Determination of $\omega_e$, $\omega_e x_e$, $B_e$, and $\alpha_e$ using potential energy functions for heteronuclear diatomic molecules via spreadsheet program

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Abstract

In order to represent the potential energy function over the whole range of $R$, many potential energy functions have been proposed. In the present paper, we employ many potential energy functions, to use Numerov method for solving the nuclear Schrödinger equation for the IF molecule, as an example of a heteronuclear diatomic molecules. Then we determine the spectroscopic constants $\omega_e$, $\omega_e x_e$, $B_e$, and $\alpha_e$ of the IF molecule from vibrational and vibration-rotation levels obtained from solution of the nuclear Schrödinger equation. Finally, by comparison of obtained values with the experimental ones, their accuracy rate is determined as well as their deviation percentages from experimental values.

Keywords: Spectroscopic constants; Potential energy functions; Heteronuclear diatomic molecules

1. Introduction

The molecular Schrödinger equation is extremely complicated to solve. The exact solution of this equation is a formidable task due to the fact that the electronic and nuclear degrees of freedom are scrambled in the related molecular Hamiltonian [1-5]. Based on the fact that nuclei are much heavier than electrons, the Born-Oppenheimer approximation is a very efficient method to treat the electronic and nuclear motions separately [6]. The electronic Schrödinger equation and nuclear Schrödinger equation are as follows:

\[ \hat{H}_{el} \psi_{el} = E_{el} \psi_{el}, \]  
\[ (\hat{T}_n + U) \psi_n = E \psi_n, \]

where $U$ is the electronic energy including internuclear repulsion which acts as the potential energy for the nuclear Schrödinger equation. For diatomic molecules, the potential energy $U$ depends only on internuclear distance $R$. So this subject is a central-force problem [7-9]. As we know, the nuclear-motion wave function is
\[ \psi_n^J = Y_n^J(\theta, \phi)P(R). \]  

(3)

where the \( Y_n^J \) functions are the spherical harmonic functions with quantum number \( J \) and \( M \), and \( P(R) \) is the radial function.

So, the Schrödinger equation can be written in the form

\[
-\frac{\hbar^2}{2\mu} F''(R) + \left[ U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] F(R) = E_n F(R). \tag{4}
\]

The latter equation looks like a one-dimensional Schrödinger equation with the effective potential energy \( U(R) + J(J+1)\hbar^2 / 2\mu R^2 \).

At first, our goal in the present paper is to solve the nuclear Schrödinger equation for heteronuclear diatomic molecules to obtain the vibration-rotation eigenvalues and eigenfunctions.

In the perturbative method, we may improve the approximation by taking further terms in the expansion of \( U \). Note that, for large \( R \), this expansion is not convergent. To represent the potential energy function over the whole range of \( R \), many potential energy functions such as Morse, Rydberg, and so on, have been proposed [10-17]. These functions contain parameters (usually three) that are evaluated from experimental quantities for the molecular electronic state of interest [18].

In this paper, the nuclear Schrödinger equation for the IF molecule as a heteronuclear diatomic molecules will be solved by the Numerov method. The potential functions of Morse [19], Rydberg [20], Varshni(II) [21], Varshni(III) [21], Varshni(VI) [21], Poschl-Teller [22], Hulburt-Hirschfelder [23], Frost-Musulin [24], Linnet [25], Lippincott [26], and Rosen-Morse [27] are used to calculate the vibrational and vibration-rotation eigenvalues and eigenfunctions. The accuracy of these potential functions are estimated by comparing the available experimental values with the numerical results which we will obtain. Thereafter we will obtain the spectroscopic constants \( \omega_e, \omega_x, B_e, \) and \( \alpha_e \) from computed vibrational and vibration-rotation energy levels.

2. Results and Discussion

2.1. Numerical solution of the vibrational Schrödinger equation of heteronuclear diatomic molecules

Since we are dealing with small quantities, to solve the Schrödinger equation by numerical methods, we should reformulate the equation using dimensionless variables. We seek to find a dimensionless reduced energy \( E_r \) and a dimensionless reduced \( x \) coordinate \( x_r \) which are defined as

\[
x_r = \frac{x}{B}, \quad E_r = \frac{E}{A},
\]

(5)

where the constant \( A \) has dimensions of energy, and \( B \) is a constant with dimensions of length. Now, for instance, we consider the Schrödinger equation with the Varshni(III) potential function. Substituting the Varshni(III) potential function into (4) with \( J = 0 \), the Schrödinger equation becomes

\[
-\frac{\hbar^2}{2\mu} \varphi''(x) + D_e \left[ 1 - \frac{r_e}{r} e^{-\beta(r^2-r_e^2)} \right]^2 \varphi = E \varphi,
\]

(6)
where \( x = r - r_e \). Equation (6) contains the three constants \( \mu \), \( \beta \), and \( h \). Thus, by using the constants, we can make the quantities of the equation dimensionless:

\[
[\beta] = L^{-2}, \quad [h] = ML^2T^{-1}, \quad [\mu] = M.
\]

(7)

Therefore

\[
A = \mu^{-1} \beta \ h^2.
\]

(8)

let \( B = \mu^a \beta^b h^c \). Therefore

\[
B = \beta^{\frac{1}{2}}.
\]

(9)

Since \( |\psi(x)|^2 \, dx \) is the probability which is dimensionless, the \( \psi(x) \) must have the dimensions of length \(-1/2\). We now rewrite the Schrödinger equation with Varshni(III) potential function in terms of the reduced variables \( D_{e,r}, x_r, \psi_r, \) and \( E_r \).

In view of (5), we have \( dx_r/dx = B^{-1} \). Substituting (5), (8) and (9) into (6), we obtain

\[
-\frac{\hbar^2}{2\mu} \left( \beta^{-1/2} \right)^5 \frac{d^2 \psi_r}{dx_r^2} + D_{e,r}(\mu^{-1} \beta \ h^2) \left[ 1 - \frac{r_{e,r}}{x_r + r_{e,r}} \right] \psi_r = E_r(\mu^{-1} \beta \ h^2) \psi_r.
\]

(10)

Dividing by \( B^{-1/2} \) and simplifying (10), we have

\[
-\frac{\hbar^2}{2\mu} \beta \frac{d^2 \psi_r}{dx_r^2} + D_{e,r}(\mu^{-1} \beta \ h^2) \left[ 1 - \frac{r_{e,r}}{x_r + r_{e,r}} \right] \psi_r = E_r(\mu^{-1} \beta \ h^2) \psi_r.
\]

(11)

Therefore,

\[
\frac{d^2 \psi_r}{dx_r^2} = \left[ 2D_{e,r} \left( 1 - \frac{r_{e,r}}{x_r + r_{e,r}} \right) e^{-(x_r^2 + 2x_r r_{e,r})} \right] - 2E_r \psi_r.
\]

(12)

Since

\[
\psi^* = G\psi,
\]

we have \( \psi^*_r = G_r \psi_r \) and hence

\[
G_r = 2D_{e,r} \left( 1 - \frac{r_{e,r}}{x_r + r_{e,r}} \right) e^{-(x_r^2 + 2x_r r_{e,r})} - 2E_r.
\]

(14)
Now, we are in the position to be able to solve the Schrödinger equation with Varshni(III) potential function via the Numerov method. In addition to finding the dimensionless expression $G_r$, we need to find relations between parameters that we need.

In order to find the relations between these parameters, we use the following three necessary conditions [16, 21, 28]:

\[
U(r_e) - U(x) = -D_e, \tag{15}
\]

\[
\left( \frac{dU}{dr} \right)_{r=r_e} = 0, \tag{16}
\]

\[
\left( \frac{d^2U}{dr^2} \right)_{r=r_e} = k_e. \tag{17}
\]

then, letting $\Delta = k_e r_e^2 / 2D_e$, we have

\[
\beta = \frac{\Delta^{1/2} - 1}{2r_e}. \tag{18}
\]

In a similar fashion, we can obtain relations between the parameters and the dimensionless expression $G_r$. Table 1 exhibits all potential functions together with their parameters and the dimensionless expression $G_r$. In the table, we make use of the symbols $\Delta = k_e r_e^2 / 2D_e$, $G = 8 \omega_e x_e / B_e$, and $F = \alpha_e \omega_e / 6B_e^2$, where $r_e$, $k_e$, $D_e$, $\omega_e$, $\omega_e x_e$, $B_e$, and $\alpha_e$ stand for the equilibrium bond length, force constant, dissociation energy, vibrational frequency, anharmonicity constant, equilibrium rotational constant, and the vibration-rotation coupling constant, respectively.

2.1.1. Determining $s_r$, $x_r,0$, and $x_r,\text{max}$

To utilize the recursion relation [2]

\[
\psi_{n+1} \approx \frac{2\psi_n - \psi_{n-1} + \frac{5}{6}G_n \psi_n^2 + \frac{1}{12}G_{n+1} \psi_{n-1}^2}{1 - G_{n+1} \psi_n^2 / 12}, \tag{19}
\]

as well as the expression $G_r$, we need to determine the initial and final values of $x_r$ and the distance $s_r$ between the adjacent points. There are different methods to determine the initial and final values of $x_r$. First, we need to locate the boundaries between the classically allowed and forbidden regions. The boundaries consist of points at which $E_r = V_r$. Table 2 demonstrates $A$, $x_r,0$, $x_r,\text{max}$, the spectroscopic numerical values, and the dimensionless expression $G_r$ for the IF molecule with various potential energy functions.
<table>
<thead>
<tr>
<th>Potential</th>
<th>Potential function</th>
<th>Relations between parameters</th>
<th>The dimensionless expression $G_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>$D_r \left[1 - e^{-a r} \right]^2$</td>
<td>$a = \left(\frac{k_e}{2D_e}\right)^{1/2}$</td>
<td>$2D_{r,e} \left[1 - e^{-b r} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Rydberg</td>
<td>$D_r \left[1 - (1 + \alpha) e^{-a r} \right]$</td>
<td>$\beta = \frac{\Delta_{1/2} - 1}{2\gamma}$</td>
<td>$2D_{r,e} \left[1 - (1 + \gamma) e^{-b r} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Varshni (II)</td>
<td>$D_r \left[1 - \frac{r_e}{r} e^{-a \left(r - r_e \right)} \right]^2$</td>
<td>$a = \frac{\Delta_{1/2} - 1}{r_e}$</td>
<td>$2D_{r,e} \left[1 - \frac{r_e}{x_r + r_{r,e}} e^{-b r} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Varshni (III)</td>
<td>$D_r \left[1 - \frac{r_e}{r} e^{-\beta \left(r - r_e \right)} \right]^2$</td>
<td>$\beta = \frac{\Delta_{1/2} - 1}{2r_e}$</td>
<td>$2D_{r,e} \left[1 - \frac{r_e}{x_r + r_{r,e}} e^{-b r} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Varshni (VI)</td>
<td>$D_r \left[1 - \frac{r_e}{r} e^{-a \left(r - r_e \right)} \right]^2$</td>
<td>$a = \frac{\Delta_{1/2} + 1}{r_e}$</td>
<td>$2D_{r,e} \left[1 - \frac{x_r + r_{r,e}}{r_{r,e}} e^{-b r} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Poschl-Teller</td>
<td>$D_x + M \cosh \left(\frac{aw}{2} \right) - N \sech \left(\frac{aw}{2} \right)$</td>
<td>$N = \frac{r_e}{\left(1 - y^2\right)^{1/2}}$, $M = N \gamma^2$, $y = \tanh \left(\frac{aw}{2}\right)$</td>
<td>$2D_{r,e} + M \cosh \left(\frac{r_{r,e} + r_{x}}{2} \right) - \tanh \left(\frac{r_{x} + r_{r,e}}{2} \right) - 2E_r$</td>
</tr>
<tr>
<td>Hulburt-</td>
<td>$D_y \left[1 + e^{2a r} - 2e^{a r} + \frac{3}{4} e^{-2a r} \right]$</td>
<td>$a = \left(\frac{k_e}{2D_e}\right)^{1/2}$</td>
<td>$2D_{r,e} \left[1 - e^{-b r} \right]^2 + e^{2a r} e^{-3r} \left(1 - br_{r,e}\right) - 2E_r$</td>
</tr>
<tr>
<td>Hirschfelder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linnet</td>
<td>$D_y + \frac{a}{r} - be^{-a r}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rosen-Morse</td>
<td>$D_x + Atanh \left(\frac{r_e}{d} \right) - \tanh \left(\frac{r_e}{d} \right)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1 continued

Potentials, relations between parameters, and the dimensionless expression $G_r$.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Potential function</th>
<th>Relations between parameters</th>
<th>The dimensionless expression $G_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lippincott</td>
<td>$D_e \left[ 1 - e^{-\alpha r} \right]^2$</td>
<td>$n = \frac{2\Delta}{r_e}$</td>
<td>$2D_e e^{-\alpha r} \left[ 1 - e^{-2\alpha r} \right] - 2E_r$</td>
</tr>
<tr>
<td>Frost-Musulin</td>
<td>$D_e + e^{-\alpha r} \left[ \frac{c}{r} - \beta \right]$</td>
<td></td>
<td>$2 \left[ D_e e^{-\alpha r} \left( \frac{c}{r} - \beta \right) - E_r \right]$</td>
</tr>
</tbody>
</table>

Table 2

$A$, $x_{r,0}$, $x_{r,max}$, the spectroscopic numerical values, and the numerical dimensionless expression $G_r$ for the IF molecule with various potential energy functions.

<table>
<thead>
<tr>
<th>Potential</th>
<th>$A$</th>
<th>$x_{r,0}$</th>
<th>$x_{r,max}$</th>
<th>Spectroscopic numerical values</th>
<th>The numerical dimensionless expression $G_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>$\hbar \mu^{-1} = 6.1770$</td>
<td>-0.5</td>
<td>0.8</td>
<td>$a = 1.740271 \times 10^8$</td>
<td>$2 \times 4879.9403 \left[ 1 - e^{-\gamma} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Rydberg</td>
<td>$\hbar \mu^{-1} = 12.3540$</td>
<td>-0.8</td>
<td>1.02</td>
<td>$a = 2.461115 \times 10^8$</td>
<td>$2 \times 2439.9701 \left[ 1 - (1 + \gamma) e^{-\gamma} \right] - 2E_r$</td>
</tr>
<tr>
<td>Varshni (II)</td>
<td>$\hbar \mu^{-1} = 3.0190$</td>
<td>-0.29</td>
<td>0.4</td>
<td>$a = 1.216645 \times 10^8$</td>
<td>$2 \times 9984.5615 \left[ 1 - \frac{2.3236}{x_r + \frac{2.3236}{x_r}} e^{-x_r} \right] - 2E_r$</td>
</tr>
<tr>
<td>Varshni (III)</td>
<td>$\hbar \mu^{-1} = 0.6497$</td>
<td>-0.19</td>
<td>0.21</td>
<td>$a = 3.185336 \times 10^5$</td>
<td>$2 \times 46397.25 \left[ 1 - \frac{1.0778}{x_r + \frac{1.0778}{x_r}} e^{-2x_r} \right] - 2E_r$</td>
</tr>
<tr>
<td>Varshni (VI)</td>
<td>$\hbar \mu^{-1} = 10.4534$</td>
<td>-0.74</td>
<td>0.86</td>
<td>$a = 2.263897 \times 10^8$</td>
<td>$2 \times 2883.5968 \left[ 1 - \frac{x_r + 4.3236}{x_r} e^{-x_r} \right] - 2E_r$</td>
</tr>
<tr>
<td>Poschl-Teller</td>
<td>$\hbar \mu^{-1} = 6.1770$</td>
<td>-0.5</td>
<td>0.7</td>
<td>$a = 1.740271 \times 10^8$</td>
<td>$2 \times 4879.9403 \left[ 1 - e^{-\gamma} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Hulburt-Hirschfelder</td>
<td>$\hbar \mu^{-1} = 6.1770$</td>
<td>-0.52</td>
<td>0.7</td>
<td>$a = 1.740271 \times 10^8$</td>
<td>$2 \times 4879.9403 \left[ 1 - e^{-\gamma} \right]^2 - 2E_r$</td>
</tr>
<tr>
<td>Frost-Musulin</td>
<td>$\hbar \mu^{-1} = 8.0979$</td>
<td>-0.6</td>
<td>0.8</td>
<td>$a = 1.992576 \times 10^9$</td>
<td>$2 \times 3722.3714 e^{-\gamma} - 2E_r$</td>
</tr>
</tbody>
</table>
Table 2 continued

\[ A, \ x_{r,0}, \ x_{r,\text{max}} \], the spectroscopic numerical values, and the numerical dimensionless expression \( G_r \) for the IF molecule with various potential energy functions

<table>
<thead>
<tr>
<th>Potential</th>
<th>( A )</th>
<th>( x_{r,0} )</th>
<th>( x_{r,\text{max}} )</th>
<th>Spectroscopic numerical values</th>
<th>The numerical dimensionless expression ( G_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linnet</td>
<td>( n^2 \mu^{-1} = 3.4653 )</td>
<td>-0.35</td>
<td>0.45</td>
<td>( n=1, 3.0347 \times 10^2 )</td>
<td>( \frac{653791.0}{(x_r + 2.4892)} - 615067.6 )</td>
</tr>
<tr>
<td>Rosen-Morse</td>
<td>( n^2 \mu^{-1} = 1.6458 )</td>
<td>-0.25</td>
<td>0.35</td>
<td>( n=1, 1.13229 \times 10^4 )</td>
<td>( 873894.3 \tanh \left( x_r + 1.7155 \right) )</td>
</tr>
<tr>
<td>Lippincott</td>
<td>( n^2 \mu^{-1} = 272.9158 )</td>
<td>-3.5</td>
<td>4.5</td>
<td>( n = 11.567585 \times 10^8 )</td>
<td>( 110.4494 \left( 1 - e^{-1.7155 x_r} \right) )</td>
</tr>
</tbody>
</table>

2.1.2. Using spreadsheet program to obtain vibrational eigenvalues and eigenfunctions

Now that our input data \( G_r, \ x_r, \ x_{r,0}, \) and \( x_{r,\text{max}} \) are obtained, we can employ (19) by some software to draw the wave function and obtain the energy levels. Here we have used Excel spreadsheet program, which has the following benefits: 1) Having a friendly environment for programming, 2) Having a high power for numerical calculations, and 3) Having a high ability for sketching the wave functions.

Now, we examine the correctness of the operation as well as the initial guess for \( E_{vib,r} \). By choosing the columns containing \( x_r \) and \( n_Psi_r \), we plot the wave function \( \psi_r \) against \( x_r \). If the sketched function has the well-behaved conditions of a wave function and its value at \( Psi_r,\text{max} \) is close to zero, then the guess for \( E_{vib,r} \) is satisfactory. But if the value of \( Psi_r,\text{max} \) is not close the zero we have to change the value of \( E_{vib,r} \). To find a better value for \( E_{vib,r} \) we proceed as follows. We first put zero for \( E_{vib,r} \) in the cell B3 and then by using the solver option we ask the program to find the amount of energy such that \( Psi_r,\text{max} \) is as close to zero as possible. The solver option in Tools menu is one of the most useful features of Excel. Since the cell F3 shows zero (Nodes = 0), we obtain the correct value of the first level of energy. To find the second level of energy we slightly increase the first level of energy. Again, by using solver option, we find a second level of energy. We must mention that the amount of increase must not be so high that the number of nodes reaches 2 or so low that the solver option can not find the next level of energy (a so-called “error”). We repeat the method for finding the next levels of energy. The number of nodes shows the kind of the state to which the energy belongs.

As a final control of the correct values of the energy levels, we have to check them against the plotted wave functions (see Appendix (B)). Finally the program multiplies the energy values \( E_{vib,r} \) into the constant \( A \) to evaluate the energy values in terms of \( \text{cm}^{-1} \) (See Appendix (A), cell K3). In the same way, one can calculate the wave function and vibrational energy of the IF molecule with potential energy functions. In Table 3, the six lower level of vibrational energy levels of the IF molecule are obtained in terms of \( \text{cm}^{-1} \), where one can also find their deviation.
percentages from the analytical calculations of the existing molecular constants [29] (in the table manual values are obtained from relation $\varepsilon = \omega_y (v + 1/2) - \omega_x x (v + 1/2)^2 + ...$).

**Table 3**
Six lower level of vibrational energy levels of the IF molecule in terms of cm$^{-1}$ and deviation percentages from the analytical calculations of the existing molecular constants.

<table>
<thead>
<tr>
<th>Potential</th>
<th>$E_0$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$E_4$</th>
<th>$E_5$</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>304.3436</td>
<td>908.3837</td>
<td>1506.205</td>
<td>2097.783</td>
<td>2683.093</td>
<td>3262.116</td>
<td>0.005553</td>
</tr>
<tr>
<td>Rydberg</td>
<td>304.3891</td>
<td>908.9551</td>
<td>1507.834</td>
<td>2101.011</td>
<td>2688.469</td>
<td>3270.194</td>
<td>0.136874</td>
</tr>
<tr>
<td>Varshni(II)</td>
<td>304.2991</td>
<td>907.6058</td>
<td>1504.009</td>
<td>2093.526</td>
<td>2676.199</td>
<td>3252.248</td>
<td>-0.16252</td>
</tr>
<tr>
<td>Varshni(III)</td>
<td>304.4331</td>
<td>909.4955</td>
<td>1509.255</td>
<td>2103.543</td>
<td>2692.186</td>
<td>3275.037</td>
<td>0.232856</td>
</tr>
<tr>
<td>Varshni(VI)</td>
<td>304.3633</td>
<td>909.0096</td>
<td>1508.038</td>
<td>2101.426</td>
<td>2689.151</td>
<td>3271.192</td>
<td>0.15136</td>
</tr>
<tr>
<td>Poschl-Teller</td>
<td>304.3511</td>
<td>908.4116</td>
<td>1506.292</td>
<td>2097.992</td>
<td>2683.509</td>
<td>3262.843</td>
<td>0.015406</td>
</tr>
<tr>
<td>Lippincott</td>
<td>303.9794</td>
<td>909.3626</td>
<td>1509.86</td>
<td>2105.443</td>
<td>2696.082</td>
<td>3281.752</td>
<td>0.285899</td>
</tr>
<tr>
<td>Hulburt-Hirschfelder</td>
<td>304.3812</td>
<td>908.3633</td>
<td>1506.076</td>
<td>2097.5</td>
<td>2682.62</td>
<td>3261.419</td>
<td>-0.00294</td>
</tr>
<tr>
<td>Frost-Musulin</td>
<td>304.3616</td>
<td>908.4998</td>
<td>1506.54</td>
<td>2098.466</td>
<td>2684.266</td>
<td>3263.928</td>
<td>0.034345</td>
</tr>
<tr>
<td>Linnet</td>
<td>304.5278</td>
<td>909.8416</td>
<td>1510.265</td>
<td>2105.797</td>
<td>2696.438</td>
<td>3282.198</td>
<td>0.33651</td>
</tr>
<tr>
<td>Rosen-Morse</td>
<td>304.3444</td>
<td>908.5784</td>
<td>1506.784</td>
<td>2098.932</td>
<td>2684.998</td>
<td>3264.957</td>
<td>0.051033</td>
</tr>
</tbody>
</table>

Manual value       | 304.34    | 908.34    | 1506.1    | 2097.62   | 2682.9    | 3261.94   |

2.2. Numerical solution of the vibration-rotation Schrödinger equation of heteronuclear diatomic molecules

Since the radial function $P(R)$ is a solution of the equation [2, 8]

$$\frac{-\hbar^2}{2\mu}\left[P''(R) + \frac{2}{R}P'(R)\right] + \frac{J(J + 1)\hbar^2}{2\mu R^2}P(R) + U(R)P(R) = E_{\text{int}}P(R). \quad (20)$$

the vibration-rotation Schrödinger equation with Varshni (III) potential function will be

$$\frac{-\hbar^2}{2\mu}\left[P''(r) + \frac{2}{r}P'(r)\right] + \frac{J(J + 1)\hbar^2}{2\mu r^2} + D_x \left[1 - \frac{r}{r_c} e^{-\beta(r^2 - r_c^2)}\right]^2]P(r) = EP(r). \quad (21)$$

therefore

$$\frac{-\hbar^2}{2\mu}F_r + \frac{J(J + 1)\hbar^2}{2\mu r^2} + D_x \left[1 - \frac{r}{r_c} e^{-\beta(r^2 - r_c^2)}\right]^2]F = EF. \quad (22)$$

then, the dimensionless form of this equation will be

$$F_{\text{r}} = \left(\frac{J(J + 1)}{r_c^2} + 2D_x \left[1 - \frac{r_{c,r}}{x_r + r_{c,r}} e^{-(r_c^2 + 2\beta r_{c,r})}\right] - 2E_r\right)F_{\text{r}}. \quad (23)$$

from (13) it follows that, dimensionless expression of $G_r$ will be
\[ G_r = \frac{J(J+1)}{\varepsilon_r^2} + 2D_{rr} \left[ 1 - \frac{r_{ee}}{x_r + r_{rr}} e^{-(x_r^2 + y_r^2)} \right]^2 - 2E_r. \]  

(24)

Comparing (24) and (14) we find out that the difference between the vibrational \( G_r \) and the vibration-rotation \( G_r \) is only in the term \( \frac{J(J+1)}{\varepsilon_r^2} \). So, we can obtain the vibration-rotation \( G_r \) for all potentials by adding the term \( \frac{J(J+1)}{\varepsilon_r^2} \) to vibrational \( G_r \), and solve the related Schrödinger equation numerically as before. Finally, we obtain the vibration-rotation energy levels of the molecule. Tables 4 and 5, demonstrate the calculated vibration-rotation energy levels of the IF molecule for the two initial vibrational states \( (v = 0 \) and \( v = 1 \)).

### Table 4
Rotational levels for vibrational state \( v = 0 \) of the IF molecule in terms of \( \text{cm}^{-1} \).

<table>
<thead>
<tr>
<th>Potential</th>
<th>( E_{0,0} )</th>
<th>( E_{0,1} )</th>
<th>( E_{0,2} )</th>
<th>( E_{0,3} )</th>
<th>( E_{0,4} )</th>
<th>( E_{0,5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>304.3436</td>
<td>304.9027</td>
<td>306.0411</td>
<td>307.6978</td>
<td>309.9224</td>
<td>312.7544</td>
</tr>
<tr>
<td>Rydberg</td>
<td>304.3891</td>
<td>304.9482</td>
<td>306.0625</td>
<td>307.7848</td>
<td>309.9804</td>
<td>312.7765</td>
</tr>
<tr>
<td>Varshni(II)</td>
<td>304.2991</td>
<td>304.8583</td>
<td>305.9866</td>
<td>307.6581</td>
<td>309.8927</td>
<td>312.6826</td>
</tr>
<tr>
<td>Varshni(III)</td>
<td>304.4331</td>
<td>304.9824</td>
<td>306.1209</td>
<td>307.7866</td>
<td>310.0256</td>
<td>312.8222</td>
</tr>
<tr>
<td>Varshni(VI)</td>
<td>304.3633</td>
<td>304.9245</td>
<td>306.0489</td>
<td>307.7188</td>
<td>309.9853</td>
<td>312.7213</td>
</tr>
<tr>
<td>Poschl-Teller</td>
<td>304.3511</td>
<td>304.9102</td>
<td>306.0386</td>
<td>307.7122</td>
<td>309.942</td>
<td>312.7389</td>
</tr>
<tr>
<td>Lippincott</td>
<td>303.9794</td>
<td>304.5386</td>
<td>305.6872</td>
<td>307.3448</td>
<td>309.5728</td>
<td>312.3682</td>
</tr>
<tr>
<td>Hulbert-Hirschfelder</td>
<td>304.3812</td>
<td>304.9403</td>
<td>306.0687</td>
<td>307.7364</td>
<td>309.9986</td>
<td>312.7429</td>
</tr>
<tr>
<td>Frost-Musulin</td>
<td>304.3616</td>
<td>304.9206</td>
<td>306.0488</td>
<td>307.7191</td>
<td>309.9684</td>
<td>312.7429</td>
</tr>
<tr>
<td>Linnet</td>
<td>304.5278</td>
<td>305.0871</td>
<td>306.2255</td>
<td>307.8863</td>
<td>310.1244</td>
<td>312.9168</td>
</tr>
<tr>
<td>Rosen-Morse</td>
<td>304.344</td>
<td>304.9032</td>
<td>306.0316</td>
<td>307.7093</td>
<td>309.9386</td>
<td>312.7345</td>
</tr>
</tbody>
</table>

### Table 5
Rotational levels for vibrational state \( v = 1 \) of the IF molecule in terms of \( \text{cm}^{-1} \).

<table>
<thead>
<tr>
<th>Potential</th>
<th>( E_{1,0} )</th>
<th>( E_{1,1} )</th>
<th>( E_{1,2} )</th>
<th>( E_{1,3} )</th>
<th>( E_{1,4} )</th>
<th>( E_{1,5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>908.3837</td>
<td>908.9429</td>
<td>910.0613</td>
<td>911.7388</td>
<td>913.9756</td>
<td>916.7715</td>
</tr>
<tr>
<td>Rydberg</td>
<td>908.9551</td>
<td>909.5143</td>
<td>910.6326</td>
<td>912.3101</td>
<td>914.5468</td>
<td>917.3426</td>
</tr>
<tr>
<td>Varshni(II)</td>
<td>907.6058</td>
<td>908.165</td>
<td>909.2833</td>
<td>910.9608</td>
<td>913.1975</td>
<td>915.9933</td>
</tr>
<tr>
<td>Varshni(III)</td>
<td>909.4955</td>
<td>910.0548</td>
<td>911.1733</td>
<td>912.8511</td>
<td>915.0882</td>
<td>917.8846</td>
</tr>
<tr>
<td>Varshni(VI)</td>
<td>909.0096</td>
<td>909.5688</td>
<td>910.6872</td>
<td>912.3648</td>
<td>914.6016</td>
<td>917.3976</td>
</tr>
<tr>
<td>Poschl-Teller</td>
<td>908.4116</td>
<td>908.9707</td>
<td>910.0891</td>
<td>911.7667</td>
<td>914.0035</td>
<td>916.7994</td>
</tr>
<tr>
<td>Lippincott</td>
<td>909.3626</td>
<td>909.9219</td>
<td>910.4043</td>
<td>912.7181</td>
<td>914.9551</td>
<td>917.7513</td>
</tr>
<tr>
<td>Hulbert-Hirschfelder</td>
<td>908.3633</td>
<td>908.9225</td>
<td>910.0409</td>
<td>911.7185</td>
<td>913.9552</td>
<td>916.7512</td>
</tr>
<tr>
<td>Frost-Musulin</td>
<td>908.4998</td>
<td>909.0589</td>
<td>910.1771</td>
<td>911.8544</td>
<td>914.0907</td>
<td>916.8862</td>
</tr>
<tr>
<td>Linnet</td>
<td>909.8416</td>
<td>910.4009</td>
<td>911.5195</td>
<td>913.1973</td>
<td>915.4343</td>
<td>918.2307</td>
</tr>
<tr>
<td>Rosen-Morse</td>
<td>908.5784</td>
<td>909.1376</td>
<td>910.2561</td>
<td>911.9338</td>
<td>914.1707</td>
<td>916.9669</td>
</tr>
</tbody>
</table>

2.3. Determination of \( \omega_e \) and \( \omega_e x_e \) from vibrational levels

As we know, vibrational energy of an anharmonic oscillator is as follows [27, 28]:

\[
\frac{E_v}{\hbar c} = Q(v) = \omega_v(v + \frac{1}{2}) - \omega_v x_v(v + \frac{1}{2})^2 + \omega_v y_v(v + \frac{1}{2})^3 + \ldots
\]

(25)

where \( \omega_v \) is vibration wavenumber and \( \omega_v x_v \) and \( \omega_v y_v \) are anharmonicity constants.
The distance between the two vibrational adjacent levels is obtained from the following relation:

$$\Delta Q = Q(v+1) - Q(v).$$

(26)

thus:

$$\Delta Q = \omega_v - \omega_v x_v (2v+2) + \omega_v y_v \left( \frac{26}{8} - 3v^2 - 6v \right) + \ldots ,$$

(27)

which becomes finally as follows:

$$\Delta Q_v \approx \omega_v - \omega_v x_v (2v+2).$$

(28)

Therefore, to determine \(\omega_v\) and \(\omega_v x_v\), it should be clear at least three vibrational levels.

Now for example, we compute \(\omega_v\) and \(\omega_v x_v\) of the IF molecule with Varshni(III) potential function. Wavenumbers of vibrational jumps of the IF molecule with Varshni(III) potential function are shown in Table 6.

According to the relation (28), if we draw the diagram \(\Delta Q_v\) in terms of \((2v+2)\), it will obtain a straight line which gives slope \(-\omega_v x_v\) and y-intercept, \(\omega_v\). According to this method, for the IF molecule with Varshni(III) potential function, we obtain \(\omega_v = 610.7818 \text{ cm}^{-1}\) and \(\omega_v x_v = 2.7768 \text{ cm}^{-1}\).

**Table 6**

Wavenumbers of vibrational jumps of the IF molecule with Varshni (III) potential function.

<table>
<thead>
<tr>
<th>((v+1) - v)</th>
<th>((2v+2))</th>
<th>(\Delta Q) in terms of (\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-0</td>
<td>2</td>
<td>605.0624</td>
</tr>
<tr>
<td>2-1</td>
<td>4</td>
<td>599.7595</td>
</tr>
<tr>
<td>3-2</td>
<td>6</td>
<td>594.2849</td>
</tr>
<tr>
<td>4-3</td>
<td>8</td>
<td>588.6461</td>
</tr>
<tr>
<td>5-4</td>
<td>10</td>
<td>582.8507</td>
</tr>
</tbody>
</table>

**2.4. Determination of \(B_v\) and \(\alpha_v\) from vibration-rotation levels**

Vibration-rotation energy of anharmonic oscillators is as follows [30-32]:

$$\varepsilon_{v,J} = Q(v) + F_v(J) = \omega_v (v + \frac{1}{2}) - \omega_v x_v (v + \frac{1}{2})^2 + \ldots + B_v J(J+1) - D_v J^2 (J+1)^2 + \ldots .$$

(29)

As we know, the selection rule of \(\Delta J = \pm 1\) ruling over transitions between rotational levels results in a branch \(R\) (\(\Delta J = +1\)) and a branch \(P\) (\(\Delta J = -1\)). Each transition becomes marked with \(R(J)\) or \(P(J)\).

In many cases, because of inequality of \(B^*\) and \(B''\), the bands of the branches \(R\) and \(P\) are asymmetric. To obtain \(B'\) and \(B''\) from spectral data, we use combination differences method. If we need to obtain some information about one series of lower states or one series of upper ones between which the transitions are occurred, then according to this method, the difference between wavenumber of transitions with common upper state, only depends upon the
characteristics of lower state. Likewise, the difference between wavenumber of transitions with common lower state only depends upon the characteristics of the upper state.

As we know, in case of a vibration-rotation band, the lines \( R(0) \) and \( P(2) \) have got a common upper state with \( J^\prime = J + 1 \) and as a result, \( \tilde{\nu}[R(0)] - \tilde{\nu}[P(2)] \) is only a function of \( B^\ast \). The transitions \( R(1) \) and \( P(3) \) are common in \( J^\prime = J + 2 \). Hence, we can say that in general \( \tilde{\nu}[R(J - 1)] - \tilde{\nu}[P(J + 1)] \) that is written as \( \Delta_2^\ast F(J) \), is only a function of \( B^\ast \). For these transitions, we have:

\[
\Delta_2^\ast F(J) = \tilde{\nu}[R(J - 1)] - \tilde{\nu}[P(J + 1)] = \left[ \tilde{\nu}_0 + B^\ast J(J + 1) - B^\ast J^2 + D^\ast J^2(J + 1)^2 \right]
- \left[ \tilde{\nu}_0 + B^\ast J(J + 1) - B^\ast J^2(J + 2)^2 + D^\ast J^2(J + 2)^2 \right]
= (4B^\ast - 6D^\ast)(J + \frac{1}{2}) - 8D^\ast(J + \frac{1}{2}).
\]

(30)

Thus, the diagram of changes \( \Delta_2^\ast F(J)/(J + 1/2) \) in terms of \((J + 1/2)^2\), gives a line with the slope \(-8D^\ast\) and y-intercept \((4B^\ast - 6D^\ast)\). As the two \( R(J) \) and \( P(J) \) are common in low states, therefore \( \tilde{\nu}[R(J)] - \tilde{\nu}[P(J)] \) is only a function of \( B^\prime \). So we will have:

\[
\Delta_1^\ast F(J) = \tilde{\nu}[R(J)] - \tilde{\nu}[P(J)] = \left[ \tilde{\nu}_0 + B^\ast J(J + 1)(J + 2) - B^\ast J^2(J + 1)^2 + D^\ast J^2(J + 1)^2 \right]
- \left[ \tilde{\nu}_0 + B^\ast J(J - 1) - B^\ast J^2(J + 1)^2 + D^\ast J^2(J + 1)^2 \right]
= (4B^\ast - 6D^\ast)(J + \frac{1}{2}) - 8D^\ast(J + \frac{1}{2}).
\]

(31)

Thus, the diagram of changes \( \Delta_1^\ast F(J)/(J + 1/2) \) in terms of \((J + 1/2)^2\), gives a line with the slope \(-8D^\prime\) and y-intercept \((4B^\prime - 6D^\prime)\). By regarding the relations (30) and (31) and also the Tables 4 and 5, the values \( B_0 \) and \( B_1 \) for the IF molecule with Varshni(III) potential function are 0.281226 and 0.279636, respectively. According to the relation [30]:

\[
B = B_1 - \alpha \left( \nu + \frac{1}{2} \right),
\]

(32)

Table 7
Spectroscopic constants of the IF molecule for all potential functions and deviation percentages from experimental values.

<table>
<thead>
<tr>
<th>Potential</th>
<th>( \omega_e (\text{cm}^{-1}) )</th>
<th>( \omega_x (\text{cm}^{-1}) )</th>
<th>( B_e (\text{cm}^{-1}) )</th>
<th>( \alpha_e (\text{cm}^{-1}) )</th>
<th>%error(\text{av})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morse</td>
<td>610.3179323</td>
<td>3.12722891</td>
<td>0.282011202</td>
<td>0.001610499</td>
<td>-3.24623872</td>
</tr>
<tr>
<td>Rydberg</td>
<td>610.2920599</td>
<td>2.855192337</td>
<td>0.283067969</td>
<td>0.002324512</td>
<td>4.19364745</td>
</tr>
<tr>
<td>Varshni(II)</td>
<td>610.0635947</td>
<td>3.412313365</td>
<td>0.28180642</td>
<td>0.001482443</td>
<td>-2.69913534</td>
</tr>
<tr>
<td>Varshni(III)</td>
<td>610.781762</td>
<td>2.776840816</td>
<td>0.28202327</td>
<td>0.001590858</td>
<td>-6.29588047</td>
</tr>
<tr>
<td>Varshni(VI)</td>
<td>610.3198872</td>
<td>2.825683996</td>
<td>0.282108683</td>
<td>0.001672717</td>
<td>-4.82356128</td>
</tr>
<tr>
<td>Poschl-Teller</td>
<td>610.2436233</td>
<td>3.090876958</td>
<td>0.281869279</td>
<td>0.001515884</td>
<td>-4.81558776</td>
</tr>
<tr>
<td>Lippincott</td>
<td>610.3398071</td>
<td>2.464203711</td>
<td>0.285706693</td>
<td>0.004056236</td>
<td>24.4029689</td>
</tr>
<tr>
<td>Hulburt-Hirschfelder</td>
<td>610.2950543</td>
<td>3.14790117</td>
<td>0.282216684</td>
<td>0.001747487</td>
<td>-1.23548709</td>
</tr>
<tr>
<td>Frost-Musulin</td>
<td>610.2711679</td>
<td>3.059656064</td>
<td>0.281896637</td>
<td>0.001568289</td>
<td>-4.36299498</td>
</tr>
<tr>
<td>Limnet</td>
<td>610.2013369</td>
<td>2.444552229</td>
<td>0.283332987</td>
<td>0.002465441</td>
<td>2.80348402</td>
</tr>
<tr>
<td>Rosen-Morse</td>
<td>610.3298391</td>
<td>3.034542904</td>
<td>0.282275484</td>
<td>0.001771445</td>
<td>-1.81748346</td>
</tr>
<tr>
<td>Experimental</td>
<td>610.24</td>
<td>3.12</td>
<td>0.2797111</td>
<td>0.0018738</td>
<td></td>
</tr>
</tbody>
</table>
$B_e$ and $\alpha_e$ become $0.28202 \text{ cm}^{-1}$ and $0.001591 \text{ cm}^{-1}$, respectively. Similarly, $B_e$ and $\alpha_e$ are computed for other heteronuclear diatomic molecules with other potential functions. The gained results for the IF molecule are inserted in Table 7.

3. Conclusions

In this paper, the nuclear Schrödinger equation for the IF molecule is solved by the Numerov method. The potential functions of Morse, Rydberg, Varshni(II), Varshni(III), Varshni(VI), Poschl-Teller, Hulburt-Hirschfelder, Lippincott, Frost-Musulin, Linnet, and Rosen-Morse are used to calculate the quantum states, vibrational energy levels, and vibration-rotation energy levels. The results are compared with the available experimental values and the accuracy of these potential functions is estimated. Our calculations have utilized more than 200 worksheets of Excel spreadsheet software. Then the spectroscopic constants $\omega_e$, $\omega_e x_e$, $B_e$, and $\alpha_e$ were computed from vibrational and vibration-rotation energy levels. To compute according to this method, 5 Excel worksheets are used for the IF molecule with all of the potential functions. The Hulburt-Hirshfelder potential function in comparison with other potential functions, forecast the values of the spectroscopic constants with a higher accuracy. Totally, the spectroscopic constants gained from this method, are in a very good accordance with experimental values.

Appendix (A)

Programming by the Excel spreadsheet to obtain vibrational levels for the IF molecule with Varshni (III) potential function is as follows (the operations to be done in each cell are written in front of each cell):

A1: Write Potential Function ($U = D_e*\left[1 - r_e/r * \exp(-\beta \times (r^2-r_e^2))^2\right]$)
A3: Write ($E_{vib,r}=$)
B3: Enter $E_{vib,r,guess}$
C3: Write ($S_r=$)
D3: Write (0.01)
A5: Write ($x_r$)
B5: Write ($G_r$)
C5: Write ($P_{si}$)
A7: Write (-0.19)
A8: Write ($A7+SDS3$)
A9-A47: Copy A8, Select A9-A47, Paste A8 in A9-A47
B7: Write ($=2*46397.2898*(1-1.0778/(A7+1.0778)*\exp(-(A7^2+2*A7*1.0778)))^2-2*BS3$)
B8-B47: Copy B7, Select B8-B47, Paste B7 in B8-B47
C7: Write (0)
C8: Write (1E-4)
C9: Write ($=(2*C8-C7+5*B8*C8*SDS3^2/6+B7*C7*SDS3^2/12)/(1-B9*SDS3^2/12))$
C10-C47: Copy C9, Select C10-C47, Paste C9 in C10-C47
D9: Write ($=IF(C9*C8<0; 1; 0))$
D10-D47: Copy D9, Select D10-D47, Paste D9 in D10-D47
E3: Write (Nodes=)
F3: Write ($=SUM(D9:D47)$)
E5: Write ($n_{pi}$)
E50: Write ($=SUMSQ(C7:C47)*SDS3$)
E7: Write ($=C7/ES50^0.5$)
E8-E47: Copy E7, Select E8-E47, Paste E7 in E8-E47
G3: Write ($\psi_i, Max=$)
Appendix (B)

The graphs of six lower vibrational wave functions versus $x_r$ for IF molecule with varshni(III) potential function.
Acknowledgements

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References