An approach to determine the diatomic vibrational energy levels: application to LiH, NO and CO molecules

I Amila*, M Janati Idrissi, A Fedoul* and S Sayouri
Laboratory of Applied Physics Informatics and Statistics
BP 1796 Fes-Atlas, Morocco
*Corresponding authors: ibrahimamila@gmail.com or afedoul@yahoo.fr

Abstract. This work presents the systematic calculation of vibrational energy levels, for diatomic molecules through an alternative approach, reposed on the Floquet representation analysis. The Morse potential function has been employed to solve the Schrodinger equation, and to obtain the vibrational energy levels of diatomic systems. As an illustration, the numerical energy values of some molecules have been computed, and compared to those of literature, revealing a good agreement, and showing the accuracy of our approach.

Keywords: Energy level; Diatomic; Floquet representation; Morse potential.

1. Introduction

In this work, we are interested in solving Schrödinger equation for Morse potential, which is a realistic model to describe the vibrational energy levels of diatomic molecules, with an appropriate approximation. Several analytical and numerical methods have been developed and applied to provide the resolution of this problem among them: the popular perturbation theory [1], Nikiforv-Uvarov method [2], tridiagonal J-matrix method [3], etc. Our motivation consists to the application of an alternative approach, based on Floquet theorem combined with the resonating average method [4] to determine the energy eigenvalues up to second order in the perturbation amplitudes, of cubic and quadric anharmonic oscillator. The analysis of this quantum anharmonic system, allowed us to obtain explicitly the expressions of vibration energy levels by introducing the Morse potential [5] and provide a useful description of diatomic molecules.

First, we give the theoretical context and the basic equations of our approach. Next, we apply it in case where the Morse potential function has developed to forth order. Therefore, we performed numerical calculations, using the established expressions as well as the parameters factors of the molecules species: LiH, NO and CO. The choice of these three molecules is for the following reasons: the molecules are different in terms of reduced mass and for the comparison with the results published in the literature. We determined the maximum quantum number energy level and we deuced the dissociation energies of the previous selected molecules.

The organisation of our paper is as follows: In section 2, we give the theoretical background and the general formulas. The section 3 contains the numerical results, comparisons with the literature and concluding comments. In section 4, we give the conclusions.
2. General Formulas

The Morse function [5] can be written as follows:

\[ V(q) = D_e (1 - e^{-\rho q})^2 \]  
\[ (1) \]

Where \( q = r - r_e \)
Moreover, where \( \rho \) is a parameter that controls the width of the potential, \( D_e \) is the depth of the potential well, \( r \) is the distance between the atoms and \( r_e \) is the equilibrium bond distance.

Since the oscillations are of small amplitudes, we can do the Taylor development of \( V(q) \) around \( q \) equal zero to forth order:

\[ V(q) = D_e \rho^2 q^2 - D_e \rho^3 q^3 + \frac{7}{12} D_e \rho^4 q^4 \]  
\[ (2) \]

Let us consider the anharmonic oscillator which the Hamiltonian such as:

\[ H(t) = \frac{p^2}{2m} + D_e \rho^2 q^2 - D_e \rho^3 q^3 + \frac{7}{12} D_e \rho^4 q^4 \]  
\[ (3) \]

Where \( P \) is the quantum momentum and \( m \) is reduced mass of the molecule.

The application of our approach to solve the Schrödinger equation according to the equation(3), leads to determine the second order energy levels as follows [6][7][8]:

\[ ^{(2a)} E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) + \mu_2 \frac{3}{4} \hbar \omega_0 \left( 2n^2 + 2n + 1 \right) - \mu_1 \frac{15 \hbar \omega_0}{4} \left( n^2 + n + \frac{11}{30} \right) \]

\[ - \mu_2 \frac{\hbar \omega_0}{8} \left( 34n^3 + 51n^2 + 59n + 21 \right) \]

Where: \( \omega_0 = \rho \sqrt{\frac{2D_e}{m}} \), \( \mu_1 = - \frac{D_e \rho^3}{m \omega_0^2} \sqrt{\frac{\hbar}{m \omega_0}} \) and \( \mu_2 = \frac{7}{12} \frac{D_e \rho^4 \hbar}{m^2 \omega_0^3} \)

\[ (4) \]

\( \mu_1 \) and \( \mu_2 \) are respectively the amplitudes of the cubic and quadric anharmonic perturbation.

We use the following identities:

\[ \left( 2n^2 + 2n + 1 \right) = 2 \left( n + \frac{1}{2} \right)^2 + \frac{1}{2} \], \( \left( n^2 + n + \frac{11}{30} \right) = \left( n + \frac{1}{2} \right)^2 + \frac{7}{60} \]

and \( \left( 34n^3 + 51n^2 + 59n + 21 \right) = 34 \left( n + \frac{1}{2} \right)^3 + \frac{67}{2} \left( n + \frac{1}{2} \right) \)

\[ (6) \]

By replacing the identities of equation (6) into equation (4), we obtain the following equation:

\[ ^{(2a)} E_n = - \hbar \omega_0 \left( \frac{7}{16} \mu_1^2 - \frac{3}{8} \mu_2 \right) + \hbar \omega_0 \left( 1 - \frac{67}{16} \mu_2^3 \right) \left( n + \frac{1}{2} \right) - \hbar \omega_0 \left( \frac{15}{4} \mu_1^2 - \frac{3}{2} \mu_2 \right) \left( n + \frac{1}{2} \right)^2 \]

\[ - \frac{17}{4} \mu_2 \left( n + \frac{1}{2} \right)^3 \]

Let us note replacing \( \mu_1 \) and \( \mu_2 \) by their expressions of equation (5) the term \( \left( \frac{7}{16} \mu_1^2 - \frac{3}{8} \mu_2 \right) = 0 \).

Since the experimental data shows the terms in \( \left( n + \frac{1}{2} \right)^3 \) are negligible, we can write the analytical expression of the vibrational energy of diatomic molecules as follows:

\[ ^{(2a)} E_n = \hbar \omega_0 \left( 1 - \frac{67}{16} \mu_2^2 \right) \left( n + \frac{1}{2} \right) - \hbar \omega_0 \left( \frac{15}{4} \mu_1^2 - \frac{3}{2} \mu_2 \right) \left( n + \frac{1}{2} \right)^2 \]

\[ (8) \]
Substituting $\omega_0$, $\mu_1$ and $\mu_2$ in equation (8), we obtain the quasi-energies formula such as:

$$
(2n)E_n = h\rho \sqrt{\frac{2D_e}{m}} \left[ 1 - \frac{3283}{18432} \frac{\hbar^2 \rho^2}{mD_e} \right] \left( n + \frac{1}{2} \right) - \frac{\hbar^2 \rho^2}{2m} \left( n + \frac{1}{2} \right)^2
$$

(9)

Note that the exact molecular spectra are usually given by the following formula:

$$
(\text{ext})E_n = \omega_e \left( n + \frac{1}{2} \right) - \omega_e \chi_e \left( n + \frac{1}{2} \right)^2
$$

(10)

Where $\omega_e$ and $\omega_e\chi_e$ are directly related to the Morse potential parameters. Thence from the equation (9), we can easily express the vibration frequency of the equilibrium $\omega_e$ and the first constant anharmonicity $\omega_e\chi_e$ as:

$$
\omega_e = h\rho \sqrt{\frac{2D_e}{m}} \left[ 1 - \frac{3283}{18432} \frac{\hbar^2 \rho^2}{mD_e} \right] \quad \omega_e\chi_e = \frac{\hbar^2 \rho^2}{2m}
$$

(11)

3. Numerical results and comparisons

The Morse potential parameters and the spectroscopies constants of the selected molecules are given on table (1) [9][10].

| Molecules | $D_e$(eV) | m(uma) | $\rho$(Å⁻¹) | $\omega_e$(eV) | $\omega_e\chi_e$(eV) |
|-----------|----------|--------|-------------|---------------|------------------|
| LiH       | 2.515287 | 0.8801221 | 1.1280     | 0.174272     | 0.016504        |
| NO        | 8.043729 | 7.46835 | 2.486737    | 0.236082     | 0.007391        |
| CO        | 11.2256  | 6.8606719 | 2.2994     | 0.269015     | 0.006124        |

As illustrations of the equations (9) and (10), inserting the Morse parameters of the selected molecules and by using the Maple software, we determine the numerical values of the vibrational energy level and the comparison of our results with the so-called exact results in the following tables:
### Table 2. Energy levels values and maximum quantum number of LiH.

| n   | $E_n$(eV)  |          |          |
|-----|------------|----------|----------|
|     | Our results| Exact results|          |
| 0   | 0.086333   | 0.086417  |          |
| 1   | 0.254469   | 0.254936  |          |
| 2   | 0.416560   | 0.417704  |          |
| 3   | 0.572608   | 0.574718  |          |
| 10  | 1.495720   | 1.512745  |          |
| 20  | 2.300737   | 2.363805  |          |
| 28  | 2.509605   | 2.630461  |          |
| 29  | 2.508517   | 2.637906  |          |
| 30  | 2.501385   | 2.639599  |          |
| 31  | 2.488210   | 2.635538  |          |
| $n_{max}$ | 28         | 30        |          |

### Table 3. Energy levels values and maximum quantum number of NO.

| n   | $E_n$(eV)  |          |          |
|-----|------------|----------|----------|
|     | Our results| Exact results|          |
| 0   | 0.117552   | 0.117605  |          |
| 1   | 0.350062   | 0.350197  |          |
| 2   | 0.579110   | 0.579300  |          |
| 3   | 0.804697   | 0.804913  |          |
| 10  | 2.286883   | 2.286480  |          |
| 30  | 5.587099   | 5.577219  |          |
| 60  | 7.941313   | 7.895800  |          |
| 67  | 8.042368   | 7.984842  |          |
| 68  | 8.042958   | 7.983602  |          |
| 69  | 8.040087   | 7.978873  |          |
| $n_{max}$ | 68         | 67        |          |

### Table 4. Energy levels values and maximum quantum number of the CO molecule.

| n   | $E_n$(eV)  |          |          |
|-----|------------|----------|----------|
|     | Our results| Exact results|          |
| 0   | 0.133361   | 0.134095  |          |
| 1   | 0.350062   | 0.350197  |          |
| 2   | 0.579110   | 0.579300  |          |
| 3   | 0.804697   | 0.804913  |          |
| 10  | 2.286883   | 2.286480  |          |
| 20  | 5.587099   | 5.577219  |          |
| 28  | 7.941313   | 7.895800  |          |
| 29  | 8.042368   | 7.984842  |          |
| 30  | 8.042958   | 7.983602  |          |
| 31  | 8.040087   | 7.978873  |          |
| $n_{max}$ | 83         | 81        |          |
For testing our results, we present in table 5, the comparisons of numerical values of the maximum quantum number \( n_{\text{max}} \), dissociation energy \( D_0 \) and the constants of anharmonicity obtained by using the quasi-energy expression of our approach, with the values calculated from the equation (10).

The maximum quantum number of vibration energy levels corresponds to the value of \( n \) beyond which the energy becomes maximum and the molecule will be dissociated, then \( n_{\text{max}} \) is the solution to the equation: \( \frac{dE_n}{dn} = 0 \), then we calculate the dissociation energy by using the expression:

\[ D_0 = E_{\text{max}} - E_0 \]

where \( E_0 \) is the zero point energy. The numerical values of the anharmonicity constants \( \omega_e \) and \( \omega_e \chi_e \) are calculated using the equation (11).

We use the established formulas (9), (10) and (11) to compute the maximum quantum number of vibrations \( n_{\text{max}} \), the dissociation energy and spectroscopies constants relating to the parameters of the LiH, NO and CO molecules are given by [10].

### Table 5. Numerical value of \( n_{\text{max}} \), \( D_0 \), \( \omega_e \) and \( \omega_e \chi_e \).

| Molecules | LiH | NO | CO |
|-----------|-----|----|----|
| \( n_{\text{max}} \) | Our results | 28 | 68 | 83 |
| | Exact results | 30 | 67 | 81 |
| \( D_0 \) (eV) | Our results | 2.425393 | 7.926653 | 11.091193 |
| | Exact results | 2.553182 | 7.867237 | 10.841943 |
| \( \omega_e \) (eV) | Our results | 0.174201 | 0.235970 | 0.268924 |
| | Exact results | 0.174272 | 0.236082 | 0.269015 |
| \( \omega_e \chi_e \) (eV) | Our results | 0.003025 | 0.001731 | 0.001610 |
| | Exact results | 0.002876 | 0.001745 | 0.001647 |

From the analysis of the results presented in the preceding table, we have shown that there is a concordance between the numerical values obtained using our approach, dismaying the maximum quantum number \( n_{\text{max}} \), the dissociation energy \( D_0 \) and the constants of anharmonicity, and the numerical values established from the equation (10) so-called exact results.
4. Conclusion

We applied the analytical approach, to determine the quasi-energies up to the second order, solutions of the Schrodinger equation, in the case of the Morse potential, which is a suitable model to describe the vibrations spectra of diatomic molecules.

From tables 2, 3 and 4, it can be seen that the calculation of energy levels values based on the formula (9) agree well, with those deduced from the Morse formula (10) when applying them to the previous diatomic molecule. Then we have applied the established analytical formulas to calculate some spectroscopic properties of diatomic systems in table 5. The comparisons of our numerical results with the literature are in good agreement and confirm the contribution of our approach.

We plan in future work to perform calculations by our approach, to determine the vibrational quasi-energies and the spectroscopy constants of anharmonicity where the Morse potential function will be developed to higher orders.

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