chapter, we have seen that the region of its convergence, the Dunham potential converges to the RKR potential derived from the energy levels of [248]

$$F_{\nu J} = \sum_{lj} Y_{lj} \left(\nu + \frac{1}{2}\right)^l J^j (J+1)^j. \tag{7.2}$$

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:

$$\begin{aligned} &\sum_{i=2}^{8} c_n \left[\left(1 + e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right)\left(\frac{R-R_e}{R}\right)\right]^n \\ &= a_0[(R-R_e)/R_e]^2 \left\{1 + \textstyle\sum_{i=1}^{\infty} a_n[(R-R_e)/R_e]^n\right\}. \end{aligned} \tag{7.3}$$

Derivatives of the two sides with respect to R have been taken and equated at $R = Re$. These resulted in expressions that relate the new potential coefficients c_n and the Dunham coefficients a_n, given by equations:

$$c_2 = \frac{1}{4} a_0; \tag{7.4}$$

$$c_3 = \frac{1}{8}\left[a_0 a_1 + 8(1+\beta)c_2\right] \tag{7.5}$$

$$c_4 = \frac{1}{16}\left[a_0 a_2 + 24(1+\beta)c_3 - 4(3\beta^2 + 4\beta + 3)c_2\right]; \tag{7.6}$$

$$\begin{aligned} c_5 = \tfrac{1}{32}&\left[a_0 a_3 + 64(1+\beta)c_4 - 4(12\beta^2 + 18\beta + 12)c_3\right. \\ &\left.+4\left(\tfrac{10}{3}\beta^3 + 6\beta^2 + 6\beta + 4\right)c_2\right]; \end{aligned} \tag{7.7}$$

$$\begin{aligned} c_6 = \tfrac{1}{64}&\left[a_0 a_4 + 160(1+\beta)c_5 - 4(40\beta^2 + 64\beta + 40)c_4\right. \\ &+4\left(18\beta^3 + 36\beta^2 + 36\beta + 20\right)c_3 \\ &\left.-4\left(3\beta^4 + \tfrac{20}{3}\beta^3 + 9\beta^2 + 8\beta + 5\right)c_2\right]; \end{aligned} \tag{7.8}$$

$$\begin{aligned} c_7 = \tfrac{1}{128}&\left[a_0 a_5 + 384(1+\beta)c_6 - 4(120\beta^2 + 200\beta + 120)c_5\right. \\ &+4\left(\tfrac{224}{3}\beta^3 + 160\beta^2 + 160\beta + 80\right)c_4 \\ &-4(22\beta^4 + 54\beta^3 + 72\beta^2 + 60\beta + 30)c_3 \\ &\left.+4\left(\tfrac{34}{15}\beta^5 + 6\beta^4 + 10\beta^3 + 12\beta^2 + 10\beta + 6\right)c_2\right]; \end{aligned} \tag{7.9}$$

$$
\begin{aligned}
c_8 = \tfrac{1}{256}\,[a_0 a_6 &+ 896(1+\beta)c_7 - 4(336\beta^2+576\beta+336)c_6 \\
&+4\left(\tfrac{800}{3}\beta^3+600\beta^2+600\beta+280\right)c_5 \\
&-4\left(\tfrac{340}{3}\beta^4+\tfrac{896}{3}\beta^3+400\beta^2+320\beta+140\right)c_4 \\
&+4\left(\tfrac{114}{5}\beta^5+66\beta^4+108\beta^3+120\beta^2+90\beta+42\right)c_3 \\
&-4\left(\tfrac{22}{15}\beta^6+\tfrac{68}{15}\beta^5+9\beta^4+\tfrac{40}{3}\beta^3+15\beta^2+12\beta+7\right)c_2\,]\,.
\end{aligned}
\tag{7.10}
$$

The potential (7.1) satisfies the necessary continuity conditions in $R = R_e$:

(a) Note that

$$
\begin{aligned}
\lim_{R\to R_e^-}\sum_{i=2}^{8} c_n\left[\left(1+e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right)\left(\frac{R-R_e}{R}\right)\right]^n &= 0 \\
\lim_{R\to R_e^+} D_e\left[\frac{(1-e^{-2\alpha(R-R_e)})}{(1+e^{-\gamma\alpha(R-R_e)})}\right]^2 &= 0.
\end{aligned}
\tag{7.11}
$$

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

$$
\begin{aligned}
\lim_{R\to R_e^-}\frac{d}{dR}\left[\sum_{i=2}^{8} c_n\left[\left(1+e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right)\left(\frac{R-R_e}{R}\right)\right]^n\right] &= 0 \\
\lim_{R\to R_e^+}\frac{d}{dR}\left[D_e\left[\frac{(1-e^{-2\alpha(R-R_e)})}{(1+e^{-\gamma\alpha(R-R_e)})}\right]^2\right] &= 0.
\end{aligned}
\tag{7.12}
$$

In addition, the new potential (7.1) satisfies the following necessary criteria [14]:

(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.

The precise calculation of Dunham's coefficients a_i, with $i > 6$, is extremely complicated (some of them can be obtained from Refs. [138, 251]). Sometimes inaccuracies are found even for a_3 or a_4. Once the proposed potential converges at $R = \infty$, Eq. (7.1) gives:

$$
D_e = \sum_n c_n, \tag{7.13}
$$

when the value of if D_e is known, the latter equation can be used to estimate an additional coefficient c_n. More precise values for parameters that depend on Dunham's highest coefficients can also be obtained in this way, ensuring correct dissociation in regions where R is large.

To quantify the accuracy of the various potentials, we used the least-squares Z-test method proposed by Murrell and Sorbie [60], described in Section 3.1.26.

7.2 Results and Discussion

The new potential energy function is very flexible, and it can have between five and eleven parameters directly obtained from experimental data. This is an important issue, especially when we consider the calculation of potential energy of diatomic systems formed by heavier atoms and/or with many electrons, such as I_2, BiI, Cs_2, Mg_2, Na_2 and others. For these types of systems, the ab initio calculation is still very expensive due to a large number of integrals [252] and the size of the base of functions that diatomic systems with these characteristics demand.

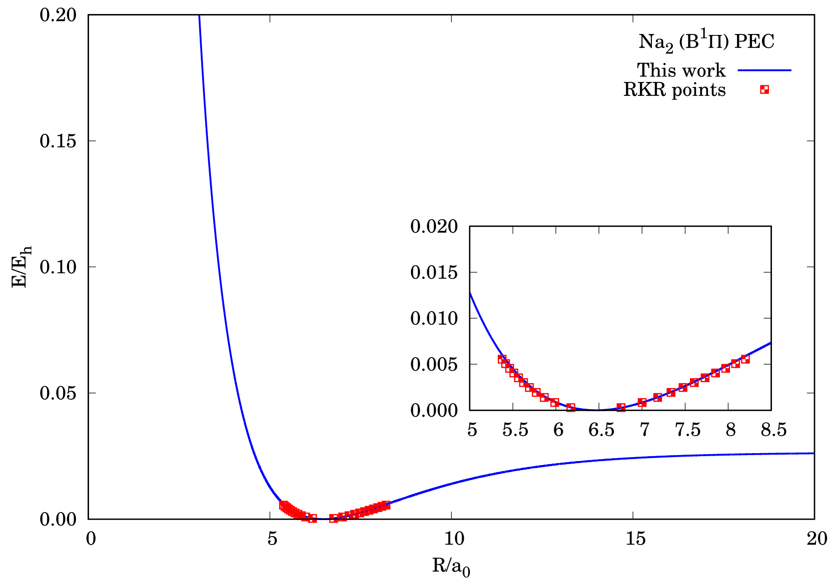


Figure 7.1: Comparison, for Na_2 ($B^1\Pi$), of the New Potential (1) with the experimental RKR points from Ref. [267].

We have calculated the parameters of the new potential (7.1) for 22 diatomic systems in their ground electronic states and some in their first excited state also. At this stage, only potentials with a single minimum were studied. We select some hydrides, some non-hydrides, and some homonuclear diatomic systems. The potential energy parameters for these systems can be seen in Tables 7.1, 7.2, 7.3 and 7.4, respectively. The Z-test has been applied and the results for chosen diatomic systems are collected in Tables 7.5 to 7.26.

Table 7.1: Potential energy parameters of some Hydrides

	H_2 ($X^1\Sigma_g^+$)	HBr ($X^1\Sigma^+$)	HCl ($X^1\Sigma^+$)	HF ($X^1\Sigma^+$)	HI ($X^1\Sigma^+$)
γ	1	1	1	1	3/2
$\beta(a_0^{-1})$	0.34163	0.317970	0.328270	0.389637	0.307710
$c_2(E_h)$	0.090648	0.238267	0.240500	0.232434	0.235315
c_3	0.049423	0.023666	-	0.061110	0.007245
c_4	0.034153	0.003340	-	0.038719	-0.010474
c_5	0.024441	-0.000250	-	0.034088	-0.006899
c_6	0.020766	-0.009964	-	0.025322	-0.033020
c_7	0.017404	-0.019620	-	-	-0.050560
c_8	0.016014	-	-	-	0.005253

Table 7.2: Potential energy parameters of some further Hydrides

	HS ($X^2\Pi$)	LiH ($X^1\Sigma^+$)	NaH ($X^1\Sigma^+$)	OH ($X^2\Pi$)	SiH ($X^2\Pi$)	
γ	3/2	1	1	1	1	
$\beta(a_0^{-1})$	0.331200	0.195723	0.188879	0.404518	0.254500	
$c_2(E_h)$	0.221300	0.074888	0.079836	0.210412	0.158300	
c_3	0.033100	0.018018	0.010030	0.057625	0.014560	
c_4	-0.038700	0.005975	0.000593	0.031385	0.003180	
c_5	-0.006899	-0.045700	-	0.016560	0.023913	-
c_6	-	-	0.019008	0.016378	-	
c_7	-	-	0.023123	0.009114	-	
c_8	-	-	0.030577	0.009353	-	

Table 7.3: Potential energy parameters of some Non-Hydrides

	BiI (XO^+)	CN ($X^2\Sigma^+$)	CN ($A^2\Pi$)	CO ($X^1\Sigma^+$)	CO^+ ($X^2\Sigma^+$)	CS ($X^1\Sigma^+$)	NO ($X^2\Pi$)
γ	3	2	1	1	1	1	1
$\beta(a_0^{-1})$	0.203530	0.206379	0.405700	0.405620	0.44137	0.324980	0.483927
$c_2(E_h)$	0.280941	0.641432	0.545495	0.694217	0.70615	0.573479	0.617586
c_3	-0.164342	-0.079323	0.011975	-	-	-0.067492	-
c_4	-0.001269	-0.097787	-0.043735	-	-	-0.061932	-
c_5	-	-0.057813	-0.052448	-	-	-0.031447	-
c_6	-	-0.035160	-	-	-	-0.022906	-
c_7	-	-0.059140	-	-	-	-0.020079	-
c_8	-	-	-	-	-	-	

Table 7.4: Potential energy parameters of some Homonuclear diatomic systems

	Cs_2 ($X^1\Sigma_g^+$)	I_2 ($X^1\Sigma_g^+$)	Mg_2 ($X^1\Sigma_g^+$)	Na_2 ($X^1\Sigma_g^+$)	Na_2 ($B^1\Pi$)
γ	3	3/2	1	3/2	1
$\beta(a_0^{-1})$	0.101230	0.327810	0.192261	0.149360	0.122779
$c_2(E_h)$	0.039596	0.350619	0.008013	0.046607	0.035002
c_3	-0.002788	-0.221393	-0.009399	0.008256	-
c_4	-	-0.114230	-	-0.008496	-
c_5	-	-0.095649	-	-0.0050160	-
c_6	-	-	-	-	-
c_7	-	-	-	-	-
c_8	-	-	-	-	-

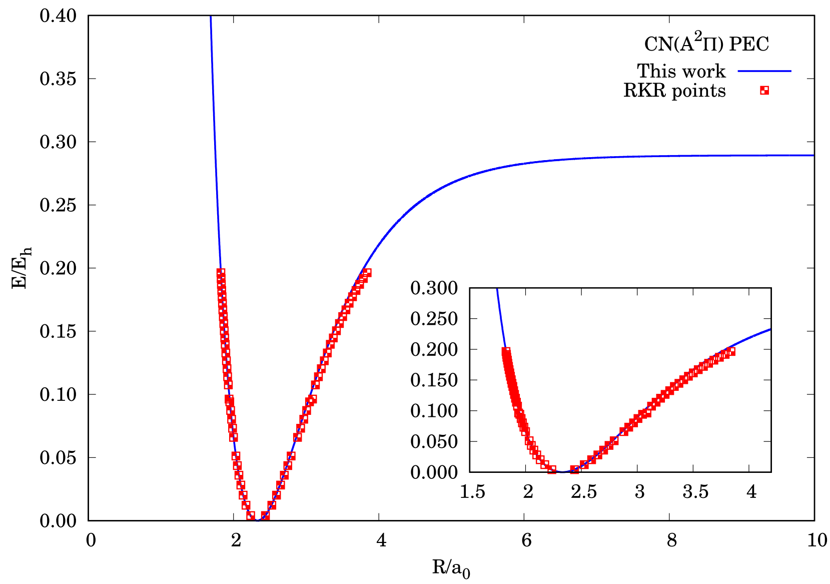


Figure 7.2: Comparison, for CN ($A^2\Pi$), of the New Potential (1) with the experimental RKR points from Ref. [256].

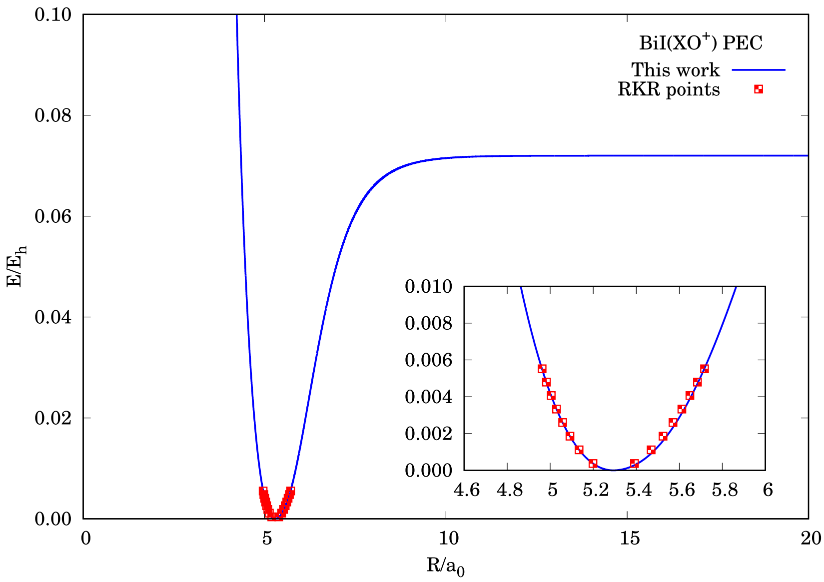


Figure 7.3: Comparison, for BiI (XO^+), of the New Potential (1) with the experimental RKR points from Ref. [254].

Specially for diatomic systems $I_2(X^1\Sigma_g^+)$, BiI(XO^+), $Cs_2(X^1\Sigma_g^+)$, $Mg_2(X^1\Sigma_g^+)$ and $Na_2(X^1\Sigma_g^+)$ the Z-test has presented very small values, all smaller than zero (remembering that Z values are given in $10^{-5}E_h{}^2\ a_0{}^{-1}$). This is an important characteristic of this new potential.

Among these cited above, two diatomic systems are especially difficult to obtain via theoretical calculation: BiI and Cs_2. Their potential energy curves are presented in Fig 7.3 and 7.4, respectively. The results of Z-test for both systems are excellent with deviations of only $0.00237\times10^{-5}E_h{}^2$ for BiI and $0.04656\times10^{-5}E_h{}^2$ for Cs_2 in whole potential range.

Furthermore, the new potential has described the diatomic systems CN($A^2\Pi$) and $Na_2(B^1\Pi)$ with good accuracy, showing that it is applicable also diatomics in their excited electronic states. The potential energy curve for $Na_2(B^1\Pi)$ and CN($A^2\Pi$) can be seen in Fig. 7.1 and 7.2, respectively.

For the ion, $CO^+(X^2\Sigma^+)$, the results of Z-test can be considered reasonable, with deviation $12.17507\times10^{-5}E_h{}^2\ a_0{}^{-1}$ in whole potential. As well as CO (see subsection 7.2.1), the potential energy function for CO^+ required only one term in the series, where $R \leq R_e$, with the potential represented by the same function (7.14).

Among the hydrides, those with the best Z-test results have been SiH($X^2\Pi$), LiH($X^1\Sigma^+$), NaH($X^1\Sigma^+$), and HI($X^1\Sigma^+$), all with Z values less than zero for three regions of the potential. See the potential energy curve for LiH($X^1\Sigma^+$) in Fig. 7.5 which presented only $0.00287\times10^{-5}E_h{}^2\ a_0{}^{-1}$ deviation from RKR points [253] in the entire potential range.

In Table 7.27 are presented the calculated and experimental values [96] of the equilibrium distance (R_e), the frequency (ω_e), the deep of the well (D_e) and the Morse

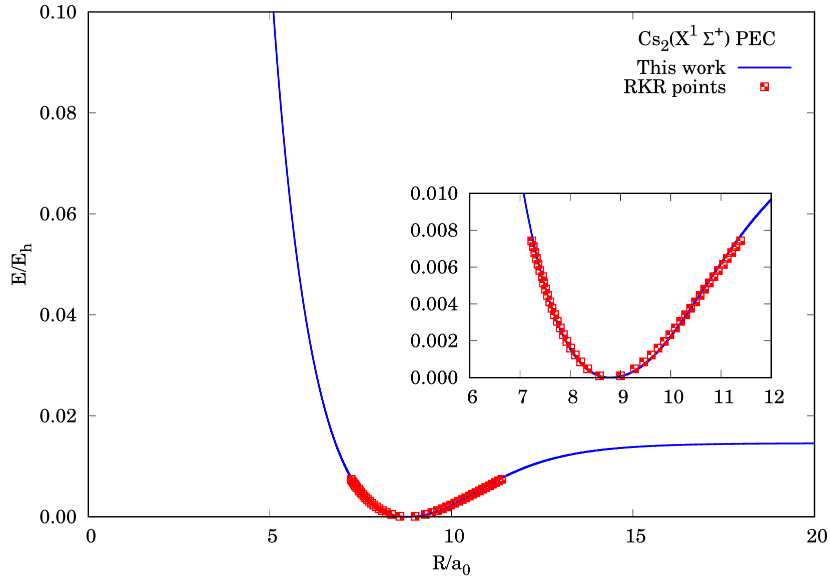


Figure 7.4: Comparison, for Cs_2 $(X^1\Sigma_g^+)$, of the New Potential (1) with the experimental RKR points from Ref. [258].

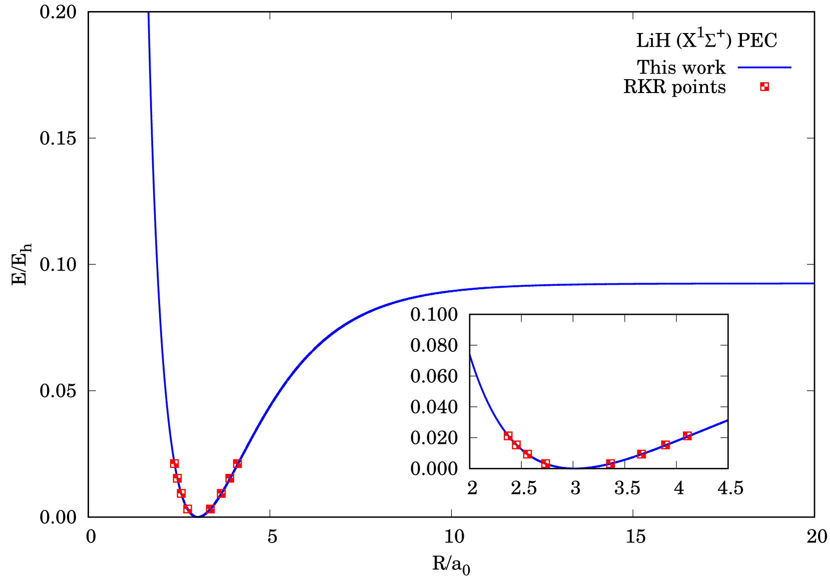


Figure 7.5: Comparison, for LiH $(X^1\Sigma^+)$, of the New Potential (1) with the experimental RKR points from Ref. [264].

parameter (α) for all 22 diatomic systems treated here. From columns 4, 7, 10, and 13 in this table, the calculated values are very near to the experimental values, and in many cases they are coincident. It is case for example of the parameters R_e and D_e for CN(X), CO^+, CS, Cs_2, H_2, HCl, Mg_2, NO, OH and SiH. The calculated values of the frequencies also differ very little from the experimental values for practically all systems. These results confirm the accuracy of the new potential proposed in this work for different types of diatomic potentials.

Table 7.5: Results of the Z-test for BiI(XO^+).

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($4.9624 < R < 5.2922$)	0.330	0.00016
Attractive branch ($5.2922 < R < 5.7170$)	0.425	0.00829
Whole potential ($4.9624 < R < 5.7170$)	0.755	0.00237

RKR experimental data from Ref. [254]

Table 7.6: Results of the Z-test for CN($X^2\Sigma^+$).

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.7983 < R < 2.2144$)	0.416	0.09108
Attractive branch ($2.2144 < R < 3.0884$)	0.874	23.41254
Whole potential ($1.7983 < R < 3.0884$)	1.290	7.94587

RKR experimental data from Ref. [255]

Table 7.7: Results of the Z-test for CN($A^2\Pi$).

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.8249 < R < 2.3306$)	0.506	0.25423
Attractive branch ($2.3306 < R < 3.8399$)	1.509	1.51046
Whole potential ($1.8249 < R < 3.8399$)	2.015	0.59740

RKR experimental data from Ref. [256]

Table 7.8: Results of the Z-test for $CO(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.6894 < R < 2.1322$)	0.443	0.51536
Attractive branch ($2.1322 < R < 3.1861$)	1.054	0.18981
Whole potential ($1.6894 < R < 3.1861$)	1.497	0.14312

RKR experimental data from Ref. [214]

Table 7.9: Results of the Z-test for $CO^+(X^2\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.6894 < R < 2.1322$)	0.344	38.40305
Attractive branch ($2.1322 < R < 3.1861$)	0.663	17.05412
Whole potential ($1.6894 < R < 3.1861$)	1.007	12.17507

RKR experimental data from Ref. [214]

Table 7.10: Results of the Z-test for $CS(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($2.4699 < R < 2.9006$)	0.431	0.01901
Attractive branch ($2.9006 < R < 3.6623$)	0.762	0.67729
Whole potential ($2.4699 < R < 3.6623$)	1.192	0.21988

RKR experimental data from Ref. [257]

Table 7.11: Results of the Z-test for $Cs_2(X^1\Sigma_g^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($7.2358 < R < 8.4471$)	1.211	0.31724
Attractive branch ($8.4471 < R < 11.3894$)	2.942	0.00091
Whole potential ($7.2358 < R < 11.3894$)	4.154	0.04656

RKR experimental data from Ref. [258]

Table 7.12: Results of the Z-test for $H_2(X^1\Sigma_g^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($0.7767 < R < 1.4011$)	0.624	110700.710
Attractive branch ($1.4011 < R < 6.1605$)	4.759	0.35020
Whole potential ($0.7767 < R < 6.1605$)	5.384	6413.83310

RKR experimental data from Ref. [259]

Table 7.13: Results of the Z-test for $HBr(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.9499 < R < 2.6729$)	0.723	0.48348
Attractive branch ($2.6729 < R < 9.0707$)	6.398	0.87706
Whole potential ($1.9499 < R < 9.0707$)	7.121	0.41871

RKR experimental data from Ref. [260]

Table 7.14: Results of the Z-test for $HCl(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.7282 < R < 2.4086$)	0.680	17.28680
Attractive branch ($2.4086 < R < 5.4386$)	3.030	2.01149
Whole potential ($1.7282 < R < 5.4386$)	3.710	2.40629

RKR experimental data from Ref. [261]

Table 7.15: Results of the Z-test for $HF(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.1735 < R < 1.7325$)	0.559	16.30813
Attractive branch ($1.7325 < R < 4.9208$)	3.188	0.70458
Whole potential ($1.1735 < R < 4.9208$)	3.747	1.51555

RKR experimental data from Ref. [262]

Table 7.16: Results of the Z-test for $HI(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch $(2.2797 < R < 3.0408)$	0.761	0.19782
Attractive branch $(3.0408 < R < 10.9604)$	7.920	0.29059
Whole potential $(2.2797 < R < 10.9604)$	8.681	0.14107

RKR experimental data from Ref. [260]

Table 7.17: Results of the Z-test for $HS(X^2\Pi)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch $(1.8321 < R < 2.5339)$	0.702	0.26094
Attractive branch $(2.5339 < R < 11.3280)$	8.794	0.29905
Whole potential $(1.8321 < R < 11.3280)$	9.496	0.14816

RKR experimental data from Ref. [263]

Table 7.18: Results of the Z-test for $I_2(X^1\Sigma_g^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch $(4.2840 < R < 5.0323)$	0.748	0.14432
Attractive branch $(5.0323 < R < 12.1831)$	7.151	0.04828
Whole potential $(4.2840 < R < 12.1831)$	7.899	0.02866

RKR experimental data from Ref. [259]

Table 7.19: Results of the Z-test for $LiH(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch $(2.3716 < R < 3.0154)$	0.644	0.00210
Attractive branch $(3.0154 < R < 4.1064)$	1.091	0.00782
Whole potential $(2.3716 < R < 4.1064)$	1.735	0.00287

RKR experimental data from Ref. [264]

Table 7.20: Results of the Z-test for $Mg_2(X^1\Sigma_g^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($6.1390 < R < 7.3520$)	1.213	0.00180
Attractive branch ($7.3520 < R < 12.7317$)	5.380	0.000002
Whole potential ($6.1390 < R < 12.7317$)	6.593	0.00018

RKR experimental data from Ref. [265]

Table 7.21: Results of the Z-test for $Na_2(X^1\Sigma_g^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($4.1877 < R < 5.8182$)	1.631	0.00229
Attractive branch ($5.8182 < R < 10.9132$)	5.095	0.00488
Whole potential ($4.1877 < R < 10.9132$)	6.726	0.00213

RKR experimental data from Ref. [266]

Table 7.22: Results of the Z-test for $Na_2(B^1\Pi)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($5.3757 < R < 6.4682$)	1.093	0.00740
Attractive branch ($6.4682 < R < 8.1997$)	1.732	0.00151
Whole potential ($5.3757 < R < 8.1997$)	2.824	0.00200

RKR experimental data from Ref. [267]

Table 7.23: Results of the Z-test for $NaH(X^1\Sigma^+)$.

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($2.6390 < R < 3.5667$)	0.928	0.00389
Attractive branch ($3.5667 < R < 5.6945$)	2.128	0.25952
Whole potential ($2.6390 < R < 5.6945$)	3.056	0.09096

RKR experimental data from Ref. [268]

Table 7.24: Results of the Z-test for NO($X^2\Pi$).

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.7556 < R < 2.1746$)	0.419	5.66391
Attractive branch ($2.1746 < R < 3.2600$)	1.085	5.22213
Whole potential ($1.7556 < R < 3.2600$)	1.504	2.67237

RKR experimental data from Ref. [269]

Table 7.25: Results of the Z-test for OH($X^2\Pi$).

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($1.6705 < R < 1.8324$)	0.162	0.78033
Attractive branch ($1.8324 < R < 2.0428$)	0.210	12.17212
Whole potential ($1.6705 < R < 2.0428$)	0.372	3.60563

RKR experimental data from Ref. [270]

Table 7.26: Results of the Z-test for SiH($X^2\Pi$).

RANGES	$\Delta R/a_0$	Z-value
Repulsive branch ($2.4283 < R < 2.8726$)	0.444	0.00023
Attractive branch ($2.8726 < R < 3.5716$)	0.699	0.01053
Whole potential ($2.4283 < R < 3.5716$)	1.143	0.00212

RKR experimental data from Ref. [253]

Table 7.27: Comparison of experimental spectroscopic parameters [96] with calculated values for 22 diatomic systems.

Diatomic system	R_e (a_0) Exp.	R_e (a_0) Calc.	$\Delta R_e/R_e$ [a] (%)	ω_e (cm^{-1}) Exp.	ω_e (cm^{-1}) Calc.	$\Delta\omega_e/\omega_e$ [b] (%)	D_e (E_h) Exp.	D_e (E_h) Calc.	$\Delta D_e/D_e$ [c] (%)	$\alpha(a_0^{-1})$ Exp.	$\alpha(a_0^{-1})$ Calc.	$\Delta\alpha/\alpha$ [d] (%)
$BiI(XO^+)$	5.29218	5.29217	0.00020	163.8800	163.91600	0.02200	0.07200	0.07200	0.00000	0.61060	0.74670	22.28960
$CN(X^2\Sigma^+)$	2.21438	2.21438	0.00000	2068.59000	2067.88800	0.033940	0.28520	0.28520	0.00000	1.19420	1.35450	13.42320
$CN(A^2\Pi)$	2.33060	2.33060	0.00000	1812.56000	1812.09400	0.025700	0.28930	0.28930	0.00000	1.21710	1.17840	3.17970
$CO(X^1\Sigma^+)$	2.13222	2.13220	0.00090	2169.81400	2169.06900	0.03430	0.41260	0.41260	0.00000	1.21690	1.21670	0.01640
CO^+ $(X^2\Sigma^+)$	2.10731	2.10731	0.00000	2214.24000	2213.46000	0.03520	0.31146	0.31146	0.00000	1.32411	1.42900	7.92150
$CS(X^1\Sigma^+)$	2.90062	2.90062	0.00000	1285.08000	1283.97100	0.08630	0.27320	0.27320	0.00000	0.97490	0.99880	2.45150
$Cs_2(X^1\Sigma_g^+)$	8.78530	8.78530	0.00000	42.02200	40.43300	3.78000	0.01460	0.01460	0.00000	0.30370	0.38990	28.38330
$H_2(X^1\Sigma_g^+)$	1.40112	1.40112	0.00000	4401.21000	4401.91000	0.01590	0.17460	0.17460	0.00000	1.02490	1.02880	0.38050
$HBr(X^1\Sigma^+)$	2.67289	2.67299	0.00370	2648.97500	2660.96700	0.45270	0.14410	0.14410	0.00000	0.95390	0.96210	0.85960
$HCl(X^1\Sigma^+)$	2.40861	2.40861	0.00000	2990.94600	2989.76000	0.03970	0.16970	0.16970	0.00000	0.98480	0.98830	0.35540
$HF(X^1\Sigma^+)$	1.73251	1.73256	0.00290	4138.32000	4135.50000	0.06810	0.22510	0.22500	0.04440	1.16890	1.17340	0.38500
$HI(X^1\Sigma^+)$	3.04076	3.04069	0.00230	2309.01400	2319.38900	0.44930	0.11750	0.11750	0.00000	0.93320	0.93090	0.24650
$HS(X^2\Pi)$	2.53393	2.53390	0.00120	2711.60000	2730.62200	0.70150	0.13660	0.13660	0.00000	0.99360	1.00470	1.11710
$I_2(X^1\Sigma_g^+)$	5.03230	5.03233	0.00060	214.50200	214.78800	0.13330	0.05720	0.05717	0.05240	0.98340	0.98430	0.09150
$LiH(X^1\Sigma^+)$	3.01544	3.01543	0.00030	1405.65000	1406.05800	0.02900	0.09250	0.09250	0.00000	0.58720	0.59680	1.63490
$Mg_2(X^1\Sigma_g^+)$	7.35198	7.35198	0.00000	51.12100	50.78500	0.65730	0.00200	0.00200	0.00000	0.57680	0.55040	4.57700
$Na_2(X^1\Sigma_g^+)$	5.81822	5.81821	0.00020	159.12400	159.13100	0.00440	0.02680	0.02682	0.00000	0.44810	0.45310	1.11580
$Na_2(B^1\Pi)$	6.46816	6.46815	0.00020	124.09000	123.90700	0.14750	0.02650	0.02650	0.00000	0.36830	0.35530	3.52970
$NaH(X^1\Sigma^+)$	3.56667	3.56667	0.00000	1172.20000	1171.69000	0.04350	0.07180	0.07176	0.05570	0.56660	0.59120	4.34170
$NO(X^2\Pi)$	2.17464	2.17464	0.00000	1904.20000	1922.47000	0.95950	0.24310	0.24310	0.00000	1.45180	1.46580	0.96430
$OH(X^2\Pi)$	1.83239	1.83239	0.00000	3737.76000	3738.01700	0.00690	0.16990	0.16990	0.00000	1.21360	1.21470	0.09060
$SiH(X^2\Pi)$	2.87257	2.87260	0.00100	2041.80000	2041.62000	0.00880	0.11710	0.11710	0.0000	0.76340	0.80950	6.03880

[a] $\Delta R_e/R_e = |R_{e_{Exp.}} - R_{e_{Calc.}}|/(R_{e_{Exp.}})$
[b] $\Delta\omega_e/\omega_e = |\omega_{e_{Exp.}} - \omega_{e_{Calc.}}|/(\omega_{e_{Exp.}})$
[c] $\Delta D_e/D_e = |D_{e_{Exp.}} - D_{e_{Calc.}}|/(D_{e_{Exp.}})$
[d] $\Delta\alpha/\alpha = |\alpha_{Exp.} - \alpha_{Calc.}|/(\alpha_{Exp.})$

7.2.1 Comparisons between different CO ($X^1\Sigma^+$) potentials

To compare the new proposed function with previously reported potentials, we select the CO ($X^1\Sigma^+$) molecule. In chapter 4, we have analyzed the behavior of fifty potential energy functions for the ground electronic state of the CO and other diatomic systems [247]. Among these potentials, we can list some that are mathematically comparable to the new potential proposed in this article, are they: Extended Morse [32] (EM), Simon-Parr-Filan [129] (SPF), Thakkar [22] (THA), Huffaker [133] (HUF), Mattera [142] (MAT), Surkus [145] (SUR), EHFACE2U [168] and Aguado-Paniagua [180] (AP) potentials. All these potentials are expansion in series of powers-type with parameters obtained by fitting them to *ab initio* energies.

To calculate the potential energy curve for the ground electronic state of CO, the functions listed above required between eight and fourteen parameters (given in parenthesis): SPF (8), AP (8), EM (9), THA (11), EHAFACE2U (12), HUF (13), MAT (14) and SUR (14), while the new potential energy function has required five (5) parameters with only one term in the power series. Thus, the new potential for CO is given by:

$$V(R) = \begin{cases} c_2\left[\left(1+e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right)\left(\frac{R-R_e}{R}\right)\right]^2, & R \le R_e \\ D_e\left[\frac{(1-e^{-2\alpha(R-R_e)})}{(1+e^{-\gamma\alpha(R-R_e)})}\right]^2, & R > R_e. \end{cases} \tag{7.14}$$

Table 7.28: Results of the Z-test for CO($X^1\Sigma^+$). Z values are given in $10^{-5}{E_h}^2\ {a_0}^{-1}$

RANGES	$\Delta R/a_0$	This work	EM	SPF	THA
Repulsive branch	0.443	0.51536	30.511	22.719	24.394
($1.6890 < R < 2.1320$)					
Attractive branch	1.054	0.18981	13.313	2.230	2.468
($2.1320 < R < 3.1860$)					
Whole potential	1.497	0.14312	9.204	4.148	4.479
($1.6890 < R < 3.1860$)					

RANGES	HUF	MAT	SUR	EHFACE2U	AP
Repulsive branch	29.796	24.742	27.268	30.706	5.872
($1.6890 < R < 2.1320$)					
Attractive branch	1.897	2.459	0.246	1.880	0.875
($2.1320 < R < 3.1860$)					
Whole potential	5.078	4.528	4.122	5.215	1.177
($1.6890 < R < 3.1860$)					

For CO, the same RKR experimental data used in Ref. [247], has been used here [214], and the new potential energy curve (7.1) proved to be more accurate (for the three different ranges of R) than all those listed above, as can be seen in the comparison presented in Table 7.28.

8 Conclusions

We have concerned with several aspects of the potentials here described: the number of parameters, its simplicity and quality in the short and long-range regions, and the diversity of diatomic systems that each function can be applied.

Nowadays, computational resources are much powerful than what we had in the recent past, making it possible, for example, to obtain excellent ab initio points and, therefore, accurate PESs. In turn, for the here studied cases, functions fitted to ab initio points did not necessarily provide better precision than those obtained without the fitting. For the latter type, the best results were for those with five parameters, highlights for the Hulburt-Hirschfelder, Huggins, and Extended Rydberg potentials. The Dmitrieva-Zenevich function with three parameters shows good results only for HeH^+. Furthermore, for CO and N_2, among the fitted functions, the more accurate has six parameters, and for HeH^+, the best choice has four adjustable parameters.

Thus, a potential energy function with only three parameters, fitted or not, is unlikely to provide the best results, as was thought possible in the past. The potential energy functions consisting of power series expansions presented good accuracy for the diatomics treated here, highlighting mainly the EHFACE2U and Aguado-Paniagua potentials. Mathematically (and physically) models containing a product of an exponential by a polynomial, with its variations, remains the ideal potential energy function. A function that escapes this configuration will hardly provide accurate results.

Since we have used the Murrell and Sorbie Z-test, it was expected the potentials obtained from spectroscopic data to be more accurate than those with adjustable coefficients. However, this was not the general trend observed. In many cases, adjustable potentials produced a smaller errors than the other.

Therefore, the accuracy of a potential related to the RKR data is directly linked to the mathematical structure of the analytical form, and not to the specific way the coefficients are obtained. After analyzing these 50 potentials and the hundred years of history that were necessary to develop them, we remain with the same opinion expressed by Varshni in 1957, and many other researchers: it is not possible to find a universal potential energy function. However, as we can see, the search for the *Holy Grail of Spectroscopy* will continue perhaps for another hundred years.

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. We have been described mathematical details to obtain good potentials.

The Extended Rydberg, Varshni III, Levine, EHFACE2U and Aguado-Paniagua potentials, besides involving exponentials and polynomials, have another characteristic in common: the correct asymptotic behaviour of the potential for dissociation into atoms. This is a necessary condition to obtain a potential which is satisfactory over all accessible values of R [56].

For this reason, in order to obtain potential energy functions, it is necessary to ensure the convergence and all other requirements described in chapter 5. In general, potentials that do not satisfy these conditions do not produce accurate results.

By using the methodology described in chapter 5, we have introduced a new generalized potential energy function for representing the inter-atomic interaction of diatomic systems. The parameters of the function are directly obtained from relations with Dunham's coefficients. The model was tested in 22 cases, comprising both ground and excited states. Among these, the interaction potential for BiI and Cs_2, in their ground electronic states, are especially accurately represented with the new function. The calculated values of the spectroscopic parameters are consistent with the observed values for all analyzed systems. Also, the new potential curve for the ground state of CO outperformed the Extended Morse, Simon-Parr-Filan, Thakkar, Huffaker, Mattera, Surkus, EHFACE2U, and Aguado-Paniagua potentials in the three described interaction regions of the potential.

9 Future Perspectives

In this work only surfaces of potential energy for diatomic systems have been considered. However, we are also researching the interaction potentials of three or more bodies. A new algebraic potential energy function for triatomic systems have been discussed, and we will present preliminary results that should be completed soon.

Triatomic molecules are of dynamical symmetric chain

$$U_1(4) \otimes U_2(4) \supset \left\{ \begin{array}{c} O_1(4) \otimes O_2(4) \\ U_{12}(4) \end{array} \right\} \supset O_{12}(4) \tag{9.1}$$

and the Hamiltonian for the chain (9.1) is

$$H = A_1 C_1 + A_2 C_2 + A_{12} C_{12}^{(1)} + A_{12}^{'} C_{12}^{(2)} + \lambda M_{12} \tag{9.2}$$

C_1, C_2, $C_{12}^{(1)}$ and $C_{12}^{(2)}$ are the Casimir operators and M_{12} is so-called Majorana operator. The classical limits of algebraic Hamiltonian will be obtained using group coherent state

$$|N_1, N_2; \xi_1, \xi_2\rangle = (N_1! N_2!)^{-1/2} [(1 - \xi_1^* \xi_1)^{1/2} \sigma_1^+ + \xi_1 \pi_1]^{N_1} \times [(1 - \xi_2^* \xi_2)^{1/2} \sigma_2^+ + \xi_2 \pi_2]^{N_2} |0\rangle \tag{9.3}$$

where ξ_1, ξ_2 are the canonical coordinates and momenta [271].

The classical Hamiltonian is

$$H_{el}(q_1, q_2, p_1, p_2) = \langle N_1, N_2; \xi_1, \xi_2| H |N_1, N_2; \xi_1, \xi_2\rangle \tag{9.4}$$

and the potential energy surface is given by:

$$\begin{aligned} & V(q_1, q_2) = H_{el}(q_1, q_2, p_1 = 0, p_2 = 0) = (A_1 + A_{12}) N_1^2 (2 - q_1^2) q_1^2 \\ & +(A_2 + A_{12}) N_2^2 (2 - q_2^2) q_2^2 + 2 A_{12} N_1 N_2 [(2 - q_1^2)(2 - q_2^2)]^{1/2} q_1 \cdot q_2 \\ & +\tfrac{1}{4} \lambda N_1 N_2 \{(2 - q_2^2) q_1^2 + (2 - q_1^2) q_2^2 \\ & -2[(2 - q_1^2)(2 - q_2^2)]^{1/2} q_1 \cdot q_2 + 2(q_1 \times q_2)^2\}. \end{aligned} \tag{9.5}$$

By using the transformation between the bond (r_i) and canonical (q_i) coordinates and the transformation between the angle between q_1 and q_2 and the bond angle [272]

$$q_i^2 = e^{-\alpha_i r_{ie}^2 (r_i - r_{ie})} \quad \text{and} \quad a_1 \cdot a_2 = [\cosh \gamma(\phi - \pi)]^{(-\gamma^2/|\gamma|^2)} \; i = 1, 2. \tag{9.6}$$

where a_i is the vector along the vector q_i and ϕ is the bond angle, γ is a parameter determined by the expansion coefficients and the molecular parameters and α_i is the Morse parameter [8].

The novel analytical PES for N_2O is given by:

$$\begin{aligned}
&V(r_1, r_2, \phi) = (A_1 + A_{12}) N_1^2 [2 - e^{-\beta_1(r_1 - r_{1e})}] e^{-\beta_1(r_1 - r_{1e})} \\
&+(A_2 + A_{12}) N_2^2 [2 - e^{-\beta_2(r_2 - r_{2e})}] e^{-\beta_2(r_2 - r_{2e})} \\
&+2A_{12} N_1 N_2 \{[2 - e^{-\beta_1(r_1 - r_{1e})}] e^{-\beta_1(r_1 - r_{1e})} \\
&\times [2 - e^{-\beta_2(r_2 - r_{2e})}] e^{-\beta_2(r_2 - r_{2e})}\}^{1/2} \cdot \cos|\gamma|(\phi - \pi) \\
&+\tfrac{1}{4}\lambda N_1 N_2 \{2e^{-\beta_1(r_1 - r_{1e})} + 2e^{-\beta_2(r_2 - r_{2e})} - 2e^{-\beta_1(r_1 - r_{1e}) - \beta_2(r_2 - r_{2e})} \\
&\times \cos^2|\gamma|(\phi - \pi) - 2[(2 - e^{-\beta_1(r_1 - r_{1e})}) e^{-\beta_1(r_1 - r_{1e})} \\
&\times (2 - e^{-\beta_2(r_2 - r_{2e})}) e^{-\beta_2(r_2 - r_{2e})}]^{1/2} \cdot \cos|\gamma|(\phi - \pi)\}
\end{aligned} \quad . \tag{9.7}$$

where we will consider $\beta_i = r_{ie}^2 \alpha_i$, $i = 1, 2$.

Parameters	Zheng-Ding [272]	Calc. [273]
N_1	134	133
N_2	163	163
A_1 (cm^{-1})	-1.7376	-3.8315
A_2 (cm^{-1})	-1.5033	-3.8406
A_{12} (cm^{-1})	-0.2787	0.8245
λ (cm^{-1})	-0.5105	-0.008683
β_1 ($Å^{-1}$)	2.7083	2.457556
β_2 ($Å^{-1}$)	2.7676	2.51568
r_{1e} (Å)	1.1273	1.09768
r_{2e} (Å)	1.1815	1.15077
γ	2.6677i	0.556i

$^\dagger\gamma$ and N are dimensionless, $1 = r_{NN}$, $2 = r_{NO}$

In summary, the algebraic approach allow us to obtain PES without ab initio points. In Fig. 7.3 and Fig. 7.4, can be seen clearly that with the new PES for N2O the well depth value was corrected by approximately 3 eV relative to the original Zheng-Ding [272] potential for both N_2 and NO diatomics. However, the correct global minimum of N_2O is approximately 0.278386 hartree [274], and the new PES provides a value around 0.5 hartree. This error is probably related to the function's symmetrization, which should be revised and corrected.

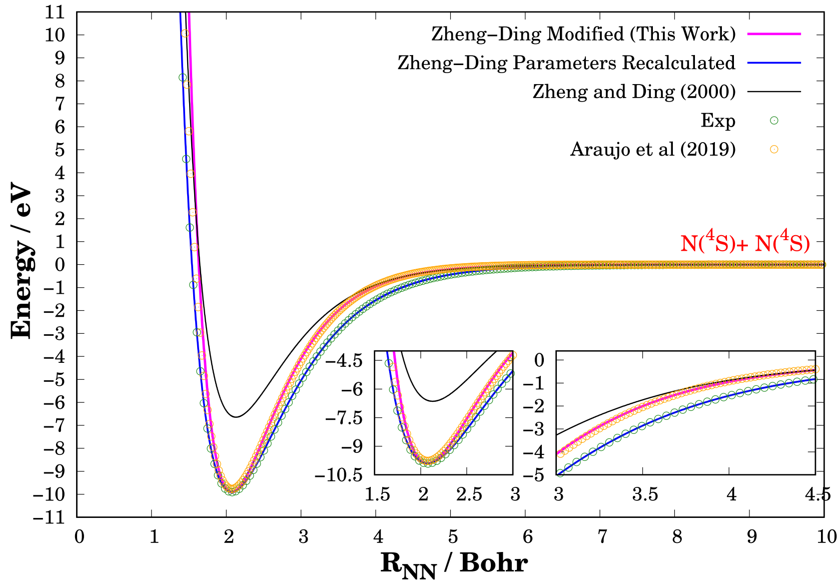


Figure 9.1: Potential energy curves of the ground electronic state of linear NNO along the R_{NN}

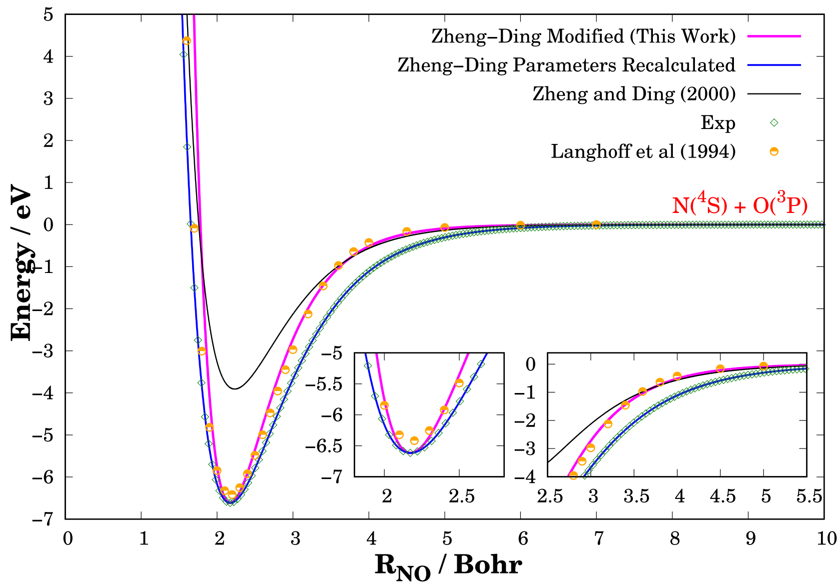


Figure 9.2: Potential energy curves of the ground electronic state of linear NNO along the R_{NO}

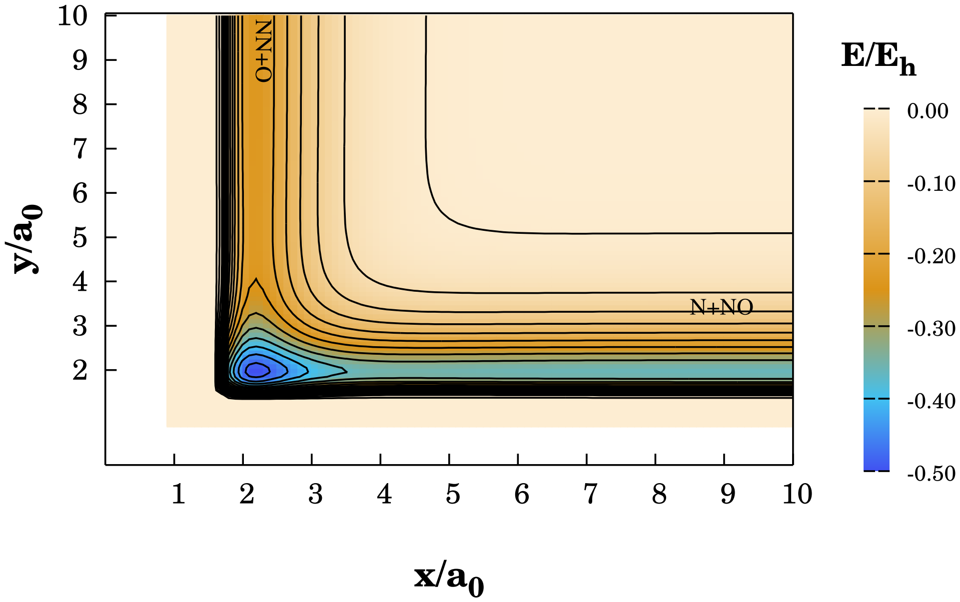


Figure 9.3: Contour plot for the channel $NN + O \rightleftharpoons N_2O \rightleftharpoons N + NO$.

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10 Appendix

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ORIGINAL PAPER

A comparative study of analytic representations of potential energy curves for O_2, N_2, and SO in their ground electronic states

Judith P. Araújo[1] · Marcos D. Alves[1] · Ramon S. da Silva[1] · Maikel Y. Ballester[1]

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Abstract

In this work, a review of six functional forms used to represent potential energy curves (PECs) is presented. The starting point is the Rydberg potential, followed by functions by Hulburt–Hirschfelder, Murrell–Sorbie, Thakkar, Hua and finalizing with the potential for diatomic systems by Aguado and Paniagua. The mathematical behavior of these functions for the short- and long-range regions is discussed. A comparison highlighting the positive and negative aspects of each representation is also presented. As study cases, three diatomic systems O_2, N_2 and SO in their respective ground electronic states were selected. To obtain spectroscopic parameters, *ab initio* energies were first calculated at multi-reference configuration interaction (MRCI) with the Davidson modification (MRCI+Q) level of theory, using aug-cc-pVXZ (X = T,Q,5,6) Dunning basis sets. Such energies were then fitted to respective functional forms. The so-obtained spectroscopic constants are compared also with available literature data.

Keywords Potential energy curves · Diatomic systems · Spectroscopic parameters · *ab initio* calculations

Introduction

The relationship between the potential energy and the internuclear distance of two atoms is of the greatest importance in physical chemistry. The study of processes like molecular scattering, photodissociation, chemical kinetics, and electric discharges relies on the knowledge of these functions [1–6]. Due to practical limitations in the solution of the Schrödinger equation for a molecular system, physically supported approximations are required. In 1927, Born and Oppenheimer, also with the contribution of Huang, presented a pathway to circumvent this problem [7].

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The Born–Oppenheimer approximation (BOA) consists of the separation of the nuclear and electron motions: once nuclei have much larger masses than the electron (more than 1838 times), they can be considered as stationary compared to the moving electrons. The mathematical formalism for such an approach can be followed elsewhere [7] and is fundamental in understanding the key concept of potential energy surface (PES). Within BOA, nuclei in a molecular system move on the PES resulting from the solution of the electronic problem. Since BOA, several researchers have been attempting to obtain analytic representations of energy as a function of the interatomic distances. Such a representation is usually required to be mathematically simple while accurately reproducing theoretical and experimental data.

The potential energy curve provides broad insight into the structure of a molecular system. The minimum in this curve defines the bond length of the diatomic molecule. Its second derivative provides the force constants, from which vibrational and rotational energy levels of the molecule can be calculated. Higher-order derivatives are required for the calculation of the anharmonicity constants.

Among the analytical representations available in the literature (over 50 to our knowledge), six functions were chosen: Rydberg, Hulburt–Hirschfelder, Murrell–Sorbie, Thakkar, Hua, and Aguado-Camacho-Paniagua.

In *Electronic Structure Calculations: An introduction* Judith de Paula Araújo presents a text dedicated mainly to undergraduate students and researchers in the fields of Physics and Theoretical Chemistry. One of the author's concerns was to produce a didactically organized text, with several examples and exercises solved step by step.

The main purpose of this book is to explore methods for obtaining solutions to the electronic Schrödinger equation for N-body systems. To this end, the author first presents a formal demonstration for the Born-Oppenheimer Approximation proving that the nuclei move according to classical mechanics. Then, the Hartree-Fock Approximation is discussed, showing that it is possible to replace the complicated problem of many electrons with a problem of one electron. In the chapter Configuration Interaction, the energy differences produced by the Hartree-Fock Approximation are calculated, that is, the correlation energies.

In a session dedicated to Second Quantization, the author shows that the Principle of Antisymmetry can be satisfied from this, as an alternative to the use of Slater Determinants. A rigorous solution of the Schrödinger equation determining the stationary states for the Harmonic Oscillator, which is one of the simplest systems, is presented. In addition, it also demonstrates how to obtain energy levels via annihilation and creation operators.

The penultimate chapter discusses the Coupled-Cluster Theory. This method is capable of recovering much of the correlation energy and can be applied to larger systems. The coupled cluster wave function provides an accurate correction to the Hartree-Fock description.

Finally, a short introduction to Many-Body Perturbation Theory is presented and exemplified by the perturbations containing two-particles interactions.

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JUDITH DE PAULA ARAÚJO
ELECTRONIC STRUCTURE CALCULATIONS
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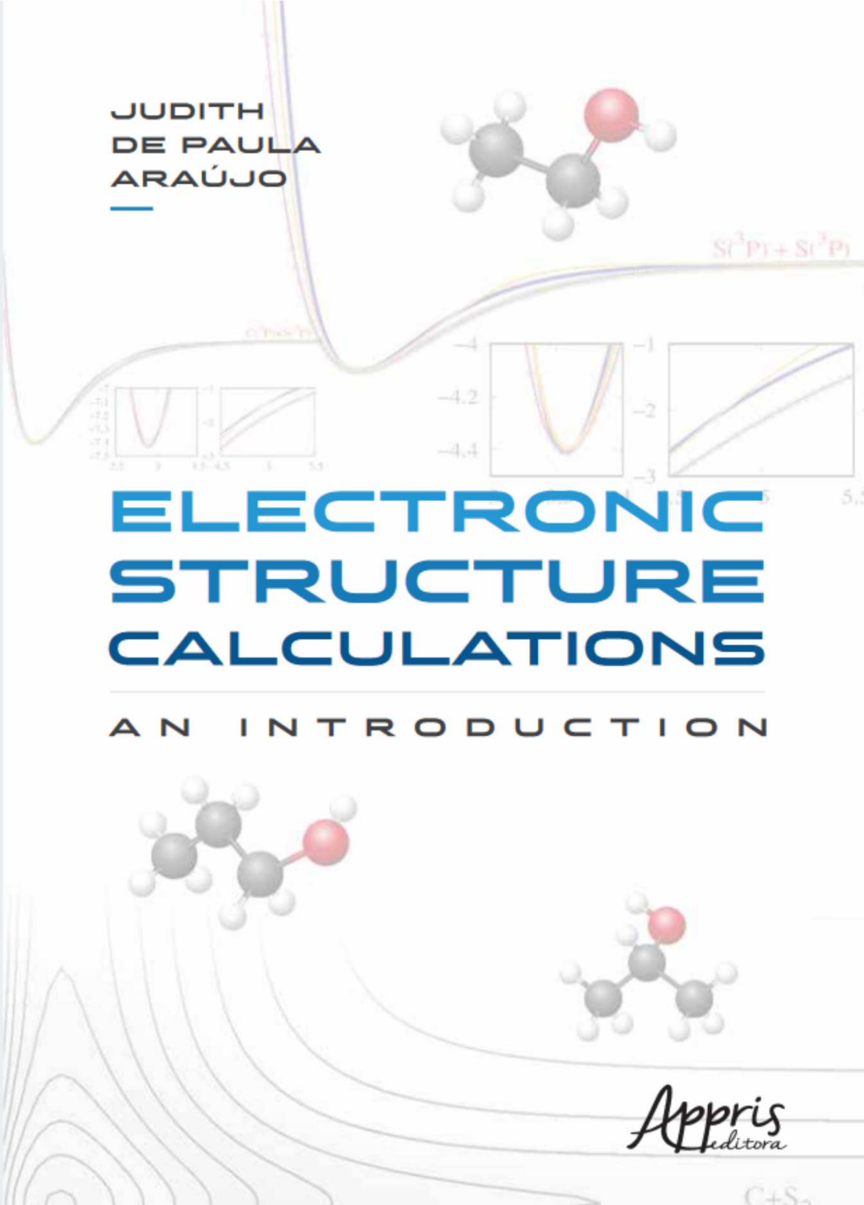

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REVIEW

Journal Section

A comparative review of fifty analytical representation of potential energy interaction for diatomic systems: One Hundred Years of History

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Interatomic potentials laid at the heart of molecular physics. They are a bridge between the spectroscopic and structural properties of molecular systems. In this paper, a century-old review from 1920 to 2020, of functional forms used to analytically represent potential energy as a function of interatomic distance for diatomic systems is presented. With such a purpose fifty functions were selected. For all of them, motivation and the main mathematical features are discussed. Our goal is to provide a chronological pathway to the reader, even with little knowledge on the subject, to understand how to calculate each parameter that composes the interatomic potentials, as well as obtain spectroscopic constants from them. Comparative evaluation for the N_2, CO, and HeH^+ systems in their ground electronic states are also presented.

KEYWORDS
potential energy curves, diatomic systems, ground electronic state, spectroscopic parameters, analytical representation

CONTENTS

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New Generalized Potential Energy Function for Diatomic Systems

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(`Dated: 23 February 2021)

A new and flexible function to represent the potential energy interactions of diatomic systems for the whole domain of internuclear separations is proposed. This function is a member of a family of functions containing a product of an exponential and a polynomial. A method for generating the parameters of the new potential as a function of Dunham's parameters is described. Coefficients for 22 selected diatomic systems with elements from the first to the sixth rows, including some ground and excited electronic states, are presented. To quantify the accuracy of the so constructed potential energy functions, the least-squares Z-test method, proposed by Murrell and Sorbie, is used. Furthermore, main spectroscopic parameters are calculated and compared with available data.

I. INTRODUCTION

The construction of accurate analytical potential energy functions for diatomic systems, within the Born-Oppenheimer Approximation (BOA), from experimental data is still an important problem in chemical and molecular physics. In recent work, we reviewed and compared fifty analytical representations of diatomic potential energy functions, which were proposed from 1920 to 2020[1]. Among them, we observed the potentials that can be obtained from the spectroscopic constants, and also those depending upon parameters obtained from fitting ab initio points. For a relatively large number of diatomic systems, the construction of an ab initio-based potential energy function is quite straightforward. However, its accuracy will be strongly linked to both, the selected function and the quality of the molecular structure calculations[1].

Despite the recent development of new and upgraded numerical approximations to solve the electronic problem, the state-of-the-art ab initio methodologies are not extensively used in systems with a large number of electrons (see for example Refs. 2,3). In turn, spectroscopic measurements, without the theoretical limitations, provide accurate data for such systems.

Therefore obtaining an accurate curve directly from experimental spectroscopic data is an interesting pathway.

Models containing a product of an exponential by a polynomial, with its variations are in general trustworthy selection for representing diatomic potential energy functions. A function that escapes this configuration will hardly provide both accurate results in the spectroscopic region and correct asymptotic behavior in the dissociation limit[4]. Furthermore, potential functions consisting of power series expansions have been considered the best models due to flexibility and precision, as is the case of the EHFACE2U[5] and Aguado-Paniagua[6] potentials.

Thus, this paper aims to introduce a new generalized potential for diatomic systems fine-tuned with spectroscopic information. Such a function is here tested for 22 diatomic systems comprising ground and excited electronic states. To quantify the accuracy of the analytical representations, we followed the least-squares Z-test method proposed by Murrell and Sorbie[7]. Spectroscopic parameters R_e, D_e and w_e, and the Morse[8] parameter α, are also calculated and compared with experimental data[9].

II. POTENTIAL ENERGY FUNCTION

The proposed generalized potential energy function for diatomic systems is given by:

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

where $\beta=\frac{1}{3}\alpha$, being α the Morse[8] parameter, γ is a fine-tuning parameter $1\leq\gamma\leq 3$, to be fixed by direct comparison with RKR data, R_e is the equilibrium distance and the c_n, $n=2,\cdots,8$ coefficients are related with the Dunham[10] coefficients.

The coefficients c_i has been obtained from relationships between derivatives of the new potential and derivatives of Dunham's potential. In the region of its convergence, the Dunham potential converges to the RKR potential derived from the energy levels of[11]

$$F_{vJ}=\sum_{lj}Y_{lj}\left(v+\frac{1}{2}\right)^l J^j(J+1)^j. \quad (2)$$

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:

$$\sum_{i=2}^{8} c_n\left[\left(1+e^{-2\beta\left(\frac{R-R_e}{R_e}\right)}\right)\left(\frac{R-R_e}{R}\right)\right]^n$$
$$=a_0[(R-R_e)/R_e]^2\left\{1+\sum_{i=1}^{\infty}a_n[(R-R_e)/R_e]^n\right\}. \quad (3)$$

Derivatives of the two sides with respect to R have been taken and equated at $R=Re$. These resulted in expressions that relate the new potential coefficients c_n and the Dunham coefficients a_n, given by equations:

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Methodology to obtain Accurate Potential Energy Functions for Diatomic Systems: A Mathematical point of view

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Abstract Insert your abstract here. Include keywords, PACS and mathematical subject classification numbers as needed.

Keywords First keyword · Second keyword · More

1 Introduction

The Born-Oppenheimer approximation is corner stone for quantum mechanically study molecular systems. 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 be thought of as the potential for the movements of atoms within a molecule or atom in collision with one other. The motion with this characteristic is called adiabatic, where the dynamic of the system are associated with a single potential energy surface [13].

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

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

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