

# A New Analytical Approach to Study the Anharmonic and Morse Potentials of Diatomic Molecules

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## Abstract

An appropriate analytical method has been used to solve the Schrödinger equation, for a polynomial anharmonic potential to obtain the eigen-energy levels, up to the second order. Moreover, the derived expression has been exploited in the case of the Morse potential that led to express the vibrational energy of diatomic molecules. The application of the proposed analytical method to some selected molecules makes it possible to obtain results that are in good agreement with those available in the literature, and proves that our approach can be a valuable aid in spectroscopic experiments.

**Keywords:** Anharmonic, Morse potential, Diatomic molecule, Energy levels.

## 1. INTRODUCTION

Due to the major role that plays harmonic and anharmonic oscillators in many branches of physics, they have been shown to furnish suitable models for describing the nature of various physical phenomena, in particular, in quantum mechanics, quantum optics and in chemical physics. Therefore, they have been widely studied in order to explain the different experimental results related to different systems and to give their interpretation.

Simple physical problems were usually treated in a first approximation, by analogy with the idealized model of the harmonic oscillator, but this assumption is not adapted anymore with the situations of real systems. Thence, the anharmonic oscillator has generated considerable effort and great interest in advanced mathematical and physical researches, to provide answers to realistic classical and quantum problems, such as the time-dependent Schrödinger equation of many quantum systems, which

is not yet exactly solved, and certain mechanisms of molecular dynamics that are not yet sufficiently explained. It can be noticed that many analytical and numerical methods have been developed and devoted to the resolution of the Schrödinger equation in the presence of anharmonic potential functions, in order to obtain an accurate energy spectrum and bound states solutions of molecular systems. Among the methods used to explore different aspects of the non-relativistic quantum mechanical systems, we cite the usual theory of perturbations [1, 2], the Lie algebraic method with canonical transformation [3], the variational method combined with the finite element method [4] and the iterative asymptotic method [5]. However, the choice of the interaction potential is essential for the description of molecular spectra. The adequate potential,  $V(r)$ , is chosen to behave correctly at its coordinate limits, i.e., at the equilibrium bond length ( $r_e$ ) of stable molecules;  $V(r_e)$  has a

minimum and  $V(\infty)$  approaches a constant. Morse (1929) has proposed an empirical potential energy [6], which is the most used model for diatomic molecules. However, the bond length of the Morse potential approaches a finite and large value, while the real potential should approach infinity. Other common interaction potentials for microscopic systems, such as those studied by Poschl-Teller [7], Varshini [8], Deng- Fan [9, 10], etc., are designed to satisfy the perfect boundary conditions, and are used to determine the precise energy spectrum in good agreement compared with the experimental data.

In previous works, we have applied an analytical approach, based on the Floquet theorem combined with the resonating averages method, to solve the Schrödinger equation for different quantum interactions. Moreover, we have successfully explored and exploited some physical properties of the derived solutions, showing the accuracy of the method [11-14].

The purpose of this paper is to extend the calculation for the Taylor expansion of the Morse potential to higher order terms. Therefore, we study the potential with the cubic, quatic, quintic and sextic terms and we present the analytically approximate solutions to this system, emphasizing the expressions obtained for the first and second order corrections. From there, we operate our approach for the Morse potential, developed in Taylor series to sixth order. This will allow us to obtain the expressions of the vibrational energy levels up to the second order for diatomic molecular systems. Besides, we note that the implementation of our proposed method can be useful to solve the Schrödinger equation for different classes of potentials. Then, using the established formulas one can express the energy spectrum as well as the dissociation energy. One can also calculate the main spectroscopic transitions of the chosen diatomic molecules (HCl, LiH, CO, NO),

according to their Morse potential parameters.

The structure of our paper is as follows. In section 2, we review the theoretical background and we give the established relationships. In section 3, we present the results of numerical calculations relative to some diatomic molecules, and we make comparisons with the literature. Finally, section 4 contains the conclusion.

## 2. MAIN THEORY

We consider the polynomial anharmonic oscillator including terms up to order six such that,

$$H = H_0 + \mu_1 \hbar \omega_0 \hat{q}^3 + \mu_2 \hbar \omega_0 \hat{q}^4 + \mu_3 \hbar \omega_0 \hat{q}^5 + \mu_4 \hbar \omega_0 \hat{q}^6 \quad (1)$$

where

$$\hat{q} = \sqrt{\frac{m\omega_0}{\hbar}} q = \frac{1}{\sqrt{2}} (a + a^\dagger) \quad (2)$$

where  $m$  and  $\omega_0$  are the mass and the frequency, respectively, and  $H_0$  is the Hamiltonian of the simple harmonic oscillator given by

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 = \hbar \omega_0 (a^\dagger a + \frac{1}{2}) \quad (3)$$

$\mu_1 \hbar \omega_0 \hat{q}^3$ ,  $\mu_2 \hbar \omega_0 \hat{q}^4$ ,  $\mu_3 \hbar \omega_0 \hat{q}^5$  and  $\mu_4 \hbar \omega_0 \hat{q}^6$  are the perturbation anharmonic terms, which amplitudes are  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$  and  $\mu_4$  respectively.

Notice that the contribution to first and second orders, due to cubic and quatic perturbations ( $\mu_1 \hbar \omega_0 \hat{q}^3$  and  $\mu_2 \hbar \omega_0 \hat{q}^4$ ), have been treated in our previous works [11, 12], and the obtained energy levels, corresponding to these systems are given by the following expressions (equations (24) and (35) of the reference [11])

$${}^{(2a)} E_1 = \hbar \omega_0 (n + \frac{1}{2}) - \frac{15}{4} \mu_1^2 \hbar \omega_0 (n^2 + n + \frac{11}{30}) \quad (4)$$

$$\begin{aligned}
^{(2a)}E_2 = \hbar\omega_0\left(n + \frac{1}{2}\right) + \frac{3}{4}\mu_2\hbar\omega_0(2n^2 \\
+ 2n + 1) - \frac{1}{8}\mu_2^2\hbar\omega_0(34n^3 + 51n^2 \\
+ 59n + 21)
\end{aligned} \quad (5)$$

The motivation of this paper is to perform calculations in order to obtain the contributions to the energy of the quintic and sextic anharmonic terms:  $\mu_3\hbar\omega_0\hat{q}^5$  and  $\mu_4\hbar\omega_0\hat{q}^6$ .

The fundamental procedure of the analytical method was detailed in our previous papers [11-14]. The similar way as in these references is applied to obtain the expressions of the average part and of the oscillating part, related to these interaction potentials, and the associated eigen-energy values are then deduced therefrom.

## 2.1. Case of the Quintic Anharmonic Potential

The Hamiltonian in this case is given by the following expression

$$H = H_0 + \mu_3\hbar\omega_0\hat{q}^5 \quad (6)$$

We express  $\hat{q}$  as a function of annihilation,  $a$ , and creation,  $a^+$ , operators; then we obtain the quantified form of Eq. (6) such that,

$$\begin{aligned}
H = \hbar\omega_0\left(a^+a + \frac{1}{2}\right) + \mu_3\frac{\hbar\omega_0}{4\sqrt{2}}[a^{+5} \\
+ 5a^{+3}(a^+a + 2) + 5a^+(2(a^+a)^2 + \\
4a^+a + 3) + 5(2(a^+a)^2 + 4a^+a + \\
3)a + 5(a^+a + 2)a^3 + a^5]
\end{aligned} \quad (7)$$

By using the following equations (Eqs. (2), (8) and (9) of reference [11])

$$U(t) = T(t)e^{-\frac{iRt}{\hbar}} \quad (8)$$

$$^{(1a)}U_I(t) = \left[1 - \frac{i\mu}{\hbar}\tilde{H}_I(t)\right]^{(1)}V_I(t) \quad (9)$$

$$\begin{aligned}
^{(2a)}U_I(t) = \left[1 - \frac{i\mu}{\hbar}\tilde{H}_I(t) \right. \\
\left. + \mu^2A_2(t)\right]\Gamma(t)
\end{aligned} \quad (10)$$

where  $U(t)$  is the time-evolution operator,  $T(t)$  is a time-periodic unitary operator and  $R$  is a constant hermitic operator (or Floquet operator). The determination of  $^{(1a)}R$  to the first order and  $^{(2a)}R$  to the second order is based on the resonating averages method [15]. This method is applied in the interaction picture of the perturbed Hamiltonian, which is written with the summation of the averaging term  $\bar{H}_I$  and the oscillating term  $\frac{d\tilde{H}_I(t)}{dt}$ .

Applying Eqs. (8) and (9), we obtain the first order Floquet operator, thence we compute the corresponding eigenvalues and deduce the eigenenergies of this system. Since  $\bar{H}_I = 0$ ; these energies remain identical to those of the simple harmonic oscillator, so there is no correction in this order due to the quintic anharmonic perturbation.

Applying the equations (8) and (10) (Eqs. (2) and (9) given in [11]), allowed us to find the improved second-order Floquet operator,

$$\begin{aligned}
^{(2a)}R = H_0 - \frac{\mu_3^2}{32}\hbar\omega_0[630(a^+a)^4 \\
+ 1260(a^+a)^3 + 2030(a^+a)^2 + \\
1400(a^+a) + 449]
\end{aligned} \quad (11)$$

Thus, we deduce the expression of the eigenenergy up to the second order as follows,

$$\begin{aligned}
^{(2a)}E_3 = \hbar\omega_0\left(n + \frac{1}{2}\right) - \frac{\mu_3^2}{32}\hbar\omega_0[630n^4 \\
+ 1260n^3 + 2030n^2 + 1400n + 449]
\end{aligned} \quad (12)$$

We point out that this perturbation affects the energy levels only from the second order.

## 2.2. Case of the Sixtic Anharmonic Potential

The Hamiltonian of this system is given by the following expression

$$H = H_0 + \mu_4 \hbar \omega_0 \hat{q}^6 \quad (13)$$

Similarly, using equations (2), (8) and (9) of reference [11], we obtained the expression for the eigenenergy to the first and second order corrections under the following form,

$$\begin{aligned} {}^{(2a)}E_4 = & \hbar \omega_0 \left( n + \frac{1}{2} \right) + \frac{5}{8} \mu_4 \hbar \omega_0 [4n^3 \\ & + 6n^2 + 8n + 3] - \frac{\mu_4^2}{64} \hbar \omega_0 [1608n^5 + \\ & 3660n^4 + 12940n^3 + 13590n^2 + \\ & 11852n + 3495] \end{aligned} \quad (14)$$

We point out that the corrections due to this perturbation appear at the first order (2<sup>nd</sup> term) and at the second order (last term) of equation (14). However, the anharmonicity effect only appears at the second order. We note that it is a similar physical fact observed in the case of quartic perturbation. Generally, we can assert that when the polynomial perturbation series contains only odd power terms (cubic, quintic,...), the first-order corrections are always equal to zero, and the corrections appear only at the second-order. However, in cases where the polynomial perturbation series contains only even power terms (quartic, sextic,...), the corrections appear at the first and at second orders [16].

## 2.3. Case of Sixth-order Polynomial Anharmonic Potential

The Hamiltonian of this system is given by the equation (1). With the help of equations (4), (5), (12) and (14), we can easily express the formula of its eigenenergy levels up to the second order as follows,

$$\begin{aligned} {}^{(2a)}E = & \frac{\hbar \omega_0}{64} (32 + 48\mu_2 + 120\mu_4 - \\ & 88\mu_1^2 - 168\mu_2^2 - 898\mu_3^2 - 3495\mu_4^2) \\ & + \frac{\hbar \omega_0}{16} (16 + 24\mu_2 + 80\mu_4 - 60\mu_1^2 \\ & - 118\mu_2^2 - 700\mu_3^2 - 2963\mu_4^2)n + \\ & + \frac{\hbar \omega_0}{32} (48\mu_2 + 120\mu_4 - 120\mu_1^2 - \\ & 204\mu_2^2 - 2030\mu_3^2 - 6795\mu_4^2)n^2 + \\ & + \frac{\hbar \omega_0}{16} (40\mu_4 - 68\mu_2^2 - 630\mu_3^2 - \\ & 3235\mu_4^2)n^3 - \frac{15}{16} \hbar \omega_0 (21\mu_3^2 + 61 \\ & \mu_4^2)n^4 - \frac{201}{8} \hbar \omega_0 \mu_4^2 n^5 \end{aligned} \quad (15)$$

The substitution of the values of the amplitudes:  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$  and  $\mu_4$  of the anharmonic perturbations into equation (15) provides the complete second-order energy spectrum of the diatomic system.

## 3. EXPLOITATION OF THE RESULTS IN THE CASE OF THE MORSE OSCILLATOR

The following relation describes the well-known function of the Morse potential [6],

$$V(q) = D_e (1 - e^{-\rho q})^2 \quad (16)$$

Where  $D_e$  is the dissociation energy,  $\rho$  is a parameter that measures the curvature of the potential well, and  $q$  is the variation of interatomic distance with respect to the equilibrium distance.

Since we are dealing with small amplitude oscillations, we can perform the Taylor series expansion of  $V(q)$  to order six around  $q$  as follows,

$$\begin{aligned} V(q) = & D_e \rho^2 q^2 - D_e \rho^3 q^3 + \frac{7}{12} D_e \\ & \rho^4 q^4 - \frac{1}{4} D_e \rho^5 q^5 + \frac{31}{360} D_e \rho^6 q^6 \end{aligned} \quad (17)$$

Then, from the expanded expression of equation (17), we assign the Hamiltonian for the Morse oscillator as,

$$H_M = \frac{p^2}{2m} + D_e \rho^2 q^2 - D_e \rho^3 q^3 + \frac{7}{12} D_e \rho^4 q^4 - \frac{1}{4} D_e \rho^5 q^5 + \frac{31}{360} D_e \rho^6 q^6 \quad (18)$$

The comparison of the coefficients of Eqs. (1) and (18) gives,

$$\omega_0 = \rho \sqrt{\frac{2D_e}{m}} \quad (19)$$

$$\mu_1 = -\frac{D_e \rho^2}{m \omega_0^2} \sqrt{\frac{\hbar}{m \omega_0}} \quad (20)$$

$$\mu_2 = \frac{7}{12} \frac{D_e \rho^4 \hbar}{m^2 \omega_0^3} \quad (21)$$

$$\mu_3 = -\frac{D_e \rho^5 \hbar}{4m^2 \omega_0^3} \sqrt{\frac{\hbar}{m \omega_0}} \quad (22)$$

$$\mu_4 = \frac{31}{360} \frac{D_e \rho^6 \hbar^2}{m^3 \omega_0^4} \quad (23)$$

Exploitation of the expressions (15) and (18), leads to the determination of the vibrational energy spectra of diatomic molecules, according to their Morse potential parameters. As an example, we have chosen the molecules HCl, LiH, CO and NO. The Morse potential parameters for these molecules are shown in Table 1.

**Table 1.** Parameters of the selected molecules.

Molecule	D (eV)	$\rho$ ( $^{\circ}\text{A}^{-1}$ )	m (amu)
HCl [17-18]	4.61907	1.8677	0.98010
LiH [17-18]	2.51528	1.1280	0.88012
CO [17-18]	11.2256	2.2994	6.86067
NO [19]	6.61350	2.7534	7.52147

Therefore, we can compute the vibrational energy values for the first five quantum number  $n$ ; by using equations

(15) and (18) with the help of the Maple software. The calculated energy level values are given in Table 2.

Furthermore, the transition energies (Table 2), can be written in wavenumber units ( $\text{cm}^{-1}$ ) such as,

$$\frac{E_n - E_m}{hc} \quad (24)$$

Where  $h$  is the Planck's constant and  $c$  is the speed of light.

Replacing ( $n = 1, m = 0$ ) for the fundamental transition:  $\nu_{0 \rightarrow 1}$ ; ( $n = 2, m = 0$ ) for the first harmonic:  $\nu_{0 \rightarrow 2}$  and ( $n = 3, m = 0$ ) for the second harmonic:  $\nu_{0 \rightarrow 3}$  are realized, respectively. Thus, the numerical values deduced for the chosen molecules are summarized in Table 3.

Moreover, the usual expression of the energy spectrum for the Morse potential, corresponding to any diatomic molecule, is given in wavenumber units ( $\text{cm}^{-1}$ ), under the following form,

$$\frac{E_n}{hc} = \omega_e \left( n + \frac{1}{2} \right) - \omega_e x_e \left( n + \frac{1}{2} \right)^2 \quad (25)$$

Where  $\omega_e$  is the harmonic wavenumber and  $\omega_e x_e$  is the first anharmonic constant. Therefore, the transition energies are,

$$\frac{E_n - E_m}{hc} = (n - m) [\omega_e - \omega_e x_e (n + m + 1)] \quad (26)$$

The spectroscopic constants  $\omega_e$  and  $\omega_e x_e$ , can be easily calculated using equations (25) and (26), and from the energy levels values of Table 2 and Table 3; when the fundamental transition:  $\nu_{0 \rightarrow 1}$ , and the first harmonic:  $\nu_{0 \rightarrow 2}$ , are realized, respectively.

On the other hand, a more general expression of the energy spectrum for the Morse potential can be written, in wave number units ( $\text{cm}^{-1}$ ), such as,

$$\frac{E_n}{hc} = \omega_e \left( n + \frac{1}{2} \right) - \omega_e x_e \left( n + \frac{1}{2} \right)^2 + \omega_e y_e \left( n + \frac{1}{2} \right)^3 \quad (27)$$

Where  $\omega_e x_e$  and  $\omega_e y_e$  are the first and second anharmonic constants, respectively. Hence, the transition energies are such as,

$$\frac{E_n - E_m}{hc} = (n - m) \left[ \omega_e - \omega_e x_e (n + m + 1) + \omega_e y_e (n^2 + m^2 - nm^2 + n^2 m + \frac{3}{2}n + \frac{3}{2}m + \frac{3}{4}) \right] \quad (28)$$

By substituting (n, m) into equation (28), one can deduce the fundamental transition:  $\nu_{0 \rightarrow 1}$ , the first harmonic:  $\nu_{0 \rightarrow 2}$  and the second harmonic:  $\nu_{0 \rightarrow 3}$ , respectively.

From this, we can deduce the following linear system equations,

$$\nu_{0 \rightarrow 1} = \omega_e - 2\omega_e x_e + \frac{13}{4}\omega_e y_e \quad (29a)$$

$$\nu_{0 \rightarrow 2} = 2\omega_e - 6\omega_e x_e + \frac{31}{2}\omega_e y_e \quad (29b)$$

$$\nu_{0 \rightarrow 3} = 3\omega_e - 12\omega_e x_e + \frac{171}{4}\omega_e y_e \quad (29c)$$

Thus, the spectroscopic constants  $\omega_e$ ,  $\omega_e x_e$  and  $\omega_e y_e$  are determined more precisely by solving the system of Eqs. (29), and from the values given in Table 3. The above analysis has been applied to the chosen molecules, and in Tables 2, 3 and 4, we have presented our calculated results. We have also reported comparisons with literature data in Table 2 [17, 18]. We note that the numerical values of bound-state energy eigenvalues ( $D - {}^{(2a)}E$ ) for various values of the vibrational quantum number, n, are in excellent agreement with those obtained by Nikiforov–Uvarov method combined with the Pekeris approximation scheme [17] and the tridiagonal J-matrix representation [18] for the HCl, LiH and CO molecules. These numerical values of the energies obtained have been used to calculate the vibrational transition frequencies and the spectroscopic constants for the selected molecules. We also note that the vibrational transition frequencies values are comparable to the experimental values presented in the work of Vu et al [20] for the CO molecule. Which proves the validity and efficiency of our analytical method.

**Table 2.** Numerical values of bound-state energy eigenvalues ( $D - {}^{(2a)}E$ ) in (eV) of HCl, LiH, CO and NO diatomic molecules for various n.

n	HCl		LiH		CO		NO
	Present study	Literature [17,18]	Present study	Literature [17,18]	Present study	Literature [17,18]	Present study
0	4.4354	4.4355	2.4288	2.4288	11.0914	11.0915	7.9261
1	4.0801	4.0797	2.2606	2.2605	10.8256	10.8258	7.6934
2	3.7412	3.7387	2.0990	2.0982	10.5630	10.5633	7.4644
3	3.4201	3.4126	1.9445	1.9420	10.3039	10.3041	7.2391
4	3.1182	3.1014	1.7974	1.7918	10.0482	10.0480	7.0175

**Table 3.** Vibrational transition frequencies in  $cm^{-1}$  for HCl, LiH, CO and NO molecules.

Transitions	HCl	LiH	CO	NO
$\nu_{0 \rightarrow 1}$	2866.5018	1356.5299	2144.2556	1876.0906
$\nu_{0 \rightarrow 2}$	5599.8367	2659.7851	4261.7426	3723.2292
$\nu_{0 \rightarrow 3}$	8189.6909	3906.2932	6351.9300	5540.7007

**Table 4.** Spectroscopic constants in  $cm^{-1}$  for HCl, LiH, CO and NO molecules.

Spectroscopic constants	HCl	LiH	CO	NO
$\omega_e$	2990.66	1406.47	2170.51	1904.35
$\omega_e x_e$	58.8481	24.0330	12.986	13.9396
$\omega_e y_e$	-1.7189	-0.57870	-0.0885	-0.1192

### 3. CONCLUSION

In this work, we have used a new analytical approach to obtain approximate solutions to the Schrödinger equation, up to the second order, for the sextic polynomial anharmonic potential. The formal identification of the obtained solutions makes it possible to express the spectral energy levels of the developed Morse potential as a sixth-order Taylor series. It is important to point out that the expressions of the eigen-energies (such as in Eqs. (4), (5), (12) and (14) among others) could not be easily found with a conventional treatment of the perturbation theory. Moreover, we note that, for all the cases considered, the anharmonicity effect appears up to second order.

To illustrate the obtained formulas, we performed the numerical calculation for the diatomic molecules: HCl, LiH, CO, and NO, according to the corresponding

Morse potential parameters. Furthermore, the method allowed us to calculate spectroscopic transition as well as the spectroscopic constant values for these selected diatomic molecules (Table 3) and (Table 4) respectively. Indeed, examination of the results obtained (Table 2), (Table 3) and (Table 4) shows that the numerical energy values agree well with those of other authors [17, 18, 20, 21].

The solutions used in the present work for the suggested polynomial anharmonic potential are of great interest when dealing with other cases of potential forms.

In future works, we project to apply our approach to the cases of the Deng-Fan [9] potential and polyatomic molecules.

### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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