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Modified ℓ-states of diatomic molecules subject to central potentials plus an angle-dependent potential

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Abstract We present modified ℓ-states of diatomic molecules by solving the radial and angle-dependent parts of the Schrödinger equation for central potentials, such as Morse and Kratzer, plus an exactly solvable angle-dependent potential $V_\theta(\theta)/r^2$ within the framework of the Nikiforov–Uvarov (NU) method. We emphasize that the contribution which comes from the solution of the Schrödinger equation for the angle-dependent potential modifies the usual angular momentum quantum number ℓ. We calculate explicitly bound state energies of a number of neutral diatomic molecules composed of a first-row transition metal and main-group elements for both Morse and Kratzer potentials plus an angle-dependent potential. We also compare the bound state energies for both potentials, taking into account spectroscopic parameters of diatomic molecules and arbitrary values of potential constants.

Keywords Bound state solution · Modified ℓ-state · Diatomic molecule · Nikiforov–Uvarov method · Central plus non-central potentials

1 Introduction

In recent years, theoretical and computational studies of molecular spectra have been one of the most valuable tools for studying on atoms and molecules. The knowledge of spectral analysis allows us to detect the presence of particular characteristics and essential components of matter. Especially, molecular spectra has been used to understand

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the motion of electrons in molecules as well as the vibration and rotation of the nuclei. The chemical interactions between atoms and molecules assist to investigate the physical properties of individual molecules. In the light of this knowledge, dissociation channels [1], centrifugal distortion constants [2], semiempirical dipole moment functions [3] and other data about the rotation, vibration and electronic energy levels [4–7] of diatomic molecules have been accurately determined by using theoretical methods. Moreover, some quantum-mechanical calculations on rotational and vibrational energy levels of diatomic molecules have been applied to the various problems in molecular physics for a number of years [8]. The modified 1/N approach has been applied to obtain energy levels of a rotational potential [9]. The formalism based on quantum groups developed for nuclei has been applied equally well to molecules [10–12], and concentrated on the rotation-vibration problem for a closed-shell molecule in a singlet electronic state [13]. Arbitrary ℓ-state solutions of the rotating Morse potential has been investigated through the exact quantization rule method [14] and other algebraic approaches and applications have been previously applied to rotational and vibrational states of special potentials [15–20].

Before discussing the exactly solvable angle-dependent potential model, it is a beneficial effort to give some information on a diatomic molecule. As is understood from the description of molecular structure, a diatomic molecule differs from an atom in having additional modes of motion caused by the ability of the molecule to rotate and vibrate about its center of mass (CM) [21]. The simplest model for the motion of a diatomic molecule is the harmonic oscillator which describes the vibrations of the two atoms along a bond direction passing through the CM and the rigid rotor which approximates the rotation of the molecule (see, Fig. 1). The rotation of a diatomic molecule is composed of two nuclei having the atomic masses M_1 and M_2. To define a reduced mass μ for a neutral molecule which is given in terms of the masses M_1 and M_2, a precise value is available according to the following expression

$$\mu = \frac{M_1 M_2}{M_1 + M_2}. \tag{1}$$

Instead of considering the rotation of atoms which can vibrate relative to each other along the internuclear distance r, the rotation of a single mass which is called a reduced mass μ at a fixed distance r from the axis of rotation can equally be preferred to determine the possible energy levels of a diatomic molecule.

In this study, the bound state energy levels are obtained by solving the Schrödinger equation for the Morse [22] and Kratzer [23] molecular potentials together with an exactly solvable angle-dependent potential, respectively,

$$V_M(r,\theta) = D_e\left(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}\right) + \frac{V_\theta(\theta)}{r^2}, \tag{2}$$

$$V_K(r,\theta) = -D_e + D_e\left(\frac{r-r_e}{r}\right)^2 + \frac{V_\theta(\theta)}{r^2}, \tag{3}$$

where subscripts M and K indicate the Morse and Kratzer potentials, respectively, a controls the width of the potential and r_e is the equilibrium internuclear distance.

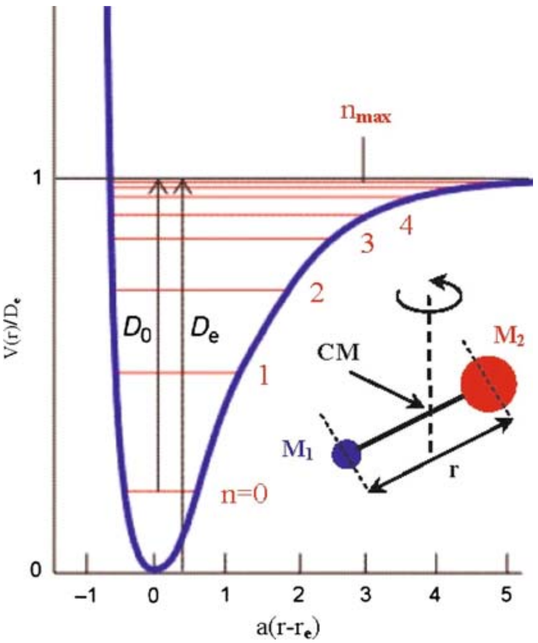

Fig. 1 Representative vibrational energy levels and rotation of a diatomic molecule. n is the vibration quantum number and D_0 is the chemical dissociation energy of the lowest ($n = 0$) vibrational level. The internuclear distance r is representatively shown in the right-hand sight of figure

The quantity D_e is the electronic (or spectroscopic) dissociation energy of the diatomic molecule and it differs slightly from the chemical dissociation energy D_0, i.e., $D_0 = D_e - \hbar\omega_e/2$, where ω_e is called harmonic vibrational parameter [24,25]. Moreover, the minimum value of $V_{M,K}(r)$ at $r = r_e$ belongs to D_e. The second term in the right-hand side of Eqs. 2 or 3 represents an angle-dependent potential and its uncovered form is given as follows

$$V_\theta(\theta) = \frac{\hbar^2}{2\mu}\left(\frac{A}{\sin^2\theta} + \frac{B}{\cos^2\theta}\right). \tag{4}$$

A and B are fixed constants or parameters obtained by some fitting procedure which is based on experimental or theoretical results; it is important to emphasize that they cannot depend on the angle θ. The factor $\hbar^2/2\mu$ is introduced in view of future convenience. The potential given in Eq. 4 has been introduced for the first time by Makarov et al. [26] classifying some non-central potential systems. The other forms of the non-central potentials have been also studied in the relativistic and the non-relativistic frameworks. In the non-relativistic case, the Schrödinger equation with non-central potentials has been solved by using the Kustaanheimo–Stiefel transformation and the energy of the levels for the ring-shaped potential has been obtained in a straightforward way from the one for the two-dimensional potential [27–30]. The accidental degeneracy and hidden symmetry of the Hartmann potential have also been discussed [31]. The Schrödinger equation for these types of angle-dependent potentials can be exactly solved to obtain the bound state energies of a diatomic molecule. It is well-known that the problem of exact solution of the Schrödinger equation for a number of special potentials has been a line of great interest in some quantum mechanical applications. The solution of this equation for several non-central potentials has been made by using some analytical methods such as classical trajectories for Hamiltonian systems with ring shaped potentials [32,33], SU(2) dynamical invariance algebra for a generalized Aharonov–Bohm plus Coulomb system [34], classical and quantum study of a generalized Kepler–Coulomb system [35,36], etc.... One of these methods is developed by Nikiforov and Uvarov [37] as a new approach to the theory of special functions. They succeeded in obtaining an unified integral representation for functions of hypergeometric type. This type of hypergeometric equation with an appropriate coordinate transformation is given as follows

$$\psi''(s) + \frac{\tilde{\tau}(s)}{\sigma(s)}\psi'(s) + \frac{\tilde{\sigma}(s)}{\sigma^2(s)}\psi(s) = 0 \tag{5}$$

where $\sigma(s)$ and $\tilde{\sigma}(s)$ are polynomials, at most second-degree, and $\tilde{\tau}(s)$ is a first-degree polynomial. The general view point of this paper is to present an analytical solution of the angle-dependent part of the Schrödinger equation for an exactly solvable angle-dependent potential $V_\theta(\theta)/r^2$ and also to obtain modified ℓ states of diatomic molecules. The solution method developed by Nikiforov and Uvarov is used for solving the Schrödinger equation. The angle-dependent part of the Schrödinger equation is investigated in detail to derive some analytical result and the solution of the radial part of the associated equation for the Morse and Kratzer potentials is extracted from the papers published previously [38,39]. The modified ℓ state expressions for the Morse and Kratzer potentials are obtained by connecting the results of the angle-dependent part with the radial one. The modified ℓ states of a number of neutral diatomic molecules composed of a first-row transition metal and main-group elements are calculated for both Morse and Kratzer potentials with an angle-dependent potential.

2 Separating variables of the Schrödinger equation in spherical coordinates

The starting point of this section is to separate the Schrödinger equation in spherical coordinates for a diatomic molecule represented by a rotating potential model. After separating the center of mass motion, the eigenvalue equation for a rotating motion in spherical coordinates is solved by using the NU method and the energy levels of the discrete spectrum are obtained for several diatomic molecules. In spherical coordinates, the Schrödinger equation is written as follows:

$$\begin{aligned}&\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\right\}\Psi_{n\ell m}(\mathbf{r})\\&+V(\mathbf{r})\Psi_{n\ell m}(\mathbf{r}) = E\Psi_{n\ell m}(\mathbf{r}).\end{aligned} \tag{6}$$

The energy E in Eq. 6 is real and it is either discrete for bound states ($E < 0$) or continuous for scattering states ($E > 0$). Introducing a new variable $x = \cos^2\theta$, Eq. 6

can be explicitly turned into the more useful one:

$$\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\left[4x(1-x)\frac{\partial^2}{\partial x^2}+2(1-3x)\frac{\partial}{\partial x}+\frac{1}{1-x}\frac{\partial^2}{\partial\varphi^2}\right]\right\}\Psi_{n\ell m}(\mathbf{r})$$
$$+\frac{2\mu}{\hbar^2}(E-V(\mathbf{r}))\Psi_{n\ell m}(\mathbf{r})=0. \tag{7}$$

Consequently, this equation is separable for a potential of the following form,

$$V(\mathbf{r})=V_{M,K}(r)+\frac{1}{r^2}\left[V_\theta(x)+\frac{1}{1-x}V_\varphi(\varphi)\right]. \tag{8}$$

If we write the wave function as $\Psi_{n\ell m}(\mathbf{r})=r^{-1}R_{n\ell}(r)\Theta_{\ell m}(\theta)\Phi_m(\varphi)$, then the wave equation in Eq. 7 with the potential in Eq. 8 is separated to a set of second-order differential equations in all three coordinates as follows:

$$\left(\frac{d^2}{dr^2}-\frac{E_\theta}{r^2}+\frac{2\mu}{\hbar^2}(E-V_{M,K}(r))\right)R_{n\ell}(r)=0, \tag{9}$$
$$\left(4x(1-x)\frac{d^2}{dx^2}+2(1-3x)\frac{d}{dx}-\frac{E_\varphi}{1-x}+E_\theta-\frac{2\mu}{\hbar^2}V_\theta(x)\right)\Theta_{\ell m}(x)=0, \tag{10}$$
$$\left(\frac{d^2}{d\varphi^2}-\frac{2\mu}{\hbar^2}V_\varphi(\varphi)+E_\varphi\right)\Phi_m(\varphi)=0, \tag{11}$$

where E_φ and E_θ are the separation constants, which are real and dimensionless. Since the wave function $\Psi_{n\ell m}(\mathbf{r})$ must be finite in all space for the bound states, the boundary conditions for Eq. 9 require $R_{n\ell}(0)=0$ and the square-integrability of $R_{n\ell}(r)$ on $(0,\infty)$, which implies that $R_{n\ell}(\infty)=0$. The finite solutions for $\Theta_{\ell m}(\theta)$ in the range $0\le\theta\le\pi$ are able to map into a differential equation of hypergeometric type. Moreover, the boundary conditions for Eq. 11 must be $\Phi_m(\varphi+2\pi)=\Phi_m(\varphi)$. If the azimuthal-dependent potential part $V_\varphi(\varphi)$ is set up to zero, then the normalized solution of Eq. 11 that satisfies the boundary conditions becomes

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi},\quad m=0,\pm1,\pm2,\ldots, \tag{12}$$

where one of the separation constants E_φ represents m^2, i.e., $E_\varphi=m^2$.

2.1 The solution of Eq. 10

It is well-known that the solution of the radial part of the Schrödinger equation gives eigenvalues and eigenfunctions for a particle moving within the interaction potentials. However, the solution of the angle-dependent part of the corresponding equation does not depends on eigenvalues presented in the solution of the radial part explicitly. It only exhibits a parameter relationship between contribution constants which come from the θ-dependent part of the potential. Such a relationship can be expressed by solving Eq. 10 in terms of E_θ. Equation 10 can then be rewritten in the following form by introducing an exactly solvable angle-dependent potential given in Eq. 4,

$$\left(4x(1-x)\frac{d^2}{dx^2}+2(1-3x)\frac{d}{dx}-\frac{E_\varphi}{1-x}+E_\theta-\left(\frac{A}{1-x}+\frac{B}{x}\right)\right)\Theta_{\ell m}(x)=0. \quad (13)$$

An arrangement of the above equation turns to a convenient form to make a comparison with the main equation of the NU method given in Eq. 5;

$$\frac{d^2\Theta_{\ell m}(x)}{dx^2}+\frac{(1-3x)}{2x(1-x)}\frac{d\Theta_{\ell m}(x)}{dx}+\frac{1}{[2x(1-x)]^2} \times\left(-E_\theta x^2+x(E_\theta-\widetilde{A}+B)-B\right)\Theta_{\ell m}(x)=0, \quad (14)$$

where $\widetilde{A}=m^2+A$ (keeping in mind the selection of $E_\varphi=m^2$). Having compared Eq. 14 with Eq. 5, the following polynomial equalities are obtained immediately

$$\widetilde{\tau}=1-3x, \quad (15)$$

$$\sigma=2x(1-x), \quad (16)$$

$$\widetilde{\sigma}=-E_\theta x^2+x(E_\theta-\widetilde{A}+B)-B. \quad (17)$$

In the next step, the basic solution procedure of the NU method given in Ref. [38] will be followed to find a solution of Eq. 14 in terms of E_θ. If polynomials given in Eqs. 15–17 are substituted into Eq. 6 of Ref. [38], π function is obtained as follows

$$\pi=\frac{1-x}{2}\pm\frac{1}{2}\sqrt{x^2(4E_\theta-8k+1)-x(4E_\theta-4\widetilde{A}+4B-8k+2)+1+4B}. \quad (18)$$

The simplest form of π can be written

$$\pi=\frac{1-x}{2}\pm\frac{1}{2}\sqrt{\alpha x^2-\beta x+\gamma}, \quad (19)$$

where $\alpha=4E_\theta-8k+1$, $\beta=4E_\theta-4\widetilde{A}+4B-8k+2$ and $\gamma=1+4B$. The possible solutions according to the plus and minus signs of Eq. 19 depend on the parameter k within the square root sign. The expression under the square root has to be the square of a polynomial, since π is a polynomial of degree at most 1. To satisfy this condition, the discriminant of the expression within the square root must be set up to zero, i.e., $\Delta=\beta^2-4\alpha\gamma=0$. This identity leads to

$$(4E_\theta-4\widetilde{A}+4B-8k+2)^2-4(4E_\theta-8k+1)(1+4B)=0, \quad (20)$$

and a second-order equation related to k is originated as follows

$$4k^2+4k(\widetilde{A}+B-E_\theta)+(\widetilde{A}-B)^2-2E_\theta(\widetilde{A}+B)+E_\theta^2-\widetilde{A}=0. \quad (21)$$

Hence, the double roots of k are derived as

$$k_{1,2} = -\frac{(\widetilde{A} + B - E_{\theta})}{2} \pm \frac{1}{2}\sqrt{\widetilde{A}(1+4B)}. \tag{22}$$

Substituting $k_{1,2}$ into Eq. 18, the four possible solutions of π are obtained

$$\pi = \frac{1-x}{2} \pm \frac{1}{2}\begin{cases} \left[\left(2\sqrt{\tilde{A}} - \sqrt{1+4B}\right)x + \sqrt{1+4B}\right], \\ \qquad \text{for} \quad k_1 = -\frac{(\tilde{A}+B-E_{\theta})}{2} + \frac{1}{2}\sqrt{\tilde{A}(1+4B)} \\ \left[\left(2\sqrt{\tilde{A}} + \sqrt{1+4B}\right)x - \sqrt{1+4B}\right], \\ \qquad \text{for} \quad k_2 = -\frac{(\tilde{A}+B-E_{\theta})}{2} - \frac{1}{2}\sqrt{\tilde{A}(1+4B)} \end{cases} \tag{23}$$

where $k_{1,2}$ is determined by means of the same procedure as in Ref. [38]. We have to choose one of the four possible forms of π to obtain the bound state solutions. Therefore, its most suitable form is established by $\pi = \frac{1-x}{2} - \frac{1}{2}\left[\left(2\sqrt{\tilde{A}} + \sqrt{1+4B}\right)x - \sqrt{1+4B}\right]$ for $k_2 = -\frac{(\tilde{A}+B-E_{\theta})}{2} - \frac{1}{2}\sqrt{\tilde{A}(1+4B)}$. The main requirement in the selection of this form is to find the negative derivative of $\tau(s)$ given by Eq. 9 of Ref. [38]. In that case, $\tau(s)$ and $\tau'(s)$ are obtained, respectively,

$$\begin{aligned} \tau(s) &= 1 + \sqrt{1+4B} - x\left(4 + 2\sqrt{\tilde{A}} + \sqrt{1+4B}\right), \\ \tau'(s) &= -\left(4 + 2\sqrt{\tilde{A}} + \sqrt{1+4B}\right) < 0. \end{aligned} \tag{24}$$

Another major polynomials given in the basic solution procedure of the NU method are λ and $\lambda_{\widetilde{n}}$ [37]. Both polynomials can be connected with each other by means of Eqs. 7 and 8 of Ref. [38]. Hence, a polynomial of degree $\widetilde{n}$ is found by using $\lambda_{\widetilde{n}} = -\widetilde{n}\tau' - \frac{\widetilde{n}(\widetilde{n}-1)}{2}\sigma''$;

$$\lambda_{\widetilde{n}} = 2\widetilde{n}^2 + 2\widetilde{n} + 2\widetilde{n}\sqrt{\tilde{A}} + \widetilde{n}\sqrt{1+4B}, \quad (\widetilde{n} = 0, 1, 2, \ldots) \tag{25}$$

taking $\sigma'' = -4$. Moreover, λ is obtained from $k_2 + \pi'$;

$$\lambda = -\frac{1}{2}\sqrt{1+4B}\left(1 + \sqrt{\tilde{A}}\right) - \frac{1}{2}\left(\tilde{A} + B - E_{\theta} + 1\right) - \sqrt{\tilde{A}} \tag{26}$$

After comparing Eq. 25 with Eq. 26 and also making some arrangements on the comparison, the separation constant E_{θ} is obtained as follows

$$\left(2\widetilde{n} + \sqrt{\tilde{A}}\right)^2 + 2\sqrt{\tilde{A}} + \sqrt{1+4B} + \left(2\widetilde{n} + \sqrt{\tilde{A}}\right)\sqrt{1+4B} + (1+B) = E_{\theta}. \tag{27}$$

It is very useful to prepare $\widetilde{\ell}(\widetilde{\ell}+1)$ as a new presentation instead of E_θ. In this case, Eq. 27 turns to

$$\left(1/2+2\widetilde{n}+\sqrt{\tilde{A}}+\sqrt{1/4+B}\right)\left(1/2+2\widetilde{n}+\sqrt{\tilde{A}}+\sqrt{1/4+B}+1\right)=\widetilde{\ell}(\widetilde{\ell}+1), \qquad (28)$$

and it becomes in terms of $\widetilde{\ell}$

$$\widetilde{\ell}=\left(1/2+2\widetilde{n}+\sqrt{\tilde{A}}+\sqrt{1/4+B}\right). \qquad (29)$$

The term $\widetilde{\ell}$ in Eq. 29 can be named the "modified" orbital angular momentum, since the contribution which comes from the angle-dependent potential damages the usual orbital angular momentum ℓ. Moreover, the result obtained in Eq. 29 is in agreement with results on the more involved case of Ref. [40]. In the limiting case $B=0$, the factor $\sqrt{1/4+B}$ in Eq. 29 should be replaced by $\pm 1/2$ so that Eq. 29 turns into $\nu+\sqrt{\tilde{A}}$, where $\nu=1+2\widetilde{n}$ for the odd functional solution or $\nu=2\widetilde{n}$ for the even functional solution [41]. The parameter $\widetilde{\ell}$ does not need to be integer. However, the difference between the parameter $\widetilde{\ell}$ and the square root terms in Eq. 29 have to be integer;

$$\widetilde{n}=\frac{1}{2}\left\{\widetilde{\ell}-\left(1/2+\sqrt{\tilde{A}}+\sqrt{1/4+B}\right)\right\}, \quad \widetilde{n}=0,1,2,\ldots \qquad (30)$$

where $\widetilde{n}$ corresponds to the number of quanta for oscillations.

2.2 The solution of Eq. 9

It is remarkable that the radial equation in Eq. 9 is independent of the angle-dependent term given in Eqs. 2 and 3 for the Morse and Kratzer cases, respectively. Equation 9 is exactly soluble by means of the NU method. However, some caution must be observed especially on the solution of the Morse potential since the exponential nature of the Morse potential and the radial behavior of the centrifugal kinetic energy term do not allow for solving the Schrödinger equation simultaneously. In the case of Kratzer potential, no caution is necessary when considering the Kratzer potential together with the centrifugal term since both terms shows the radial behaviors. In the following subsections, the solution of both potentials is briefly investigated by using the NU method.

2.2.1 The Morse case

Adopting the Morse potential to Eq. 9, the radial Schrödinger equation turns into the following form

$$\left(\frac{d^2}{dr^2}-\frac{E_\theta}{r^2}+\frac{2\mu}{\hbar^2}\left(E-D_e\left(e^{-2a(r-r_e)}-2e^{-a(r-r_e)}\right)\right)\right)R_{n\ell}(r)=0. \qquad (31)$$

Disadvantage of Eq. 31 is that analytical solutions cannot be found because of the centrifugal kinetic energy term of the potential proportional to E_θ/r^2 is included into the radial Schrödinger equation. In order to obtain an analytical solution of Eq. 31, the term E_θ/r^2 has to be approximated to the exponential one. Using an accurate approximate treatment suggested by Pekeris [42], this term can be translated into the following form

$$\frac{E_\theta}{r^2} \cong \frac{E_\theta}{r_e^2}\left(D_0 + D_1 e^{-ar_e x} + D_2 e^{-2ar_e x}\right), \tag{32}$$

where x is a coordinate transformation represented by $(r - r_e)/r_e$ and D_i is the coefficients which are given in Eq. 18 of Ref. [38] $(i = 0, 1, 2)$. Substituting Eq. 32 into Eq. 31 and using a new variable of the form $s = e^{-ar_e x}$, the resulting Schrödinger equation becomes

$$\frac{d^2 R_{n\ell}(s)}{ds^2} + \frac{1}{s}\frac{dR_{n\ell}(s)}{ds} + \frac{1}{s^2}\left[-\varepsilon_1^2 + \varepsilon_2 s - \varepsilon_3 s^2\right] R_{n\ell}(s) = 0, \tag{33}$$

where $-\varepsilon_1^2 = 2\mu\left(E - \frac{E_\theta D_0}{r_e^2}\right)/\hbar^2 a^2$, $\varepsilon_2 = 2\mu\left(2D_e - \frac{E_\theta D_1}{r_e^2}\right)/\hbar^2 a^2$ and $\varepsilon_3 = 2\mu\left(D_e - \frac{E_\theta D_2}{r_e^2}\right)/\hbar^2 a^2$. Comparing this equation with that of Eq. 21 of Ref. [38] and following the solution steps of the NU method, the energy spectrum according to the quantum numbers n, $\widetilde{n}$ and m is obtained as

$$E_{n\widetilde{n}m} = \frac{\hbar^2 E_\theta}{2\mu r_e^2}\left(1 - \frac{3}{ar_e} + \frac{3}{a^2 r_e^2}\right) - \frac{\hbar^2 a^2}{2\mu}\left[C_{\widetilde{n}m} - \left(n + \frac{1}{2}\right)\right]^2, \tag{34}$$

where

$$C_{\widetilde{n}m} = \frac{1}{\sqrt{\frac{2\mu a^2 D_e}{\hbar^2} + \frac{a^2 E_\theta D_2}{r_e^2}}}\left[\frac{2\mu D_e}{\hbar^2} - \frac{E_\theta}{r_e^2}\left(\frac{2}{ar_e} - \frac{3}{a^2 r_e^2}\right)\right], \tag{35}$$

and E_θ is given by Eq. 28, keeping in mind $\tilde{A} = m^2 + A$. The highest vibrational quantum number n_{max} can be directly estimated from the condition $dE_{n\widetilde{n}m}/dn = 0$;

$$n_{max} = C_{\widetilde{n}m} - \frac{1}{2}. \tag{36}$$

n_{max} is generally limited to obtain the number of bound states in the case of the Morse potential and its maximum value depends on the potential parameters of a given diatomic molecule as well as the quantum numbers $\widetilde{n}$ and m.

2.2.2 The Kratzer case

Among many two-particle interaction models, one of the most interesting potential types is the Kratzer potential because it can be exactly solved for the general case of rotation states different from zero. The first term on the right-hand side of Eq. 4 is the central Kratzer potential and the radial part of the Schrödinger equation in the presence of this potential can be written as follows, recalling Eq. 9,

$$\left(\frac{d^2}{dr^2}-\frac{E_\theta}{r^2}+\frac{2\mu}{\hbar^2}\left[E+D_e-D_e\left(\frac{r-r_e}{r}\right)^2\right]\right)R_{n\ell}(r)=0. \tag{37}$$

Using the transformation $s \to r/r_e$ and letting the dimensionless notations

$$-\varepsilon_1^2=\frac{2\mu r_e^2 E}{\hbar^2},\quad \varepsilon_2=\frac{4\mu D_e r_e^2}{\hbar^2},\quad \varepsilon_3=E_\theta+\frac{2\mu D_e r_e^2}{\hbar^2}, \tag{38}$$

Equation 37 can be rewritten in a simple form as follows

$$\frac{d^2R_{n\ell}(s)}{ds^2}+\frac{1}{s^2}\left(-\varepsilon_1^2 s^2+\varepsilon_2 s-\varepsilon_3\right)R_{n\ell}(s)=0. \tag{39}$$

The complete solution of Eq. 39 by means of the NU method can be found in Ref. [39], after having made of some notation setting. Hence, the energy spectrum with respect to the quantum numbers n, $\widetilde{n}$ and m is obtained as

$$E_{n\widetilde{n}m}=-\frac{\hbar^2}{2\mu}\left[\left(\frac{4\mu D_e r_e}{\hbar^2}\right)^2\left(1+2n+\sqrt{1+4D_{\widetilde{n}m}}\right)^{-2}\right], \tag{40}$$

where

$$D_{\widetilde{n}m}=\frac{2\mu D_e r_e^2}{\hbar^2}+\left(1/2+2\widetilde{n}+\sqrt{m^2+A}+\sqrt{1/4+B}\right)\times\left(1/2+2\widetilde{n}+\sqrt{m^2+A}+\sqrt{1/4+B}+1\right). \tag{41}$$

The derivative of Eq. 41 according to n gives the maximum vibrational quantum number n_{max} in the case of Kratzer potential;

$$\frac{dE_{n\widetilde{n}m}}{dn}=\frac{\frac{8\mu D_e^2 r_e^2}{\hbar^2}}{\left(1+2n_{max}+\sqrt{1+4D_{\widetilde{n}m}}\right)^3}=0. \tag{42}$$

The condition which requires to satisfy the equality on the right-hand side of Eq. 42 is that n_{max} must be supported by an infinite number of vibrational levels.

2.3 Remarks and calculations for the modified ℓ states

In order to discuss the behavior of energy spectrums of a diatomic molecule when the values of quantum numbers n, $\widetilde{n}$ and m differ, it is very useful to select some diatomic

Table 1 Spectroscopic parameters and reduced masses for some diatomic molecules composed of a first-row transition metal and main-group elements (H-F). The complete list of this table can be found from Ref. [49]

Molecule	D_e (eV)	r_e (Å)	ω_e (cm^{-1})	a (Å^{-1})	μ (a.m.u)	Reference
ScH	2.25	1.776	1572	1.41113	0.986040	[43]
TiH	2.05	1.781	1407	1.32408	0.987371	[43]
VH	2.33	1.719	1635	1.44370	0.988005	[43]
CrH	2.13	1.694	1647	1.52179	0.988976	[43]
MnH	1.67	1.753	1530	1.59737	0.989984	[43]
CuLi	1.74	2.310	392	1.00818	6.259494	[44]
TiC	2.66	1.790	592	1.52550	9.606079	[45]
NiC	2.76	1.621	874	2.25297	9.974265	[46]
ScN	4.56	1.768	726	1.50680	10.682771	[47]
ScF	5.85	1.794	713	1.46102	13.358942	[48]

molecules composed of a first-row transition metal and main-group elements (H-F). One or two of these molecules are the first-row transition metal hydrides such as ScH, TiH, VH, CrH and MnH [43]. Transition metal hydrides are chemical compounds formed when hydrogen gas reacts with transition metal atoms. These are of considerable importance in chemical synthesis as intermediates and in solid matrix samples for infrared spectroscopic study. Another diatomic molecule containing the transition metal element copper (Cu) and the main group element lithium (Li) is CuLi, which elucidates the nature of the bonding in mixed transition metal lithides [44]. Presently the transition metal carbide molecules such as TiC and NiC represent a very active field of research, especially due to the desire for a quantitative understanding of their chemical bonds [45,46]. Moreover, diatomic scandium nitride molecule ScN has excellent physical properties of high temperature stability as well as electronic transport properties, which are typical of transition metal nitride [47]. Furthermore, the scandium fluoride molecule ScF is the best studied transition metal halide and it has been fairly well characterized [48]. Diatomic molecules which consist of transition metal and main group elements are challenging theoretically and computationally, but recent advancements in computational methods have made such molecules more accessible to investigations. Their spectroscopic parameters have been accurately determined by using ab-initio calculations. One of these calculations is called the multi-configuration self-consistent field (MCSCF) and it seems qualitatively correct. In Table 1, the spectroscopic parameters of the above mentioned diatomic molecules are summarized using MCSCF results [49]. However, choice of the parameter a is not a simple issue. Solution of the Schrödinger equation for the Morse potential gives the following well-known relation (see p.132 of Ref. [25]);

$$a = \frac{\omega_e}{2r_e\sqrt{B_e D_e}}, \tag{43}$$

Table 2 The variation of bound state energies (in eV) for various values of n, $\widetilde{n}$, m, A and B

Molecule	n	$\widetilde{n}$	m	Morse potential			Kratzer potential		
				$A = 1$ $B = 9$	$A = 1$ $B = 1$	$A = 9$ $B = 1$	$A = 1$ $B = 9$	$A = 1$ $B = 1$	$A = 9$ $B = 1$
ScH	0	0	0	−2.13697	−2.14733	−2.13645	−2.19509	−2.20526	−2.19459
	1	1	0	−1.93560	−1.95052	−1.93490	−2.10731	−2.12154	−2.10665
	3	2	1	−1.56637	−1.58578	−1.56832	−1.95151	−1.96918	−1.95327
	3	3	2	−1.53010	−1.55582	−1.53794	−1.91920	−1.94202	−1.92611
	5	4	3	−1.17869	−1.20852	−1.19224	−1.76519	−1.79029	−1.77652
	5	5	4	−1.12534	−1.16101	−1.14521	−1.72169	−1.75058	−1.73769
TiH	0	0	0	−1.94719	−1.95748	−1.94668	−1.99713	−2.00721	−1.99663
	1	1	0	−1.76538	−1.78019	−1.76469	−1.91331	−1.92738	−1.91266
	3	2	1	−1.43216	−1.45141	−1.43409	−1.76537	−1.78272	−1.76710
	3	3	2	−1.39624	−1.42170	−1.40400	−1.73372	−1.75607	−1.74048
	5	4	3	−1.07703	−1.10651	−1.09041	−1.58802	−1.61244	−1.59903
	5	5	4	−1.02440	−1.05957	−1.04398	−1.54584	−1.57383	−1.56133
VH	0	0	0	−2.21203	−2.22307	−2.21148	−2.27210	−2.28293	−2.27156
	1	1	0	−2.00226	−2.01816	−2.00153	−2.17978	−2.19492	−2.17908
	3	2	1	−1.61793	−1.63859	−1.62000	−2.01624	−2.03499	−2.01810
	3	3	2	−1.57935	−1.60671	−1.58769	−1.98197	−1.07718	−1.98929
	5	4	3	−1.21343	−1.24513	−1.22783	−1.82048	−1.84705	−1.83247
	5	5	4	−1.15677	−1.19465	−1.17787	−1.77450	−1.80503	−1.79140
CrH	0	0	0	−2.01092	−2.02226	−2.01036	−2.07289	−2.08400	−2.07234
	1	1	0	−1.80031	−1.81659	−1.79956	−1.96202	−1.98219	−1.96113
	3	2	1	−1.41769	−1.43870	−1.41980	−1.8247	−1.84369	−1.82659
	3	3	2	−1.37846	−1.40627	−1.38694	−1.79010	−1.81452	−1.79749
	5	4	3	−1.01871	−1.05067	−1.03322	−1.63474	−1.66128	−1.64671
	5	5	4	−0.96162	−0.99978	−0.98287	−1.58901	−1.61934	−1.60579
MnH	0	0	0	−1.55956	−1.57012	−1.55904	−1.61987	−1.63018	−1.61936
	1	1	0	−1.36574	−1.38081	−1.36504	−1.54231	−1.55656	−1.54165
	3	2	1	−1.01943	−1.03864	−1.02136	−1.40762	−1.42489	−1.40934
	3	3	2	−0.98358	−1.00900	−0.99133	−1.37632	−1.39839	−1.38298
	5	4	3	−0.66694	−0.69570	−0.68000	−1.24530	−1.26892	−1.25593
	5	5	4	−0.61561	−0.64992	−0.63471	−1.20492	−1.23166	−1.21969
CuLi	0	0	0	−1.71422	−1.71519	−1.71417	−1.72804	−1.72901	−1.72799
	1	1	0	−1.66482	−1.66626	−1.66475	−1.70610	−1.70752	−1.70603
	3	2	1	−1.56867	−1.57064	−1.56886	−1.66395	−1.66586	−1.66414
	3	3	2	−1.56497	−1.56759	−1.56577	−1.66038	−1.66291	−1.66115
	5	4	3	−1.46933	−1.47256	−1.47080	−1.61763	−1.62070	−1.61903
	5	5	4	−1.46352	−1.46741	−1.46569	−1.61213	−1.61581	−1.61419
TiC	0	0	0	−2.62172	−2.62278	−2.62167	−2.61837	−2.61941	−2.61832
	1	1	0	−2.54773	−2.54930	−2.54766	−2.59060	−2.59213	−2.59052

Table 2 continued

Molecule	n	$\widetilde{n}$	m	Morse potential			Kratzer potential		
				$A = 1$ $B = 9$	$A = 1$ $B = 1$	$A = 9$ $B = 1$	$A = 1$ $B = 9$	$A = 1$ $B = 1$	$A = 9$ $B = 1$
	3	2	1	−2.40344	−2.40559	−2.40366	−2.53690	−2.53898	−2.53711
	3	3	2	−2.39942	−2.40228	−2.40029	−2.53301	−2.53577	−2.53385
	5	4	3	−2.25676	−2.26028	−2.25836	−2.47861	−2.48196	−2.48013
	5	5	4	−2.25042	−2.25467	−2.25279	−2.47257	−2.47661	−2.47482
NiC	0	0	0	−2.70409	−2.70533	−2.70402	−2.74321	−2.74445	−2.74315
	1	1	0	−2.59598	−2.59781	−2.59589	−2.71217	−2.71398	−2.71208
	3	2	1	−2.38692	−2.38942	−2.38717	−2.65228	−2.65473	−2.65252
	3	3	2	−2.38223	−2.38556	−2.38325	−2.64768	−2.65094	−2.64868
	5	4	3	−2.17893	−2.18301	−2.18079	−2.58698	−2.59093	−2.58878
	5	5	4	−2.17157	−2.17650	−2.17432	−2.57987	−2.58463	−2.58252
ScN	0	0	0	−4.51353	−4.51451	−4.51348	−4.54157	−4.54255	−4.54152
	1	1	0	−4.42292	−4.42437	−4.42285	−4.50668	−4.50812	−4.50662
	3	2	1	−4.24493	−4.24693	−4.24513	−4.43862	−4.44058	−4.43881
	3	3	2	−4.24119	−4.24385	−4.24200	−4.43494	−4.43755	−4.43573
	5	4	3	−4.06444	−4.06774	−4.06594	−4.36611	−4.36932	−4.36757
	5	5	4	−4.05850	−4.06248	−4.06072	−4.36033	−4.36420	−4.36249
ScF	0	0	0	−5.80466	−5.80542	−5.80462	−5.83194	−5.83270	−5.83190
	1	1	0	−5.71576	−5.71689	−5.71571	−5.79735	−5.79848	−5.79730
	3	2	1	−5.54042	−5.54198	−5.54057	−5.72950	−5.73104	−5.72965
	3	3	2	−5.53749	−5.53957	−5.53813	−5.72661	−5.72866	−5.72723
	5	4	3	−5.36298	−5.36556	−5.36415	−5.65811	−5.66064	−5.65926
	5	5	4	−5.35832	−5.36144	−5.36006	−5.65355	−5.65660	−5.65525

where $B_e = \frac{hc}{8\pi^2 \mu c^2 r_e^2}$. Notice that the parameter a is used to calculate the energy spectrum of the Morse potential. Another considerable effort for the Morse potential is that the highest vibrational quantum number n_{max} changes according to the spectroscopic parameters of diatomic molecules as well as the parameters $\widetilde{n}$, m, A and B, keeping in mind Eq. 36. As an example, the value of n_{max} for ScH is 20 in the fixed values of $A = 1$ and $B = 9$ and under the conditions of $\widetilde{n} \leq 10$ and $m \leq 10$. The values of n_{max} for TiH, VH, CrH, MnH, CuLi, TiC, NiC, ScN and ScF molecules given in Table 1 are aligned 20, 20, 17, 14, 70, 71, 50, 100 and 131, respectively, in the same values of parameters and conditions.

To calculate the bound state energies of diatomic molecules given in Table 1, Eqs. 34 and 40 must be recalled for the Morse and Kratzer cases, respectively. Taken into account spectroscopic parameters of diatomic molecules and arbitrary values of A and B, the bound state energies can be compared for both potentials. This type of comparison is given in Table 2. As can be seen from Table 2, when parameters A and B are fixed to 1 and 1, respectively, for different values of n, $\widetilde{n}$ and m, the bound state energies become lower than that of other values. A comparison of $A = 1$ and $B = 9$ with $A = 9$ and $B = 1$ shows that the bound state energies obtained for $A = 1$ and $B = 9$ are a little smaller than the energies obtained for $A = 9$ and $B = 1$ in small values of $n, \widetilde{n}$ and m, especially 0 and 1. For large values of the quantum numbers, the bound state energies obtained for $A = 9$ and $B = 1$ tend to become more separately spaced than the energies obtained for $A = 1$ and $B = 9$.

3 Conclusions

An interesting extension of this work is to study the effect of an angle-dependent potential to the Morse and Kratzer potentials and to examine the partial changes on the usual ℓ states. The analysis presented in this work suggests that the bound state energies of diatomic molecules depend on the quantum numbers $n, \widetilde{n}, m$ and also the parameters A and B. Moreover, the energy spectrum obtained in Eq. 34 is an approximate description of the quantum aspects of diatomic molecules for the Morse potential together with angle-dependent potential while the spectrum obtained in Eq. 40 is a complete description for the Kratzer potential together with angle-dependent potential. Furthermore, the solution procedure presented in this paper is also systematical and efficient for solving the angle-dependent part of the Schrödinger equation.

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