A New Perturbation–Theoretic Approach to the Rovibronic Transition Matrix Elements of Diatomics

Mahmoud Korek\textsuperscript{1} and Bassam Hamdoun\textsuperscript{2}

\textsuperscript{1} Faculty of Science, Beirut Arab University, P.O. Box 11–5020, Beirut, Lebanon
\textsuperscript{2} Faculty of Engineering, University of Lebanon, P.O. Box 30014, Choueifat, Lebanon

Received: August 280, 2003; Revised: October 24, 2003; Accepted: December 15, 2003; Published: May 31, 2004

Citation of the article:
A New Perturbation–Theoretic Approach to the Rovibronic Transition Matrix Elements of Diatomics

Mahmoud Korek¹,* and Bassam Hamdoun²

¹ Faculty of Science, Beirut Arab University, P.O. Box 11–5020, Beirut, Lebanon
² Faculty of Engineering, University of Lebanon, P.O. Box 30014, Choueifat, Lebanon

Received: August 280, 2003; Revised: October 24, 2003; Accepted: December 15, 2003; Published: May 31, 2004

Abstract

The line intensities of the transitions \( \nu J \leftrightarrow \nu' J' \) where \( |J'-J| \geq 1 \) are proportional to the matrix elements \( R_{\nu J}^{\nu' J'} = \langle \Psi_{\nu J} | f(r) | \Psi_{\nu' J'} \rangle \). In the conventional Rayleigh–Schrödinger perturbation theory these matrix elements are expressed in terms of the transition number \( m = (\lambda - \lambda')/2 \) where \( \lambda = J(J + 1) \) and \( \lambda' = J'(J' + 1) \). In order to reduce the complexity in the calculation of these matrix elements for the high order corrections in the perturbation theory (because of the transition from \( \lambda \) and \( \lambda' \) – representations of \( \Psi_{\nu J} \) and \( \Psi_{\nu' J'} \) to the \( m \)–representation of \( R_{\nu J}^{\nu' J'} \) the eigenvalue and the eigenfunction of the two states \( (\nu J) \) and \( (\nu' J') \) are expanded in terms of one variable \( m \) as

\[
E_{\nu m} = \sum_{i=0} E^{(i)}_{\nu m} i^1, \quad \Psi_{\nu m} = \sum_{i=0} \phi^{(i)}_{\nu m} i^1, \quad E_{\nu' m} = \sum_{i=0} E^{(i)}_{\nu' m} i^1, \quad \Psi_{\nu' m} = \sum_{i=0} \phi^{(i)}_{\nu' m} i^1
\]

where the coefficients \( E^{(i)}_{\nu m} \), \( \phi^{(i)}_{\nu m} \), \( E^{(i)}_{\nu' m} \) and \( \phi^{(i)}_{\nu' m} \) are given by analytical expressions by using the canonical functions method. This new approach in the perturbation theory is valid for any transition (infrared, Raman, …), any operator \( f(r) \) and any potential function either empirical or of the RKR–type. The numerical application, in Raman transitions, to the ground state of the molecule CO shows that the values of \( E_{\nu m} \) and \( \Psi_{\nu m} \) calculated by using the present formulation (up to sixth order) are in good agreement with those computed by a numerical direct method.

Keywords. Rovibronic transition matrix elements of diatomics.

1 INTRODUCTION

The Rayleigh–Schrödinger perturbation theory [1] (RSPT) applied to the diatomic vibration–rotation problem allows one to write the eigenfunction and the eigenvalue of a state \( (\nu J) \) respectively by:

\[ \]

* Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.
* Correspondence author; phone: 961–1–300110; fax: 961–1–818402; E–mail: fkorek@cyberia.net.lb.
\[ \Psi_{vJ} = \sum_{i=0}^{\infty} \Psi_{v}^{(i)} \chi_{iJ} \]  
\[ E_{vJ} = \sum_{i=0}^{\infty} e_{v}^{(i)} \chi_{iJ} \]  

(1a)  

(1b)

where \( \Psi_{v}^{(0)} \) is the pure vibration wavefunction and \( \Psi_{v}^{(i)} \) are the rotational corrections, \( E_{v0} \) is the pure vibrational energy, \( e_{v}^{(1)} = B_{v} \) is the rotational constant, \( e_{v}^{(2)} = -D_{v} \), \( e_{v}^{(3)} = H_{v} \), ..., are the centrifugal distortions constants (CDC) and \( \lambda = J(J+1) \). In the transitions \( v J \leftrightarrow v'J' \) (\( J' - J = j \)) with \( |j| > 0 \) the eigenfunction and the eigenvalue of the upper state \( (v'J') \) are given respectively by

\[ \Psi_{v'J'} = \sum_{i=0}^{\infty} \Psi_{v'}^{(i)} \chi_{iJ'} \]  
\[ E_{v'J'} = \sum_{i=0}^{\infty} e_{v'}^{(i)} \chi_{iJ'} \]  

(2a)  

(2b)

where \( \lambda' = J'(J'+1) \).

In the literature, the line intensities \( S_{v}^{\psi}(m) \) of the vibrational–rotational transitions \( v J \leftrightarrow v'J' \) at temperature \( T \) in infrared transitions are expressed in terms of \( m \) as [2,3]

\[ S_{v}^{\psi} = \frac{8\pi^{3}\omega(m)}{3hc} \left| R_{v}^{0}(m) \right|^{2} \frac{N_{0}m^{2}}{Q} \exp\left[ -E(m)/k_{B}T \right] \]  

(3)

where the transition number \( m \) relates the two rotational quantum numbers \( J \) and \( J' \) of the two considered states as \( m = [J'(J'+1) - J(J+1)]/2 \), \( \omega(m) \) is the frequency at the line center, \( N_{0} \) is the number of molecules per unit volume, \( Q \) is the rotational partition function, \( \left| R_{v}^{\psi}(m) \right|^{2} \) is the square of the transition dipole moment matrix element which is the product of a rotationless factor \( R_{v}^{\psi}(0) \) and a rotational factor (or Herman–Wallis factor) [4–7]

\[ \left| R_{v}^{\psi}(m) \right|^{2} = \left| R_{v}^{\psi}(0) \right|^{2} (1 + C_{v}m + D_{v}m^{2}) \]  

(4)

Similarly, the line intensities in the Raman transitions are proportional to the matrix elements \( R_{vJ}^{vJ'} \) which are also expressed in terms of the transition number \( m \) [8–10].

The conventional approach for the calculation of this rotational factor [11–13] (i.e. the Herman–Wallis coefficients \( C_{v} \) and \( D_{v} \)) in the perturbation theory is by the transition from \( \lambda \) and \( \lambda' \)–representations of \( E_{vJ}, \Psi_{vJ}, E_{v'J'}, \) and \( \Psi_{v'J'} \) to \( m \)–representation for the rotational factor \( R_{v}^{\psi}(m) \) (Eq.(4)). This change in representation from \( \lambda \) and \( \lambda' \) to \( m \) leads to a mathematical...
complexity if high accuracy is required (high order corrections) and to the limitation of this approach to the solution of the radial Schrödinger equation in case of the empirical Dunham potential. In order to avoid these problems, one may find it judicious to express \( E_{vJ}, E_{v'J'}, \Psi_{vJ} \) and \( \Psi_{v'J'} \), in terms of one variable \( m \) instead of two parameters \( \lambda \) and \( \lambda' \) as:

\[
\Psi_{vm} = \sum_{i=0}^{\infty} \phi_{v}^{(i)} m^i
\]

\[
E_{vm} = \sum_{i=0}^{\infty} E_{v}^{(i)} m^i
\]

\[
\Psi_{v'm} = \sum_{i=0}^{\infty} \phi_{v'}^{(i)} m^i
\]

\[
E_{v'm} = \sum_{i=0}^{\infty} E_{v'}^{(i)} m^i
\]

The aim of this work is to give to the functions \( E_{v}^{(i)}, \phi_{v}^{(i)}, \Psi_{v}^{(i)} \) and \( \Psi_{v'}^{(i)} \) simple analytical expressions by using the canonical functions approach [14–16]. Under this form of the perturbation theory, the calculation of the matrix elements (Eq.(4b)) for the considered transitions is greatly simplified and all the calculation can be done by using only one parameter \( m \). The numerical application to the ground state of the molecule CO showed the validity and the high accuracy of the present formulation.

\section*{2 THEORETICAL}

\subsection*{2.1 Expressions of \( E_{v}^{(i)} \) in terms of \( e_{v}^{(i)} \)}

In the \( vJ \leftrightarrow v'J' \) transitions the rotational quantum numbers \( J \) and \( J' \) are related as \( J' = J + j \) where \( j = \pm 1 \) in the infrared transitions and \( j = 0, \pm 2 \) in the Raman transitions. By expressing \( \lambda \) and \( \lambda' \) in terms of \( j \) and \( m \) (for \( j = \pm 1, \pm 2, \ldots \)) one obtains [5]:

\[
\lambda = \frac{j^2 - 1}{4} - m + \frac{m^2}{j^2}
\]

\[
\lambda' = \frac{j^2 - 1}{4} + m + \frac{m^2}{j^2}
\]

or more generally \( \lambda \) or \( \lambda' \) can be written as:

\[
\Lambda = \sum_{i=0}^{\infty} a_i m^i
\]
where:

\[
a_0 = \frac{j^2 - 1}{4}, \quad a_1 = \pm 1 \quad \text{and} \quad a_2 = \frac{1}{j^2}
\]  

(6d)

with \(a_1 = -1\) and \(a_1 = +1\) are for the lower and upper state respectively.

By replacing \(\Lambda\) (Eq.(6c)) in (1b) we obtain the “m–representation” of the eigenvalue as:

\[
E_{vm} = \sum_{i=0}^{\infty} E_v^{(i)} m^i
\]

(7)

where

\[
E_v^{(0)} = \sum_{i=0}^{\infty} a_0^{(i)} e_v^{(i)}
\]

(8a)

\[
E_v^{(1)} = a_1 \sum_{i=1}^{\infty} i a_0^{(i)} e_v^{(i)}
\]

(8b)

\[
E_v^{(2)} = \sum_{i=1}^{\infty} i[a_0^{(i)} a_2^{(i)} + \frac{(i-1)}{2} a_1^{(i)} a_0^{(i)} e_v^{(i)}]
\]

(8c)

\[
E_v^{(3)} = \sum_{i=2}^{\infty} i(i-1)[a_0^{(i)} a_2^{(i)} + \frac{(i-1)}{2} a_1^{(i)} a_0^{(i)} e_v^{(i)}]
\]

(8d)

\[
E_v^{(4)} = \sum_{i=2}^{\infty} \frac{i(i-1)}{2} [a_0^{(i)} a_2^{(i)} + (i-2) a_0^{(i-2)} a_2^{(i)} + \frac{(i-2)(i-3)}{12} a_1^{(i)} a_0^{(i)} e_v^{(i)}]
\]

(8e)

\[
E_v^{(5)} = \sum_{i=3}^{\infty} \frac{i(i-1)(i-2)}{2} [a_0^{(i)} a_2^{(i)} + \frac{(i-3)}{3} a_0^{(i-3)} a_2^{(i)} + \frac{(i-3)(i-4)}{60} a_1^{(i)} a_0^{(i)} e_v^{(i)}]
\]

(8f)

2.2 Expression of \(\phi_v^{(i)}\) in terms of \(\Psi_v^{(i)}\)

By replacing (6c) in (1a) we obtain the “m–representation” of the eigenfunctions in the form

\[
\Psi_{vm} = \sum_{i=0}^{\infty} \phi_v^{(i)} m^i
\]

(9)

where the functions \(\phi_v^{(i)}\) have the same expressions as \(E_v^{(i)}\) (Eqs.(8)) by substituting \(e_v^{(i)}\) by \(\Psi_v^{(i)}\).

By using Eqs.(8) and (9) the coefficients \(E_v^{(i)}\) and \(\phi_v^{(i)}\) can be determined (up to the sixth order) with high precision because the determination of the highly accurate large order coefficients \(e_v^{(i)}\), and \(\Psi_v^{(i)}\) is a solved problem [17].
2.3 Analytic Expression for $E^{(i)}_v$

Within the Born–Oppenheimer apprxiotion [18], a rovibrational state $(v,J)$ of a diatomic molecule is characterized by the eigenvalue $E_{vJ}$ and the eigenfunction $\Psi_{vJ}$ of the radial Schrödinger equation

$$\frac{d^2\psi_{vJ}}{dr^2} + \{k[E_{vJ} - U_0(r)] - \frac{\lambda}{r^2}\} \psi_{vJ} = 0 \quad (10a)$$

where $U_0(r)$ is the rotationless potential, $r$ is the internuclear distance and $k = \frac{2\mu}{\hbar^2}$, $\mu$ and $\hbar$ having their usual significations. By replacing Eqs.(5a), (5b) and (6c) in Eq.(10a), one can find:

$$\frac{d^2\psi_{vm}}{dr^2} + \{k[E_{vm} - U_0(r)] - \frac{\sum_{i=0}^{2} a_i m^i}{r^2}\} \psi_{vm} = 0 \quad (10b)$$

$$\frac{d}{dr} \sum_{i} \phi^{(i)}_v m^i + \{k[\sum_{i} E^{(i)}_v m^i - U_0(r)] - \frac{\sum_{i=0}^{2} a_i m^i}{r^2}\} \sum_{i} \phi^{(i)}_v m^i = 0 \quad (10c)$$

Since this equation is satisfied for any $m$, we obtain:

$$\phi^{(0)}_v'' + k[E^{(0)}_v - U(r)]\phi^{(0)}_v = 0 \quad (11)$$

$$\phi^{(n)}_v'' + k[E^{(0)}_v - U(r)]\phi^{(n)}_v = -\sum_{i=1}^{n} B_i \phi^{(n-i)}_v \quad (12)$$

where:

$$U(r) = U_0(r) + \frac{a_0}{kr^2}$$

$$B_1 = kE^{(1)}_v - \frac{a_1}{r^2} \quad (1)$$

$$B_2 = kE^{(2)}_v - \frac{a_2}{r^2}$$

$$B_i = kE^{(i)}_v \text{ for } i \geq 3$$

Eqs.(12) can be written in the general form:

$$\phi^{(n)}_v''(r) + k[E^{(0)}_v - U]\phi^{(n)}_v = S_n(r) \quad (13)$$

By using the Rayleigh–Schrödinger perturbation approach [19] we can find:
If we replace the successive values of $S_n$ (Eq.(12)) in (14) and by defining:

$$I_{in} = \langle \phi_v^{(i)} | \phi_v^{(n)} \rangle$$  

$$R_{in}^{(P)} = \langle \phi_v^{(i)} | B_{P} | \phi_v^{(n)} \rangle$$  

$$T_q = \langle \phi_v^{(0)} | \frac{a_q}{r^2} | \phi_v^{(0)} \rangle$$

one can obtain for $E_v^{(i)}$ the analytic expressions:

$$E_v^{(1)} = T_1 / kI_{00}$$

$$E_v^{(2)} = (T_2 - R_{01}^{(1)}) / kI_{00}$$

$$E_v^{(3)} = -(R_{02}^{(1)} + R_{01}^{(2)}) / kI_{00}$$

and for $n \geq 4$:

$$E_v^{(n)} = -(R_{0(n-1)}^{(1)} + R_{0(n-2)}^{(2)}) + \sum_{i=4}^{n} B_{(i-1)}^{I_{00}} [0(n-i+1)] / kI_{00}$$

### 2.4 Analytic Expressions for the Rovibrational Wave Function $\Psi_{vm}$

The radial Schrödinger equation (10b) can be simply represented by:

$$\frac{d^2 \Psi_{vm}}{dr^2} = f_{vm}(x) \Psi_{vm}(x)$$

with $x = r - r_c$ and:

$$f_{vm} = -k[E_{vm} - U_{0}(x)] - \sum_{i=0}^{2} \frac{a_i m_i}{(x + r_c)^2}$$

By replacing Eq.(5b) in (18) one obtains:

$$f_{vm}(x) = \sum_{i=0}^{2} C_i(x) m_i$$
where:

\[
C_0(x) = -k[E_v^{(0)} - U_0(x)] + a_0
\]  
\[\text{(20a)}\]

\[
C_1(x) = -kE_v^{(1)} + a_1/(x + r_c)^2
\]  
\[\text{(20b)}\]

\[
C_2(x) = -kE_v^{(2)} + a_2/(x + r_c)^2
\]  
\[\text{(20c)}\]

\[
C_i(x) = -kE_v^{(i)} \text{ for } i \geq 3
\]  
\[\text{(20d)}\]

Equation (17) is equivalent to the second type of Volterra equation [20]:

\[
\Psi_{vm}(x) = \Psi_{vm}(0) + x\Psi_{vm}'(0) + \int_0^x (x-t)f_{vm}(x)\Psi_{vm}(t)dt
\]  
\[\text{(21)}\]

in the sense that the solution of one is the solution of other [21]. By replacing \[\Psi_{vm}(t)\] within the integral by its expressions in Eq.(12) an infinity of time, one can write:

\[
\Psi_{vm}(x) = \sum_{i=0}^{\infty} D_i(x)
\]  
\[\text{(22)}\]

where:

\[
D_i(x) = \int_0^x (x-t)f_{vm}(t)D_{i-1}(t)dt
\]  
\[\text{(23a)}\]

with:

\[
D_0(x) = \Psi_{vm}(0) + x\Psi_{vm}'(0)
\]  
\[\text{(23b)}\]

if \[D_0\] is replaced in \[D_1\] and \[D_2\], and so one can obtain the solution of Eq.(17) in the form:

\[
\Psi_{vm}(x) = \Psi_{vm}(0)\alpha_{vm}(x) + \Psi_{vm}'(0)\beta_{vm}(x)
\]  
\[\text{(24)}\]

where:

\[
\alpha_{vm}(x) = \sum_{i=0}^{\infty} H_i(x)
\]  
\[\text{(25a)}\]

\[
H_i(x) = \int_0^x (x-t)f_{vm}(t)H_{i-1}(t)dt
\]  
\[\text{(25b)}\]

\[H_0(x) = 1\]  
\[\text{(25c)}\]
with the initial values $\alpha_{\text{vm}}(0) = 1$ and $\alpha'_{\text{vm}}(0) = 0$ and:

$$\beta_{\text{vm}}(x) = \sum_{i=0}^{\infty} G_i(x) \quad (26a)$$

$$G_i(x) = \int_{0}^{x} f_{\text{vm}}(t) G_{i-1}(t) dt \quad (26b)$$

$$G_0(x) = x \quad (26c)$$

with $\beta_{\text{vm}}(0) = 0$ and $\beta'_{\text{vm}}(0) = 1$. The initial values $\Psi_{\text{vm}}(0)$ and $\Psi'_{\text{vm}}(0)$ (Eq.(24)) are determined by the boundary conditions of the wave function:

$$\Psi_{\text{vm}}(x) \rightarrow 0 \text{ as } x \rightarrow \infty \text{ and } x \rightarrow -r_e \quad (27)$$

By using this condition in Eq. (24):

$$\frac{\Psi'_{\text{vm}}(0)}{\Psi_{\text{vm}}(0)} = \lim_{x \rightarrow \infty} \frac{\alpha_{\text{vm}}(x)}{\beta_{\text{vm}}(x)} \text{ as } x \rightarrow \infty \text{ and } x \rightarrow -r_e \quad (28)$$

For the un–normalized wave function and without any loss of the generality of the problem we take:

$$\Psi_{\text{vm}}(0) = 1 \quad (29)$$

Thus an analytic expression is obtained for the wave function $\Psi_{\text{vm}}$ without any restriction on the potential function of the considered electronic state.

### 2.5 Analytic Expressions for the Functions $\phi^{(i)}_v$

In order to have successively the analytic expressions for the functions $\phi^{(i)}_v$, Eq.(11) can be written in the form:

$$\phi^{(0)}_v'' + f_v(r)\phi^{(0)}_v = 0 \quad (30)$$

where:

$$f_v(r) = k(E^{(0)}_v - U(r)) \quad (31)$$
Table 1. Values of the pure vibrational energy $E_v$, the rotational constant $B_v$ and the centrifugal distortion constants for several vibrational levels for a Dunham potential of the ground state of the molecule CO calculated by using the highly accurate method of Ref. [17]. The number in parentheses is a multiplicative power of 10.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$E_v$</th>
<th>$B_v$</th>
<th>$D_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1081.776 425 149</td>
<td>1.922 528 872 188 4</td>
<td>6.119 538 190 045 7 (–6)</td>
</tr>
<tr>
<td>1</td>
<td>3225.047 998 885</td>
<td>1.905 023 764 516 8</td>
<td>6.118 442 023 764 5 (–6)</td>
</tr>
<tr>
<td>2</td>
<td>7432.218 208 258</td>
<td>1.870 382 123 4</td>
<td>6.116 916 977 780 7 (–6)</td>
</tr>
<tr>
<td>3</td>
<td>11.534.025 078 516</td>
<td>1.835 034 533 221 6</td>
<td>6.118 847 356 162 4 (–6)</td>
</tr>
<tr>
<td>4</td>
<td>15.531.120 784 273</td>
<td>1.800 652 049 6</td>
<td>6.118 385 027 782 3 (–6)</td>
</tr>
<tr>
<td>5</td>
<td>19.424.385 126 713</td>
<td>1.765 193 201 18</td>
<td>6.116 667 143 7 (–6)</td>
</tr>
<tr>
<td>6</td>
<td>23.215.178 762 636</td>
<td>1.730 502 372 1</td>
<td>6.099 007 253 955 3 (–6)</td>
</tr>
<tr>
<td>7</td>
<td>26.908.787 935 516</td>
<td>1.696 248 430 9</td>
<td>6.058 008 738 369 0 (–6)</td>
</tr>
<tr>
<td>8</td>
<td>30.500.138 111 400</td>
<td>1.662 765 453 069 8</td>
<td>5.968 651 638 803 7 (–6)</td>
</tr>
<tr>
<td>9</td>
<td>34.004.814 019 292</td>
<td>1.630 796 697 133 4</td>
<td>5.798 185 471 819 9 (–6)</td>
</tr>
<tr>
<td>10</td>
<td>37.430.275 022 813</td>
<td>1.601 269 809 6</td>
<td>5.510 807 274 654 1 (–6)</td>
</tr>
<tr>
<td>11</td>
<td>40.793.837 404 836</td>
<td>1.575 495 583 9</td>
<td>5.289 444 773 890 7 (–6)</td>
</tr>
<tr>
<td>12</td>
<td>44.109.660 979 866</td>
<td>1.550 371 123 7</td>
<td>5.064 021 249 617 0 (–6)</td>
</tr>
<tr>
<td>13</td>
<td>47.407.110 167 608</td>
<td>1.528 476 578 9</td>
<td>4.843 843 647 370 3 (–6)</td>
</tr>
<tr>
<td>14</td>
<td>50.707.803 288 057</td>
<td>1.507 303 959 3</td>
<td>4.623 155 001 388 3 (–6)</td>
</tr>
<tr>
<td>15</td>
<td>54.032.686 216 679</td>
<td>1.486 230 124 0</td>
<td>4.404 258 358 857 2 (–6)</td>
</tr>
</tbody>
</table>

By using Eq.(21) and by applying the same approach used in the calculation of $\Psi_{vm}$ one can obtain

$$\phi_{v}^{(0)}(x) = \phi_{v}^{(0)}(0) a_v(x) + \phi_{v}^{(0)'}(0) b_v(x)$$

(32)

where the canonical functions $a_v(x)$ and $b_v(x)$ are given by the analytic expressions (25) and (26) in which $f_{vm}(x)$ (Eq.(19)) is substituted by $f_v(x)$ (Eq.(31)) with the same initial conditions

$$a_v(0) = 1 \quad a_v'(0) = 0$$

(33a)

$$b_v(0) = 0 \quad b_v'(0) = 1$$

(33b)

$$\phi_{v}^{(0)'}(0) = -\lim_{x \to \infty} \frac{a_v(x)}{b_v(x)} \quad \text{as} \quad x \to \infty \quad \text{and} \quad x \to -r_e$$

(33c)
Table 2. Values of the coefficients $E_v^{(i)}$ calculated from Eq. (16) (first entry) compared to those calculated from Eq. (8) by taking $a_1 = +1$ (second entry) for the Dunham potential of the ground state of the molecule CO

<table>
<thead>
<tr>
<th>$v$</th>
<th>$E_v^{(0)}$</th>
<th>$E_v^{(1)}$</th>
<th>$E_v^{(2)}$</th>
<th>$E_v^{(3)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1083.218 318 361</td>
<td>1039.241 519 890 9</td>
<td>4.806 238 036 976 0 (–1)</td>
<td>0.059 756 768 437 4 (–6)*</td>
</tr>
<tr>
<td>1</td>
<td>3226.476 764 786</td>
<td>3184.701 727 249 4</td>
<td>4.762 480 341 347 1 (–1)</td>
<td>0.059 411 660 050 0 (–6)</td>
</tr>
<tr>
<td>2</td>
<td>7433.620 723 103</td>
<td>7307.187 976 874 9</td>
<td>4.764 976 826 874 1 (–1)</td>
<td>0.059 209 609 573 9 (–6)</td>
</tr>
<tr>
<td>3</td>
<td>11535.401 350 97</td>
<td>11408.968 974 584 7</td>
<td>4.674 976 826 874 1 (–1)</td>
<td>0.059 447 650 103 5 (–6)</td>
</tr>
<tr>
<td>4</td>
<td>15532.470 836 82</td>
<td>15406.029 472 274 2 (–1)</td>
<td>4.587 502 198 081 9 (–1)</td>
<td>0.059 407 029 436 6 (–6)</td>
</tr>
<tr>
<td>5</td>
<td>19425.709 018 35</td>
<td>19299.278 982 218 6</td>
<td>4.412 900 173 973 4 (–1)</td>
<td>0.057 323 210 585 9 (–6)</td>
</tr>
<tr>
<td>6</td>
<td>23216.476 600 08</td>
<td>23091.063 558 780 8</td>
<td>4.326 172 399 732 4 (–1)</td>
<td>0.034 491 546 849 3 (–6)</td>
</tr>
<tr>
<td>7</td>
<td>26907.060 100 22</td>
<td>26782.649 515 430 4</td>
<td>4.240 477 073 656 4 (–1)</td>
<td>0.032 988 531 997 2 (–6)</td>
</tr>
<tr>
<td>8</td>
<td>30501.385 182 13</td>
<td>30376.973 567 810 1</td>
<td>4.156 831 536 986 1 (–1)</td>
<td>0.029 842 327 261 3 (–6)</td>
</tr>
<tr>
<td>9</td>
<td>34006.037 113 55</td>
<td>33881.624 989 884 3</td>
<td>4.076 912 018 245 4 (–1)</td>
<td>0.026 905 976 567 7 (–6)</td>
</tr>
<tr>
<td>10</td>
<td>37431.457 988 91</td>
<td>37307.043 528 218 6</td>
<td>4.003 154 901 621 3 (–1)</td>
<td>0.023 548 177 053 2 (–6)</td>
</tr>
<tr>
<td>11</td>
<td>40793.018 984 29</td>
<td>40669.605 466 405 8</td>
<td>3.938 537 805 230 2 (–1)</td>
<td>0.020 003 422 989 8 (–6)</td>
</tr>
<tr>
<td>12</td>
<td>44110.826 755 61</td>
<td>44026.412 546 944 4</td>
<td>3.885 865 209 983 3 (–1)</td>
<td>0.017 271 819 782 1 (–6)</td>
</tr>
<tr>
<td>13</td>
<td>47408.264 215 28</td>
<td>47323.850 549 607 4</td>
<td>3.846 780 549 607 4 (–1)</td>
<td>0.014 561 751 665 1 (–6)</td>
</tr>
<tr>
<td>14</td>
<td>50708.949 651 76</td>
<td>50624.536 542 542 2</td>
<td>3.817 172 371 597 4 (–1)</td>
<td>0.012 046 536 565 6 (–6)</td>
</tr>
<tr>
<td>15</td>
<td>54033.828 453 83</td>
<td>53949.422 380 542 2</td>
<td>3.087 723 120 177 1 (–1)</td>
<td>0.009 055 454 786 6 (–6)</td>
</tr>
</tbody>
</table>

\[ \phi_i(1) = 1 \]  

(33d)

and the boundary condition [22]:

\[ \phi_v^{(0)}(x) \rightarrow 0 \quad \text{as} \quad x \rightarrow \infty \quad \text{and} \quad x \rightarrow r_e \]  

(34)

By repeating the same way of calculation to Eq.(13) for \( n \geq 1 \) one obtains:

\[ \phi_v^{(i)}(x) = \phi_v^{(i)}(0) \alpha_v(x) + \phi_v^{(i)}(0) \beta_v(x) + \gamma_v^{(i)}(x) \]  

(35)

where \( \alpha_v(x) \) and \( \beta_v(x) \) are those of Eq.(32) and \( \gamma_v^{(i)}(x) \) is a particular solution of the inhomogeneous differential equation (Eq.(13)) which is given by:

\[ \gamma_v^{(i)}(x) = \sum_{p=0}^{\infty} F_p(x) \]  

(36a)
By using the Boundary conditions (28) and (34) in (5a):

$$\phi_V^{(i)}(x) \rightarrow 0 \text{ as } x \rightarrow \infty \text{ and } x \rightarrow -r_e$$  \hspace{1cm} (37)

and by replacing the conditions (29) and (33d) in (5a) one finds:

$$\phi_V^{(i)}(0) = 0 \text{ for } i \neq 0$$  \hspace{1cm} (38)

from this condition a function $\phi_V^{(i)}(x)$ will be given by:

\begin{align*}
F_p(x) &= \int_0^x (x-t)S_1(t)F_p -1(t)dt \\
F_0(x) &= \int_0^x (x-t)S_1(t)\phi_V^{(0)}(t)dt
\end{align*}
\hspace{1cm} (36b)
\hspace{1cm} (36c)
Table 3. Values of the function $\phi^{(i)}_V (0 \leq i \leq 5)$ (Eqs. (32), (39)) and the wave function $\Psi_{vm}$ calculated from $\sum \phi^{(i)}_V m^i$ (Eq. (5a)) compared to $\Psi_{vm}$ calculated from a direct numerical method [24] for $m = -3$ and $v = 0, 5, 10$ at $x = 0.03 \text{ Å}, 0.06 \text{ Å}, 0.09 \text{ Å}.$

\[\begin{array}{c|ccc}
X(\text{Å}) & \text{ } & v = 0 & v = 5 & v = 10 \\
\hline
\text{(0)} & m = -5 & m = 5 & m = 10 \\
\hline
\phi^{(0)}_V & 0.853 779 042 & -0.628 689 912 & -0.746 271 835 \\
\phi^{(1)}_V & -0.403 364 851 (–4)* & -0.237 123 424 (–3) & -0.167 721 066 (–3) \\
\phi^{(2)}_V & 0.100 850 055 (–4) & 0.592 703 387 (–4) & 0.419 651 635 (–4) \\
\phi^{(3)}_V & -0.467 024 033 (–9) & 0.525 321 283 (–8) & -0.174 617 832 (–7) \\
\phi^{(4)}_V & 0.583 868 998 (–10) & 0.653 260 291 (–9) & 0.219 100 921 (–8) \\
\phi^{(5)}_V & -0.266 885 116 (–14) & 0.101 705 210 (–11) & 0.248 965 974 (–11) \\
\hline
\psi_{vm} & \frac{5}{5} \sum \phi^{(i)}_V m^i & 0.854 232 945 & -0.626 032 598 & -0.744 380 541 \\
\psi_{vm}** & 601 & 38 \\
\hline
\phi^{(0)}_V & 0.503 481 580 & -0.509 123 121 & 0.344 191 238 \\
\phi^{(1)}_V & -0.474 923 607 (–4) & 0.204 739 736 (–3) & 0.333 499 906 (–3) \\
\phi^{(2)}_V & 0.118 753 084 (–4) & -0.511 753 561 (–4) & -0.834 411 834 (–4) \\
\phi^{(3)}_V & -0.110 919 296 (–8) & -0.478 427 792 (–8) & 0.331 292 250 (–7) \\
\phi^{(4)}_V & 0.138 691 949 (–9) & 0.595 140 409 (–9) & -0.415 725 968 (–8) \\
\phi^{(5)}_V & -0.128 497 528 (–13) & 0.867 989 493 (–12) & 0.483 729 440 (–11) \\
\hline
\psi_{vm} & \frac{5}{5} \sum \phi^{(i)}_V m^i & 0.504 016 150 & -0.511 425 236 & 0.304 430 655 \\
\psi_{vm}** & 0 & 4 & 48 \\
\end{array}\]

\[\phi^{(i)}_V(x) = \phi^{(i)}_V(0) \beta_\cdot V(x) + \gamma^{(i)}_V(x) \quad (39)\]

where $\phi^{(i)}_V(0)$ is obtained from the boundary condition:
\[ \phi_v^{(i)}(0) = \lim_{x \to \infty} \frac{\gamma_v^{(i)}(x)}{\beta_v(x)} \quad \text{as} \quad x \to \infty \quad \text{and} \quad x \to -r_e \]  

(40)

### Table 3. (Continued)

<table>
<thead>
<tr>
<th>( v )</th>
<th>( \phi_v^{(0)} )</th>
<th>( \phi_v^{(1)} )</th>
<th>( \phi_v^{(2)} )</th>
<th>( \phi_v^{(3)} )</th>
<th>( \phi_v^{(4)} )</th>
<th>( \phi_v^{(5)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.210 338 145</td>
<td>0.107 123 434</td>
<td>0.237 413 614</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-0.297 156 762 \times 10^{-4})</td>
<td>(-0.116 825 775 \times 10^{-3})</td>
<td>(-0.460 495 292 \times 10^{-3})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.743 102 987 \times 10^{-5}</td>
<td>(-0.291 972 731 \times 10^{-4})</td>
<td>(-0.115 212 696 \times 10^{-3})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-0.104 300 028 \times 10^{-8})</td>
<td>(-0.458 203 437 \times 10^{-8})</td>
<td>(-0.444 719 366 \times 10^{-7})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.130 435 703 \times 10^{-9}</td>
<td>0.570 723 262 \times 10^{-9}</td>
<td>0.558 104 009 \times 10^{-8}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-0.182 029 512 \times 10^{-13})</td>
<td>0.609 060 117 \times 10^{-12}</td>
<td>(-0.662 164 445 \times 10^{-11})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\Psi_{vm} = \sum_{i=0}^{5} \phi_v^{(i)} m^i 
\]

\[
\Psi_{vm}^{**} = 1 \quad 1 \quad 85
\]

* Number between parentheses is a multiplicative power of 10
** Ref [24]
*** Omitted figures are identical to those in the leading entry

### 3 NUMERICAL APPLICATION

The present formulation is applied to the ground state of the molecule CO by using a Dunham potential [23] in the case of Raman transitions where \( J' - J = j = \pm 2 \) with \( a_0 = \frac{3}{4}, a_1 = -1 \) and \( a_2 = \frac{1}{4} \) (Eq. (6d)). In order to have the successive values of \( E_v^{(i)} \) and \( \phi_v^{(i)} \), the \( \phi_v^{(0)} \) are computed from Eqs (32), (33) and (34) and then by using alternatively Eqs (16) and (39). The values of \( E_v^{(i)} \) for \( i = 0, 1, 2 \ldots 6 \) and \( 0 \leq v < 29 \) are presented in Table 2 (first entry); the comparison of these values to those calculated from Eqs. (8) (second entry), by using the data of Table 1 (calculated by using a highly accurate method [17]), shows the excellent agreement up to 10 significant figures and more. The values of \( \phi_v^{(i)} \) (0 \( \leq i \leq 5 \)) calculated from Eqs. (32) and (39) for \( m = -5, x = 0.03, 0.06 \) and 0.09 for the different vibrational levels \( v = 0,5,10 \) are showed in Table 3.

The comparison of the wave function calculated from \( \sum \phi_v^{(i)} m^i \) (Eq. (5a)) to those calculated by direct numerical method [24] shows an excellent agreement between these values up to seven
significant figures, or more, for the considered vibrational levels and for the different values of x.

<table>
<thead>
<tr>
<th>m</th>
<th>v = 0</th>
<th>v = 5</th>
<th>v = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.503 481 503</td>
<td>-0.591 231 205</td>
<td>0.344 191 238</td>
</tr>
<tr>
<td>1</td>
<td>0.503 624 057</td>
<td>-0.509 737 339</td>
<td>0.343 190 738</td>
</tr>
<tr>
<td>2</td>
<td>0.503 730 935</td>
<td>-0.510 197 917</td>
<td>0.342 439 767</td>
</tr>
<tr>
<td>3</td>
<td>0.503 730 965</td>
<td>-0.510 197 788</td>
<td>0.342 438 873</td>
</tr>
<tr>
<td>4</td>
<td>0.503 730 976</td>
<td>-0.510 197 740</td>
<td>0.342 438 536</td>
</tr>
<tr>
<td>5</td>
<td>0.503 730 976</td>
<td>-0.510 197 741</td>
<td>0.342 438 355</td>
</tr>
</tbody>
</table>

In Table 3 the wave function $\Psi_{vm}(x)$ is represented by successive approximations as:

\[
S_0 = \phi_v^{(0)}
\]

\[
S_1 = S_0 + \phi_v^{(1)} m
\]

\[
S_2 = S_1 + \phi_v^{(2)} m^2
\]
for \( m = -3, \ x = 0.03 \, \text{Å}, 0.06 \, \text{Å}, 0.09 \, \text{Å} \) and for the vibrational levels \( \nu = 0, 5, 10 \). The comparison of \( \Psi_{\nu m} \) calculated by direct method [24] shows an excellent agreement between these values up to seven significant figures, or more, for all the considered vibrational levels and for the different values of \( x \). The comparison of \( \Psi_{\nu} \) to \( \Psi_{\nu m} \) calculated by a numerical method [24] shows that (i) a good agreement can be obtained by third order of correction; if highly accurate wave functions are needed the fourth and the fifth order of correction are required; (ii) the agreement decreases slightly with the increasing value of \(|m|\), this is may explained by the perturbative aspect of the present formulation.

## 4 CONCLUSIONS

For any transition \( \mathbf{vJ} \leftrightarrow \mathbf{v'J'} \) (infrared, Raman, …), the corresponding eigenfunctions and eigenvalues are expressed for the two considered states in terms of the same transition number \( m \) as:

\[
\begin{align*}
E_{\nu m} &= \sum_{i=0} E_{\nu}^{(i)} m^i \\
\Psi_{\nu m} &= \sum_{i=0} \phi_{\nu}^{(i)} m^i
\end{align*}
\]

where the coefficients \( E_{\nu}^{(i)} \) and \( \phi_{\nu}^{(i)} \) are given by analytical expressions (Eqs.(16), (32) and (39)). This approach is governed by three coefficients \( a_0, a_1, a_2 \) (Eqs. (3d)). The type of a transition is defined by the value of \( j \) in \( a_0 \) and \( a_2 \) (\( j = \pm1 \) in infrared and \( j = \pm2 \) in Raman transitions) and the rovibrational state is defined by the sign of \( a_1 \) (\( a_1 = -1 \) for the lower state and \( a_1 = +1 \) for the upper state). The numerical application to the ground state of the molecule CO in Raman transitions shows the excellent accuracy of the \( m \)–representation of the eigenvalue and the eigenfunction. By using this formulation, the calculation of the matrix elements for a transition is greatly simplified.

## 5 REFERENCES


