Non-Relativistic Ro-Vibrational Energies of Chlorine Molecule for Molecular Attractive Potential Model

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Abstract. We obtained the solutions of the radial Schrödinger equation with the modified molecular attractive potential model by employing the supersymmetric WKB method, and present the non-relativistic rotation-vibrational energy equation for diatomic molecules. Using the energy equation and the spectroscopic parameters of chlorine molecule, we computed the vibrational energy eigenvalues for various quantum states. The calculated results are found to be in agreement with the experimental values.

Keywords: Wave equation; eigensolutions; bound state; Schrödinger equation.

Introduction

Based on the usefulness of internuclear energy potential function that describes the molecular structure, there has been a radical interest devoted to the determination of energy spectrum of diatomic molecules. The potential function involves usually consists of three spectroscopic parameters. Using the spectroscopic parameters, several authors have studied different molecules under different energy potential models in terms of vibration transitional frequency and validated their results by comparing it with the experimental data [1-8]. Depending on the potential function and the molecule to be studied, some calculated results fairly agreed with the experimental values while others are in good agreement with the experimental values. In ref. [1], the authors obtained the average absolute deviation of Morse potential function for \( \chi^1\Sigma^+ \) of scadium monoiodide as 0.0344%. Liu et al. [5], obtained average deviation of improved Rosen-Morse potential model and the Morse
The potential function for $3^1\Sigma^+_g$ of cesium dimer was calculated as 0.036% of $D_e$ and 0.121% of $D_e$ respectively. These authors also obtained the average deviation of the same potentials for $5^3\Delta_g$ state of sodium molecule as 0.225% of $D_e$ and 0.792% of $D_e$. Recently, Onate and coauthors [6], modified an attractive potential to a molecular attractive potential model and used it to study $3^1\Sigma^+_g$ state of cesium and $a^3\Sigma^+_u$ state of lithium molecules via the methodology of parametric Nikiforov-Uvarov. Their calculated results were found to agree with the experimental values. They deduced the percentage average deviation of the calculated results from the experimental values. Precisely, the percentage average deviation for cesium molecule is 0.4415% while that of lithium molecule is 0.0007%. Though the two results are in good agreement with the experimental values, the potential model fits the computation of lithium molecule compared to cesium molecule.

The molecular attractive potential function is given as [6]

$$U(x) = D_e \left[ \frac{\lambda_1 e^{2\alpha x} e^{-2\alpha x} + \lambda_2 e^{\alpha x} e^{-\alpha x} + \lambda_3}{(1 - e^{-\alpha x})^2} \right],$$

(1)

where $D_e$ is the dissociation energy, $x$ is the internuclear separation, $\alpha$ is a screening parameter, and $\lambda_1$, $\lambda_2$, and $\lambda_3$ are potential parameters whose values for computation depend on the author. For molecules, the screening parameter can be determined from the given potential (1) noting that

$$\frac{d^2V(x)}{dx^2} \bigg|_{x=r_e} = k_e (4\mu \pi c^2 \omega_e^2).$$

(2)

Simplifying the above equation along with potential (1) gives

$$\alpha = 2\pi \omega_e \sqrt{\frac{\mu}{D_e (20\lambda_1 + 13\lambda_2 + 8\lambda_3)}} - \frac{32\pi^4 c^2 \mu \lambda_1 r_e^4 \omega_e^2}{3h^2} - \frac{1}{r_e}.$$ \hspace{1cm} (3)

Following the value of the screening parameter above, the potential parameters are given as $\lambda_2 = 2(\lambda_0 - 1)$ and $\lambda_3 = \lambda_1 + \lambda_2 - 2$ where $-\infty < \lambda_0 < +\infty$. Motivated by the interest in the molecular attractive potential function, the present study wants to examine the molecular attractive potential function for $1^1\Sigma^+_g$ state of $^{35}\text{Cl}_2$. The shape of molecular attractive potential is shown in Fig. 1:
**Bound State Solutions**

The Schrödinger equation for a quantum system with a non-relativistic energy \( E \) and an interacting potential \( V(r, \theta, \varphi) \) coupled with a reduced mass \( \mu \) is given by

\[
\left[ \frac{-\hbar^2}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) - E + V(r, \theta, \varphi) \right] \psi(r, \theta, \varphi) = 0, \quad (4)
\]

where \( \hbar \) is the reduced Planck’s constant and \( \psi(r, \theta, \varphi) \) is the total wave function. Putting the wave function in the form

\[
\psi(r, \theta, \varphi) = \frac{R_{v,j}(r)}{r} Y_{j,m}(\theta, \varphi),
\]

where \( Y_{j,m}(\theta, \varphi) \) is the spherical harmonic function, and consider the Schrödinger equation with

\[
\frac{j(j+1)}{r^2},
\]

the radial part of Eq. (4) becomes

\[
\left[ \frac{-\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r) - \frac{\hbar^2}{2\mu} \frac{j(j+1)}{r^2} \right] R_{v,j}(r) = 0, \quad (5)
\]

where \( V \) is the vibrational quantum number and \( j \) is the rotational quantum number. In order to obtain the analytical solutions of Eq. (5) for any arbitrary \( j^- \) state, one must approximate the centrifugal term when \( \alpha \ll 1 \). Several approximation schemes were developed to deal with the centrifugal term [9, 10]. In this study, we employ an improved Greene-Aldrich approximation scheme [11] to get rid of the centrifugal term.

\[
\frac{1}{r^2} \approx \alpha^2 \left( C_0 + \frac{e^{-ar}}{(1-e^{-ar})^2} \right), \quad (6)
\]
The constant in Eq. (6) is a dimensionless constant with numerical value as 1/12 that is obtained using the following power series

\[ \alpha^2 \left( C_0 + \frac{e^{-ar}}{(1 - e^{-ar})^2} \right) = \alpha^2 \left[ C_0 + \frac{1}{(ar)^2} - \frac{1}{12} + \frac{(ar)^2}{240} - \frac{(ar)^4}{6048} + 0(ar)^6 \right]. \quad (7) \]

If the constant \( C_0 = 0 \), then, Eq. (6) reduces to the conventional Greene-Aldrich approximation scheme. Plugging Eq. (1) and Eq. (6) into Eq. (5), we have the following second-order Schrödinger-like equation of the form

\[ \frac{d^2 R_{v,j}(r)}{dr^2} = \left[ \frac{2\mu\lambda \hat{D}}{\hbar^2} + \frac{2\mu\lambda \hat{D}e^{ar}}{\hbar^2} + j(j+1)\alpha^2 \right] e^{-ar} + \frac{2\mu\lambda \hat{D}e^{2ar}e^{-2ar}}{\hbar^2} \right] R_{v,j}(r). \quad (8) \]

where we have used the following for mathematical simplicity

\[ \overline{E}_T = j(j+1)C_0\alpha^2 - \frac{2\mu E_{v,j}}{\hbar^2}. \quad (9) \]

Having obtained Eq. (8), we now employ the basic concept and formalism of the supersymmetric approach to solve the Schrödinger-like equation given in Eq. (8). On the basis of the formalism of supersymmetric approach, the ground state wave function \( R_{0,j}(r) \) can be written in the form

\[ R_{0,j}(r) = \exp \left( -\int Q(r)dr \right), \quad (10) \]

where \( Q(r) \) is called a superpotential function in supersymmetric quantum mechanics [12 - 17]. Invoking Eq. (10) on Eq. (8), we have a non-linear Riccati equation satisfied by the superpotential function \( Q(r) \),

\[ Q^2(r) - Q'(r) = \overline{E}_T + \frac{2\mu\lambda \hat{D}}{\hbar^2} + \frac{2\mu\lambda \hat{D}e^{ar}}{\hbar^2} + j(j+1)\alpha^2 \right] e^{-ar} + \frac{2\mu\lambda \hat{D}e^{2ar}e^{-2ar}}{\hbar^2} \right]. \quad (11) \]

For compatibility of the property of both the left hand side and the right hand side of Eq. (11), the superpotential function can be put forward in the following form

\[ Q(r) = \rho_0 + \frac{\rho e^{-ar}}{1-e^{-ar}}, \quad (12) \]
where $\rho_0$ and $\rho_1$ are superpotential parameters that will be determined later. Eq. (12) is actually a solution to Eq. (11). The difference between its squared and its first derivative into Eq. (11) results to a comparison of the two sides of Eq. (11) that leads to the determination of the two superpotential parameters. However, this study only consider the bound state solutions that demands the wave function $R_{v,j}(r)$ satisfying the boundary conditions as $R_{v,j}(r)/r$ becomes zero when $r$ is infinite, and $R_{v,j}(r)/r$ is finite when $r$ goes to zero.

The regularity condition thus, leads us to have a restriction condition that $\rho_0 > 0$ and $\rho_1 < 0$. Following the restriction, when we plug Eq. (12) into Eq. (11) with some mathematical algebraic simplification, we now have the superpotential parameters as

$$\rho_0 = \frac{2\mu D_e(\lambda_0 e^{2ar_0} - \lambda_1)}{\hbar^2} + j(j+1) - \rho_1^2, \quad (13)$$

$$\rho_1 = \frac{\alpha}{2} \left(-1 \pm \sqrt{(1 + 2j)^2 + \frac{8\mu D_e(\lambda_0 e^{2ar_0} + \lambda_2 e^{ar_0} + \lambda_3)}{\alpha^2 \hbar^2}}\right), \quad (14)$$

$$\rho_0^2 = j(j+1)C_0\alpha^2 + \frac{2\mu(\lambda_3D_e - E_{v,j})}{\hbar^2}. \quad (15)$$

Using the formalism of supersymmetric approach, the construction of the partner potentials is significant as these give the choice of mapping function for the derivation of recurrence relations. Hence, using Eq. (12), it becomes very easy to construct a pair of supersymmetric partner potentials

$$U_\pm(r) = Q^2(r) \pm \frac{dQ(r)}{dr},$$

in the following forms

$$U_+(r) = \left(\frac{2\mu D_e(\lambda_0 e^{2ar_0} - \lambda_1)}{\hbar^2} + j(j+1) - \rho_1^2\right)^2 + \frac{2\mu D_e(\lambda_0 e^{2ar_0} - \lambda_1)}{\hbar^2} + j(j+1) - 2\rho_1^2 \frac{e^{ar}}{1-e^{ar}} + \frac{\rho_1(\rho_1 - \alpha)e^{ar}}{(1-e^{ar})^2}, \quad (16)$$

$$U_-(r) = \left(\frac{2\mu D_e(\lambda_0 e^{2ar_0} - \lambda_1)}{\hbar^2} + j(j+1) - \rho_1^2\right)^2 + \frac{2\mu D_e(\lambda_0 e^{2ar_0} - \lambda_1)}{\hbar^2} + j(j+1) - 2\rho_1^2 \frac{e^{-ar}}{1-e^{-ar}} + \frac{\rho_1(\rho_1 - \alpha)e^{-ar}}{(1-e^{-ar})^2}. \quad (17)$$

Eq. (16) and Eq. (17) are connected via a simple formula/relation that satisfied the partner potentials $U_\pm$:
\[ U_+ (r, a_0) = U_+ (r, a_1) + R(a_1), \]  

where \( a_1 \) is a new set of parameters uniquely determined from \( a_0 \) an old set of parameter via mapping of the form \( a_1 = h(a_0) = a_0 - \alpha \), and the remainder \( R(a_1) \) is independent of the variable \( r \). The energy spectrum can be exactly be determined following supersymmetric WKB quantization condition [16]

\[ \int_{r_1}^{r_2} \sqrt{\mathcal{E}^{(-)}_r - Q^2(r)} dr = \pi \nu, \quad \nu \geq 0. \]  

The integral limits are two turning points that are determined by the equation. Following the concept and formalism of supersymmetric approach and the standard WKB method [17, 18], the exact energy spectra of the shape invariance potential can be determined. Considering Eq. (12) and Eq. (13), the supersymmetric WKB quantization condition shown in Eq. (19) can now be written as

\[ \int_{r_1}^{r_2} \sqrt{\mathcal{E}^{(-)}_r - Q^2(r)} dr = \pi \nu. \]  

Defining a transformation of the form \( y = \frac{1 + e^{-ar}}{1 - e^{-ar}} \) and invoke it on Eq. (20), we have the following equation whose integral limits and derivative changes from that of Eq. (20)

\[ \int_{y_L}^{y_H} \frac{\rho_1}{\alpha} \frac{1}{y^{-1}} \sqrt{y_r (y - y_L) - y (y + y_L)} dy = \pi \nu. \]  

The turning points in Eq. (21) are given by

\[ y_R = -\frac{2}{\rho_1} \left( \frac{2 \mu D_e (\lambda_1 e^{2ar} - \lambda_3) + j(j+1)}{\mathcal{E}^{(-)}_r + \frac{\hbar^2}{2\rho_1}} \right), \]  

\[ y_L = -\frac{2}{\rho_1} \left( \frac{2 \mu D_e (\lambda_1 e^{2ar} - \lambda_3) + j(j+1)}{-\mathcal{E}^{(-)}_r + \frac{\hbar^2}{2\rho_1}} \right). \]
Solving Eq. (21), the term \( \bar{E}_T^{(-)} \) can be obtained as
\[
\bar{E}_T^{(-)} = \left( \frac{2 \mu D_e (\lambda_3 e^{2a\tau} - \lambda_3)}{\hbar^2} + j(j+1)\rho_1^2 - \frac{2 \mu D_e (\lambda_3 e^{2a\tau} - \lambda_3)}{\hbar^2} + j(j+1) - (\rho_1 - \alpha \nu)^2 \right)^2 ,
\]
where we have used the integral of the form
\[
\int_a^b \frac{1}{\sqrt{(y-a)(b-y)}} dy = \frac{\pi}{2} \left[ \sqrt{(a+1)(b+1)} - \sqrt{(a-1)(b-1)} - 2 \right] .
\]

Using Eq. (8) and Eq. (17), we have the following equation
\[
\bar{E}_T = \bar{E}_T^{(-)} = \left( \frac{2 \mu D_e (\lambda_3 e^{2a\tau} - \lambda_3)}{\hbar^2} + j(j+1)\rho_1^2 \right)^2 .
\]

Plugging Eq. (24) into Eq. (26), the ro-vibrational energy equation for a system interacting with a molecular attractive potential is obtained as
\[
E_{v,j} = \lambda_3 D_e + \frac{\alpha^2 \hbar^2}{2 \mu} \left[ j(j+1)C_0 - \left( \frac{2 \mu D_e (\lambda_3 e^{2a\tau} - \lambda_3)}{\alpha^2 \hbar^2} + j(j+1) - \frac{2 \nu + 1 \pm R_f}{4} \right)^2 \right] .
\]

\[
R_f = \sqrt{(1+2j)^2 + \frac{8 \mu D_e (\lambda_3 e^{2a\tau} + \lambda_3 e^{a\tau} + \lambda_3)}{\alpha^2 \hbar^2}} .
\]

If we consider \( R_f \) as negative \( (-R_f) \), then, the energy equation in Eq. (27) becomes
\[
E_{v,j} = \lambda_3 D_e + \frac{\alpha^2 \hbar^2}{2 \mu} \left[ j(j+1)C_0 - \left( \frac{2 \mu D_e (\lambda_3 e^{2a\tau} - \lambda_3)}{\alpha^2 \hbar^2} + j(j+1) - \frac{2 \nu + 1 - R_f}{4} \right)^2 \right] .
\]
The Radial Wave Function

To obtain the radial wave function, we define $y = e^{-ar}$, and substitute it into Eq. (8) to have

$$\begin{align*}
\frac{d^2}{dy^2} + \frac{1}{y} \frac{d}{dy} + \left\{ -P_1 y^2 + P_2 y - \frac{j(j+1)C_0 + 2\mu(\lambda_2 D_e e^{2\alpha_r} - E_{v,j})}{\alpha^2 h^2} \right\} y^2 (1-y)^2 R_{v,j}(y) &= 0, \\
\frac{d^2}{dy^2} + \frac{1}{y} \frac{d}{dy} + \frac{j(j+1)C_0 + 2\mu(\lambda_2 D_e e^{2\alpha_r} - E_{v,j})}{\alpha^2 h^2} y^2 (1-y)^2 R_{v,j}(y) &= 0,
\end{align*}$$

(30)

$$P_1 = j(j+1)C_0 + \frac{2\mu(\lambda_2 D_e e^{2\alpha_r} - E_{v,j})}{\alpha^2 h^2},$$

(31)

$$P_2 = -j(j+1)(2C_0 + 1) - \frac{2\mu(\lambda_2 D_e e^{2\alpha_r} - 2E_{v,j})}{\alpha^2 h^2}.$$  

(32)

Analyzing the asymptotic behaviour of Eq. (30) at origin and at infinity, it can be tested that when $r \to 0(y \to 1)$, and $r \to \infty(y \to 0)$, Eq. (30) has a solution of the form $R_{v,j}(y) = (1-y)^\delta y^T$, where

$$\delta = \frac{1}{2} + \frac{1}{2} \sqrt{(1+2j)^2 + \frac{8\mu D_e (A e^{2\alpha_r} + B e^{\alpha_r} + C)}{\alpha^2 h^2}},$$

(33)

$$T = \sqrt{\frac{8\mu(D_e - E_{v,j})}{\alpha^2 h^2}}.$$  

(34)

Consider a trial wave function of the form $R_{v,j}(y) = y^T (1-y)^\delta f(y)$ and substitute it into Eq. (30), we have

$$f'(y) + \left( \frac{(2T+1)-(2T+2\delta+1)y}{y(1-y)} \right) f'(y) - \left( \frac{(\delta+T)^2 + P_1}{y(1-y)} \right) f(y) = 0.$$  

(35)

Eq. (35) is a differential equation satisfied by hypergeometric function. Hence, its solution is obtain via

$$f(y) = {}_2F_1(-n,n+2(\delta+T);2t+1,y).$$  

(36)

Replacing the function $f(y)$ by the hypergeometric function, we have a complete radial wave function as
\[ R_{v,i}(y) = Ny^{T}(1-y)^{\delta} \sum_{n=0}^{\infty} \frac{(-n, n + 2(\delta + T); 2T + 1, y)}. \]  

(37)

Fig. 2. Variation of energy against the screening parameter for molecular attractive potential with \( \hbar = \mu = \ell = 1, \lambda = 2, r_e = 0.55 \) and \( D_e = 10 \).

Fig. 3. Variation of energy against the screening parameter for molecular attractive potential (a) and improved Rosen-Morse potential (b) with \( \hbar = \mu = \ell = 1, \lambda = 2, \alpha = 0.15 \) and \( r_e = 0.55 \).
Table 1. Comparison of the energy of the attractive molecular potential for various quantum states and angular quantum states with $h = \mu = \ell = 1$, $\lambda_0 = 2$, $\alpha = 0.25$ and $r_c = 0.25$.

| $n$ | $\ell$ | $D_c = 5$ Present | [6] | $D_c = 10$ Present | [6] |
|-----|--------|------------------|-----|------------------|-----|
| 0   | 0      | 3.977598260      | 3.977598297 | 6.798286894       | 6.798287056 |
| 1   | 1      | 4.809523564      | 4.792524933 | 9.108667476       | 9.075571808  |
| 2   | 2      | 4.976039762      | 4.967085778 | 9.723414912       | 9.696564702  |
| 3   | 3      | 5.003831145      | 4.999752546 | 9.872914437       | 9.882375036  |
| 4   | 4      | 5.012890620      | 4.980612046 | 9.966101890       | 9.981247750  |

Table 2. Comparison of the observed values and calculated values of the Chlorine molecule (Cl$_2$)

| $v$ | RKR (cm$^{-1}$) [19] | calculated results |
|-----|---------------------|-------------------|
|     |                     | $j = 0$           | $j = 1$           |
| 0   | 279.15              | 272.0144          | 272.4928          |
| 1   | 833.43              | 815.8936          | 816.3721          |
| 2   | 1382.33             | 1359.5343         | 1360.0128         |
| 3   | 1925.79             | 1902.9364         | 1903.4150         |
| 4   | 2463.80             | 2446.0997         | 2446.5783         |
| 5   | 2996.28             | 2989.0242         | 2989.5029         |
| 6   | 3523.40             | 3531.7099         | 3532.1887         |
| 7   | 4044.80             | 4074.1566         | 4074.6354         |
| 8   | 4560.50             | 4616.3643         | 4616.8432         |
| 9   | 5070.50             | 5158.3328         | 5158.8118         |
| 10  | 5574.70             | 5700.0622         | 5700.5412         |

Discussion

The shape of the molecular attractive potential for chlorine molecule is shown in Fig. 1. The effect of the screening parameter on the energy of the attractive potential is shown in Fig. 2. The energy varies directly with the screening parameter. However, as the screening parameter increases above 2, the energy of the system has turning point starting from the energy of the highest quantum state. In Fig. 3, we examined the effect of the dissociation energy on the energy of the molecular attractive potential. The energy of the system increases monotonically as the dissociation energy increases gradually for all the quantum states. Figures 2 and 3 are plotted using Eq. (29).

The comparison of the present results and the previous results for attractive molecular potential are presented in Table 1. The present results and the previous results agreed with one another. Imputing the
Experimental data $D_e = 3341470\text{cm}^{-1}$, $r_e = 1.762\text{Å}$, $\alpha_e = 2.511\text{cm}^{-1}$ and $\omega_e = 255.380\text{cm}^{-1}$ into equation (29), we obtained the rotational vibrational energy for chlorine molecule. The comparison of the experimental values and the calculated values are presented in Table 2. The experimental values are obtained from ref. [19, 20]. The calculated results showed a good agreement with the observed values. To ascertain the degree of accuracy of the calculated values, we obtained the percentage deviation from the observed values. The percentage deviation for the present calculation with $j = 0$ is 0.0589 % while the percentage deviation with $j = 1$ is 0.0603 %. The percentage deviation is obtained using the formula

$$\sigma = \frac{100}{N} \sum_{i=0}^{N} \left( \frac{E_{\text{ex}} - E_{\text{cal}}}{E_{\text{ex}}} \right),$$

where, $E_{\text{ex}}$ is the experimental data, $E_{\text{cal}}$ is the calculated value and $N$ is the number of data points.

**Conclusion**

The solution of the radial Schrödinger equation was obtained under the attractive molecular potential model. It was observed that two different energy equations can be obtained under this potential. Then, one of the energy equations obtained was used to generate numerical values for chlorine molecule which perfectly agreed with the experimental values. The deviation of the calculated values from the experimental values is approximately 0.0589 % for $j = 0$ and 0.0603 % for $j = 1$. Thus, the attractive molecular potential perfectly fits the computation for Chlorine molecule.

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