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

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

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Abstract

The line intensities of the transitions $v\,J \leftrightarrow v'J'$ where $|J'-J| \geq 1$ are proportional to the matrix elements $R_{v\,J}^{v'J'} = \langle \Psi_{v\,J} | f(r) | \Psi_{v'\,J'} \rangle$. 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 λ and λ' – representations of Ψ_{vJ} and $\Psi_{v'J'}$ to the m–representation of $R_{v\,J}^{v'J'}$) the eigenvalue and the eigenfunction of the two states $(v\,J)$ and $(v'J')$ are expanded in terms of one variable m as $E_{vm} = \sum_{i=0} E_v^{(i)} m^i$, $\Psi_{vm} = \sum_{i=0} \phi_v^{(i)} m^i$, $E_{v'm} = \sum_{i=0} E_{v'}^{(i)} m^i$ and $\Psi_{v'm} = \sum_{i=0} \phi_{v'}^{(i)} m^i$ where the coefficients $E_v^{(i)}, \phi_v^{(i)}$, $E_{v'}^{(i)}$ and $\phi_{v'}^{(i)}$ 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_{vm} and Ψ_{vm} 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 (vJ) respectively by:

[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

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$$\Psi_{vJ} = \sum_{i=0} \Psi_v^{(i)}\lambda^i \tag{1a}$$

$$E_{vJ} = \sum_{i=0} e_v^{(i)}\lambda^i \tag{1b}$$

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

$$\Psi_{v'J'} = \sum_{i=0} \Psi_{v'}^{(i)}\lambda'^i \tag{2a}$$

$$E_{v'J'} = \sum_{i=0} e_{v'}^{(i)}\lambda'^i \tag{2b}$$

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

In the literature, the line intensities $S_v^{v'}(m)$ 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]

$$S_v^{v'} = \frac{8\pi^3\omega(m)}{3hc}\left|R_v^0(m)\right|^2 \frac{N_0|m|}{Q}\exp\left[-E(m)/k_BT\right] \tag{3}$$

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, $\left|R_v^{v'}(m)\right|^2$ is the square of the transition dipole moment matrix element which is the product of a rotationless factor $R_v^{v'}(0)$ and a rotational factor (or Herman–Wallis factor) [4–7]

$$\left|R_v^{v'}(m)\right|^2 = \left|R_v^{v'}(0)\right|^2(1 + C_v m + D_v m^2) \tag{4}$$

Similarly, the line intensities in the Raman transitions are proportional to the matrix elements $R_{vJ}^{v'J'}$ 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 λ and λ'–representations of E_{vJ}, Ψ_{vJ} , $E_{v'J'}$ and $\Psi_{v'J'}$ to m–representation for the rotational factor $R_v^{v'}(m)$ (Eq.(4)). This change in representation from λ and λ' 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}, $E_{v'J'}$, Ψ_{vJ} and $\Psi_{v'J'}$ in terms of one variable m instead of two parameters λ and λ' as:

$$\Psi_{vm} = \sum_{i=0} \phi_v^{(i)} m^i \tag{5a}$$

$$E_{vm} = \sum_{i=0} E_v^{(i)} m^i \tag{5b}$$

$$\Psi_{v'm} = \sum_{i=0} \phi_{v'}^{(i)} m^i \tag{5c}$$

$$E_{v'm} = \sum_{i=0} E_{v'}^{i} m^i \tag{5d}$$

The aim of this work is to give to the functions $E_v^{(i)}$, $\phi_v^{(i)}$, $E_{v'}^{(i)}$ and $\phi_{v'}^{(i)}$ 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.

2 THEORETICAL

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 = ±1 in the infrared transitions and j = 0, ± 2 in the Raman transitions. By expressing λ and λ' in terms of j and m (for j = ±1, ±2,…) one obtains [5]:

$$\lambda = \frac{j^2 - 1}{4} - m + \frac{m^2}{j^2} \tag{6a}$$

$$\lambda' = \frac{j^2 - 1}{4} + m + \frac{m^2}{j^2} \tag{6b}$$

or more generally λ or λ' can be written as:

$$\Lambda = \sum_{i=0}^{2} a_i m^i \tag{6c}$$

where:

$$a_0 = \frac{j^2 - 1}{4} \quad a_1 = \pm 1 \quad \text{and} \quad a_2 = \frac{1}{j^2} \tag{6d}$$

with $a_1 = -1$ and $a_1 = +1$ are for the lower and upper state respectively.

By replacing Λ (Eq.(6c)) in (1b) we obtain the "m–representation" of the eigenvalue as:

$$E_{vm} = \sum_{i=0} E_v^{(i)} m^i \tag{7}$$

where

$$E_v^{(0)} = \sum_{i=0} a_0^i e_v^{(i)} \tag{8a}$$

$$E_v^{(1)} = a_1 \sum_{i=1} i a_0^{i-1} e_v^{(i)} \tag{8b}$$

$$E_v^{(2)} = \sum_{i=1} i[a_0 a_2 + \frac{(i-1)}{2} a_1^2] a_0^{i-2} e_v^{(i)} \tag{8c}$$

$$E_v^{(3)} = \sum_{i=2} i(i-1)[a_0 a_1 a_2 + \frac{(i-1)}{6} a_1^3] a_0^{i-3} e_v^{(i)} \tag{8d}$$

$$E_v^{(4)} = \sum_{i=2} \frac{i(i-1)}{2} [a_0^2 a_2^2 + (i-2) a_0 a_1^2 a_2 + \frac{(i-2)(i-3)}{12} a_1^4] a_0^{i-4} e_v^{(i)} \tag{8e}$$

$$E_v^{(5)} = \sum_{i=3} \frac{i(i-1)(i-2)}{2} [a_0^2 a_1 a_2^2 + \frac{(i-3)}{3} a_0 a_1^3 a_2 + \frac{(i-3)(i-4)}{60} a_1^5] a_0^{i-5} e_v^{(i)} \tag{8f}$$

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

$$\Psi_{vm} = \sum_{i=0} \phi_v^{(i)} m^i \tag{9}$$

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 $E_v^{(i)}$

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

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

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

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

$$\frac{d}{dr^2}\sum\phi_v^{(i)} m^i + \{k[\sum_i E_v^{(i)} m^i - U_o(r)] - \frac{\sum_{i=0}^{2} a_i m^i}{r^2}\}\sum\phi_v^{(i)} m^i = 0 \tag{10c}$$

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

$$\phi_v^{(0)''} + k[E_v^{(0)} - U(r)]\phi_v^{(0)} = 0 \tag{11}$$

$$\phi_v^{(n)''} + k[E_v^{(0)} - U(r)]\phi_v^{(n)} = -\sum_{i=1}^{n} B_i\phi_v^{(n-i)} \tag{12}$$

where:

$$\begin{aligned} U(r) &= U_0(r) + \frac{a_0}{kr^2} \\ B_1 &= kE_v^{(1)} - \frac{a_1}{r^2} \\ B_2 &= kE_v^{(2)} - \frac{a_2}{r^2} \\ B_i &= kE_v^{(i)} \text{ for } i \geq 3 \end{aligned} \tag{1}$$

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

$$\phi_v^{(n)''}(r) + k(E_v^{(0)} - U)\phi_v^{(n)} = S_n(r) \tag{13}$$

By using the Rayleigh–Schrödinger perturbation approach [19] we can find:

$$< S_n \mid \phi_0 >= 0 \tag{14}$$

If we replace the successive values of S_n (Eq.(12)) in (14) and by defining:

$$I_{in} =< \phi_v^{(i)} \mid \phi_v^{(n)} > \tag{15a}$$

$$R_{in}^{(P)} =< \phi_v^{(i)} \mid B_P \mid \phi_v^{(n)} > \tag{15b}$$

$$T_q =< \phi_v^{(0)} \mid \frac{a_q}{r^2} \mid \phi_v^{(0)} \tag{15c}$$

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

$$E_v^{(1)} = T_1 / kI_{00} \tag{16a}$$

$$E_v^{(2)} = (T_2 - R_{01}^{(1)})/kI_{00} \tag{16b}$$

$$E_v^{(3)} = -(R_{02}^{(1)} + R_{01}^{(2)})/kI_{00} \tag{16c}$$

and for $n \geq 4$:

$$E_v^{(n)} = -(R_{0(n-1)}^{(1)} + R_{0(n-2)}^{(2)} + \sum_{i=4}^{n} B_{(i-1)} I_{0(n-i+1)})/kI_{00} \tag{16n}$$

2.4 Analytic Expressions for the Rovibrational Wave Function Ψ_{vm}

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

$$\frac{d^2\Psi_{vm}}{dr^2} = f_{vm}(x)\Psi_{vm}(x) \tag{17}$$

with $x = r - r_e$ and:

$$f_{vm} = -k[E_{vm} - U_0(x)] - \frac{\sum_{i=0}^{2} a_i m^i}{(x + r_e)^2} \tag{18}$$

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

$$f_{vm}(x) = \sum_{i=0} C_i(x) m^i \tag{19}$$

where:

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

$$C_1(x) = -kE_v^{(1)} + a_1/(x + r_e)^2 \tag{20b}$$

$$C_2(x) = -kE_v^{(2)} + a_2/(x + r_e)^2 \tag{20c}$$

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

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

$$\Psi_{vm}(x) = \Psi_{vm}(0) + x\Psi'_{vm}(0) + \int_0^x (x-t) f_{vm}(x) \Psi_{vm}(t) dt \tag{21}$$

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:

$$\Psi_{vm}(x) = \sum_{i=0}^{\infty} D_i(x) \tag{22}$$

where:

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

with:

$$D_0(x) = \Psi_{vm}(0) + x\Psi'_{vm}(0) \tag{23b}$$

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

$$\Psi_{vm}(x) = \Psi_{vm}(0)\alpha_{vm}(x) + \Psi'_{vm}(0)\beta_{vm}(x) \tag{24}$$

where:

$$\alpha_{vm}(x) = \sum_{i=0}^{\infty} H_i(x) \tag{25a}$$

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

$$H_0(x) = 1 \tag{25c}$$

with the initial values $\alpha_{vm}(0)=1$ and $\alpha'_{vm}(0)=0$ and:

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

$$G_i(x)=\int_o^x (x-t)f_{vm}(t)G_{i-1}(t)dt \tag{26b}$$

$$G_0(x)=x \tag{26c}$$

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

$$\Psi_{vm}(x) \longrightarrow 0 \text{ as } x\to\infty \text{ and } x\to -r_e \tag{27}$$

By using this condition in Eq. (24):

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

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

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

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

2.5 Analytic Expressions for the Functions $\phi_v^{(i)}$

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

$$\phi_v^{(0)''}+f_v(r)\phi_v^{(0)''}=0 \tag{30}$$

where:

$$f_v(r)=k(E_v^{(0)}-U(r)) \tag{31}$$

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.

v	E_V	B_V	$-D_V$
0	1081.776 425 149	1.922 528 872 188 4	6.119 538 190 045 7 (–6)
1	3225.047 998 885	1.905 025 790 139 1	6.118 847 356 162 4 (–6)
3	7432.218 208 258	1.870 024 382 123 4	6.118 442 023 764 5 (–6)
5	11 534.025 078 516	1.835 034 533 221 6	6.118 916 977 780 7 (–6)
7	15 531.120 784 273	1.800 074 652 049 6	6.118 835 020 782 3 (–6)
9	19 424.385 126 713	1.765 193 700 211 8	6.114 667 766 143 7 (–6)
11	23 215.178 726 636	1.730 502 504 372 1	6.099 007 253 955 3 (–6)
13	26 908.787 935 516	1.696 224 148 430 9	6.058 008 738 369 0 (–6)
15	30 500.138 111 400	1.662 765 453 060 0	5.968 651 638 803 7 (–6)
17	34 004.814 019 292	1.630 796 697 133 4	5.798 185 471 813 9 (–6)
19	37 430.275 022 813	1.601 292 269 809 6	5.510 807 274 654 1 (–6)
21	40 791.837 404 834	1.575 443 095 583 9	5.086 158 954 178 (–6)
23	44 109.660 979 866	1.554 371 069 123 7	4.542 834 647 370 3 (–6)
25	47 407.110 167 068	1.538 733 907 593 9	3.943 315 001 388 3 (–6)
27	50 707.803 288 057	1.528 487 461 578 9	3.366 069 995 680 3 (–6)
29	54 032.686 216 679	1.522 958 023 124 0	2.868 259 358 857 2 (–6)

v	H_V	L_V	M_V	N_V
0	5.800 826 482 892 8 (–12)	–3.644 482 113 419 8 (–17)	–4.870 538 869 963 6 (–23)	–7.944 618 716 339 6 (–28)
1	5.655 626 063 842 2 (–12)	–3.716 016 607 411 7 (–17)	–5.286 977 841 264 2 (–23)	–8.202 443 291 416 1 (–28)
3	5.365 876 871 694 4 (–12)	–3.840 930 389 967 2 (–17)	–5.089 190 415 662 8 (–23)	–5.288 444 773 890 7 (–28)
5	5.100 690 261 986 4 (–12)	–3.839 743 171 656 5 (–17)	–4.866 633 096 387 6 (–24)	9.150 377 344 462 3 (–28)
7	4.932 289 995 031 5 (–12)	–3.449 062 155 861 5 (–17)	1.566 345 996 261 6 (–22)	5.064 021 249 616 7 (–27)
9	5.022 385 897 233 7 (–12)	–1.833 458 850 797 7 (–17)	4.990 141 089 048 2 (–19)	2.938 202 183 981 9 (–20)
11	5.684 743 329 402 5 (–12)	1.039 384 933 693 1 (–17)	1.427 381 293 340 6 (–21)	3.195 998 779 024 7 (–26)
13	7.452 630 055 244 9 (–12)	7.432 746 772 842 4 (–17)	2.925 094 083 798 7 (–21)	5.521 533 857 341 4 (–26)
15	1.108 041 639 771 3 (–11)	1.825 444 440 164 4 (–16)	4.867 535 563 102 5 (–21)	6.356 304 977 879 1 (–26)
17	1.729 779 154 024 6 (–11)	3.268 583 332 567 7 (–16)	5.958 112 543 524 7 (–21)	6.090 934 472 050 2 (–27)
19	2.609 769 172 949 7 (–11)	4.490 900 358 934 6 (–16)	3.588 471 931 149 9 (–21)	–1.522 000 620 963 7 (–25)
21	3.587 918 796 732 2 (–11)	4.427 018 935 523 4 (–16)	–3.576 155 155 178 6 (–21)	–2.990 705 692 095 9 (–25)
23	4.306 012 294 688 8 (–11)	2.435 905 824 561 2 (–16)	–1.145 728 429 560 5 (–20)	–2.175 228 870 606 3 (–25)
25	4.505 851 450 193 0 (–11)	–6.701 838 700 304 7 (–17)	–1.340 294 820 845 1 (–20)	5.393 700 232 923 6 (–26)
27	4.162 041 023 015 1 (–11)	–3.257 048 076 239 1 (–16)	–8.727 350 300 273 3 (–21)	2.305 178 768 225 7 (–25)
29	3.493 022 271 198 7 (–11)	–4.440 110 903 356 3 (–16)	–2.388 998 298 361 8 (–21)	2.134 111 939 782 5 (–25)

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

$$\phi_v^{(0)}(x) = \phi_v^{(0)}(0)\alpha_v(x) + \phi_v^{(0)'}\beta_v(x) \tag{32}$$

where the canonical functions $\alpha_v(x)$ and $\beta_v(x)$ 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

$$\alpha_v(0) = 1 \quad \alpha_v^{'}(0) = 0 \tag{33a}$$

$$\beta_v(0) = 0 \quad \beta_v^{'}(0) = 1 \tag{33b}$$

$$\phi_v^{'(0)}(0) = -\lim \frac{\alpha_v(x)}{\beta_v(x)} \text{ as } x \to \infty \text{ and } x \to -r_e \tag{33c}$$

Table2. 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

v	$E_v^{(0)}$	$E_v^{(1)}$	$E_v^{(2)}$	$E_v^{(3)}$
0	1083.218 318 361 1	−1.922 519 692 890 9 9**	4.806 238 036 976 0 (−1) 0	3.059 756 768 437 4 (−6)* 0
1	3226.476 764 786 6	−1.905 016 611 877 6 6	4.762 480 341 347 7 (−1) 7	3.059 411 660 050 0 (−6) 1 6
3	7433.620 723 103 3	−1.870 015 204 496 4 4	4.674 976 826 874 1 (−1) 1	3.059 209 609 573 9 (−6) 80 2
5	11535.401 350 97 7	−1.835 025 354 854 7 7	4.587 502 198 081 9 (−1) 9	3.059 447 650 103 5 (−6) 2 1
7	15532.470 836 82 2	−1.800 065 473 805 4 4	4.500 102 496 274 2 (−1) 2	3.059 407 029 436 6 (−6) 5
9	19425.709 018 54 4	−1.765 184 528 218 6 6	4.412 900 173 982 0 (−1) 0	3.057 323 210 585 9 (−6) 387 2
11	23216.476 600 08 8	−1.730 493 355 870 8 8	4.326 172 399 732 4 (−1) 4	3.049 491 546 849 3 (−6) 52 0
13	26907.060 100 22 2	−1.696 215 061 430 4 4	4.240 477 073 656 4 (−1) 4	3.028 988 531 997 2 (−6) 87 7
15	30501.385 182 13 3	−1.662 756 500 101 2 2	4.156 831 563 986 0 (−1) 0	2.984 302 272 661 3 (−6) 75 1
17	34006.037 113 55 5	−1.630 787 999 884 3 3	4.076 912 018 245 4 (−1) 4	2.899 055 976 567 7 (−6) 2 8
19	37431.457 988 91 1	−1.601 284 003 642 7 7	4.003 154 901 621 3 (−1) 3	2.755 348 177 053 2 (−6) 9 7
21	40793.018 984 29 9	−1.575 435 466 405 8 8	3.938 537 805 230 4 (−1) 4	2.543 003 422 989 8 (−6) 3 037 5
23	44110.826 755 61 1	−1.554 364 254 944 4 3	3.885 865 209 983 3 (−1) 3	2.271 325 819 782 1 (−6) 843 2
25	47408.264 215 28 8	−1.538 727 992 697 4 4	3.846 780 549 607 4 (−1) 4	1.971 561 751 665 1 (−6) 741 0
27	50708.949 651 76 5	−1.528 482 412 544 2 2	3.821 172 371 597 4 (−1) 4	1.682 946 536 556 6 (−6) 604 6
29	54033.828 453 83 3	−1.522 980 720 793 9 9	3.087 723 120 177 1 (−1) 1	1.434 055 454 786 6 (−6) 8 3

$$\phi_0(1) = 1 \tag{33d}$$

and the boundary condition [22]:

$$\phi_v^{(0)}(x) \longrightarrow 0 \text{ as } x \to \infty \text{ and } x \to -r_e \tag{34}$$

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

$$\phi_v^{(i)}(x) = \phi_v^{(i)}(0)\alpha_v(x) + \phi_v^{(i)'}(0)\beta_v(x) + \gamma_v^{(i)}(x) \tag{35}$$

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:

$$\gamma_v^{(i)}(x) = \sum_{p=0}^{\infty} F_p(x) \tag{36a}$$

Table2. (Continued)

v	$E_v^{(4)}$	$E_v^{(5)}$	$E_v^{(6)}$
0	–3.824 659 706 429 0 (–7) 8 6	–1.087 598 020 226 6 (–12) 368 4	9.062 253 850 262 3 (–14) 1 566 4
1	–3.824 229 228 467 9 (–7) 9 4	–1.060 371 823 904 0 (–12) 4 068 8	8.835 348 015 738 2 (–14) 6 753 6
3	–3.823 978 467 341 3 (–7) 9 2	–1.006 041 898 609 9 (–12) 350 5	8.382 562 205 548 3 (–14) 438 9
5	–3.824 277 684 419 2 (–7) 7 5	–9.563 194 281 071 6 (–13) 2 657 6	7.968 028 641 368 6 (–14) 2 607 9
7	–3.824 227 960 974 8 (–7) 6	–9.247 504 833 815 3 (–13) 719 9	7.705 248 087 127 4 (–14) 6 938 1
9	–3.811 828 903 616 9 (–7) 468 9	–9.416 713 398 707 6 (–13) 09 900 223 4	7.864 849 466 319 4 (–14) 598 934 896 3
11	–3.811 828 903 616 9 (–7) 9 9	–1.065 905 622 938 6 (–12) 739 4	8.882 850 334 435 6 (–14) 2 875 4
13	–3.786 189 083 921 5 (–7) 09 8	–1.397 484 289 007 0 (–12) 444 0	1.164 787 095 410 6 (–13) 769 2
15	–3.730 308 582 975 6 (–7) 92 8	–2.077 863 328 520 7 (–12) 3 338 0	1.732 085 305 094 2 (–13) 0 193 0
17	–3.623 711 850 114 9 (–7) 08 8	–3.243 846 664 527 1 (–12) 639 7	2.704 159 025 256 6 (–13) 364 3
19	–3.444 022 096 144 1 (–7) 51 9	–4.894 069 548 288 8 (–12) 7 282 2	4.079 701 217 280 4 (–13) 6 426 1
21	–3.178 530 583 585 0 (–7) 644 7	–6.711 164 444 817 4 (–12) 3 257 5	5.593 928 170 343 1 (–13) 68 999 1
23	–2.838 888 141 956 9 (–7) 2 033 7	–8.074 153 596 316 5 (–12) 5 166 0	6.729 171 543 795 4 (–13) 2 542 7
25	–2.464 170 575 793 5 (–7) 888 2	–8.448 366 675 083 3 (–12) 298 1	7.040 109 789 316 0 (–13) 458 3
27	–2.103 423 052 496 5 (–7) 556 0	–7.803 317 953 736 3 (–12) 886 1	6.501 814 791 836 0 (–13) 916 9
29	–1.792 351 017 356 9 (–7) 9 0	–6.548 722 977 305 7 (–12) 6 969 0	5.455 974 061 424 4 (–13) 123 6

$$F_p(x) = \int_0^x (x-t)S_i(t)F_{p-1}(t)dt \tag{36b}$$

$$F_0(x) = \int_0^x (x-t)S_i(t)\phi_v^{(0)}(t)dt \tag{36c}$$

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

$$\phi_v^{(i)}(x) \longrightarrow 0 \text{ as } x \to \infty \text{ and } x \to -r_e \tag{37}$$

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

$$\phi_v^{(i)}(0) = 0 \text{ for } i \neq 0 \tag{38}$$

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

Table 3. Values of the function $\phi_{v}^{(i)}$ ($0 \le i \le 5$) (Eqs. (32), (39)) and the wave function Ψ_{vm} calculated from $\sum \phi_{v}^{(i)} m^{i}$ (Eq. (5a)) compared to Ψ_{vm} calculated from a direct numerical method [24] for m = –3 and v = 0, 5, 10 at x = 0.03 Å, 0.06 Å, 0.09 Å.

		m = –5		
X(A°)		v = 0	v = 5	v = 10
0.03	$\phi_{v}^{(0)}$	0.853 779 042	–0.628 689 912	–0.746 271 835
	$\phi_{v}^{(1)}$	–0.403 364 851 (–4)*	–0.237 123 424 (–3)	–0.167 721 066 (–3)
	$\phi_{v}^{(2)}$	0.100 850 055 (–4)	0.592 703 387 (–4)	0.419 651 635 (–4)
	$\phi_{v}^{(3)}$	–0.467 024 033 (–9)	0.525 321 283 (–8)	–0.174 617 832 (–7)
	$\phi_{v}^{(4)}$	0.583 868 998 (–10)	0.653 260 291 (–9)	0.219 100 921 (–8)
	$\phi_{v}^{(5)}$	–0.266 885 116 (–14)	0.101 705 210 (–11)	0.248 965 974 (–11)
	$\Psi_{vm} = \sum_{i=0}^{5} \phi_{v}^{(i)} m^{i}$	0.854 232 945	–0.626 032 598	–0.744 380 541
	Ψ_{vm}^{**}	5***	601	38
0.06	$\phi_{v}^{(0)}$	0.503 481 580	–0.509 123 121	0.344 191 238
	$\phi_{v}^{(1)}$	–0.474 923 607 (–4)	0.204 739 736 (–3)	0.333 499 906 (–3)
	$\phi_{v}^{(2)}$	0.118 753 084 (–4)	–0.511 753 561 (–4)	–0.834 411 834 (–4)
	$\phi_{v}^{(3)}$	–0.110 919 296 (–8)	–0.478 427 792 (–8)	0.331 292 250 (–7)
	$\phi_{v}^{(4)}$	0.138 691 949 (–9)	0.595 140 409 (–9)	–0.415 725 968 (–8)
	$\phi_{v}^{(5)}$	–0.128 497 528 (–13)	0.867 989 493 (–12)	0.483 729 440 (–11)
	$\Psi_{vm} = \sum_{i=0}^{5} \phi_{v}^{(i)} m^{i}$	0.504 016 150	–0.511 425 236	0.304 430 655
	Ψ_{vm}^{**}	0	4	48

$$\phi_{v}^{(i)}(x) = \phi_{v}^{(i)'}(0)\beta_{v}(x) + \gamma_{v}^{(i)}(x) \tag{39}$$

where $\phi_{v}^{'(i)}(0)$ is obtained from the boundary condition:

$$\phi_v'^{(i)}(0) = \lim \frac{\gamma_v^{(i)}(x)}{\beta_v(x)} \text{ as } x \to \infty \text{ and } x \to -r_e \tag{40}$$

Table3. (Continued)

0.09	$\phi_v^{(0)}$	0.210 338 145	0.107 123 434	0.237 413 614
	$\phi_v^{(1)}$	–0.297 1567 762 (–4)	0.116 825 775 (–3)	–0.460 495 292 (–3)
	$\phi_v^{(2)}$	0.743 102 987 (–5)	–0.291 972 731 (–4)	0.115 212 696 (–3)
	$\phi_v^{(3)}$	–0.104 300 028 (–8)	–0.458 203 437 (–8)	–0.444 719 366 (–7)
	$\phi_v^{(4)}$	0.130 435 703 (–9)	0.570 723 262 (–9)	0.558 104 009 (–8)
	$\phi_v^{(5)}$	–0.182 029 512 (–13)	0.609 060 117 (–12)	–0.662 164 445 (–11)
	$\Psi_{vm} = \sum_{i=0}^{5} \phi_v^{(i)} m^i$	0.210 672 711	0.106 993 121	0.242 605 476
	Ψ_{vm}^{**}	1	1	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…6 and $0 \le v < 29$ 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 10 significant figures and more. The values of $\phi_v^{(i)}$ ($0 \le i \le 5$) 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 4. Values of the successive approximations of the wave function $\Psi_{vm}(x) = S_p$, (Eqs. (32), (39)) compared to Ψ_{vm} calculated from a direct numerical method [24] from m = –3, –7, –11 and v = 0, 5, 10 at x = 0.06 Å

			x = 0.06 Å	
m		v = 0	v = 5	v = 10
–3	S_0	0.503 481 503	–0.591 231 205	0.344 191 238
	$S1$	0.503 624 057	–0.509 737 339	0.343 190 738
	$S2$	0.503 730 935	–0.510 197 917	0.342 439 767
	S_3	0.503 730 965	–0.510 197 788	0.342 438 873
	$S4$	0.503 730 976	–0.510 197 740	0.342 438 536
	S_5	0.503 730 976	–0.510 197 741	0.342 438 535
	$\Psi_{vm}=\sum_{i=0}^{5}\phi_v^{(i)}m^i$ Ψ_{vm}^{**}	0.503 730 976 6*	–0.510 197 741 1	0.342 438 535 5
–7	S_0	0.503 481 580	–0.509 123 120	0.344 191 238
	$S1$	0.503 814 026	–0.510 556 298	0.341 856 738
	$S2$	0.504 395 917	–0.513 063 891	0.337 768 121
	S_3	0.504 396 297	–0.513 062 250	0.337 756 757
	$S4$	0.504 396 630	–0.513 060 821	0.337 746 776
	S_5	0.504 396 631	–0.513 060 835	0.337 746 694
	$\Psi_{vm}=\sum_{i=0}^{5}\phi_v^{(i)}m^i$ Ψ_{vm}^{**}	0.504 396 631 1	–0.513 060 835 44	0.337 746 694 47
–11	S_0	0.503 481 580	–0.509 123 120	0.344 191 238
	$S1$	0.504 003 996	–0.511 375 257	0.340 522 739
	$S2$	0.505 440 908	–0.517 567 475	0.330 426 356
	S_3	0.505 442 385	–0.517 561 107	0.330 382 261
	$S4$	0.505 444 514	–0.517 552 394	0.330 321 394
	S_5	0.505 444 417	–0.517 552 534	0.330 320 615
	$\Psi_{vm}=\sum_{i=0}^{5}\phi_v^{(i)}m^i$ Ψ_{vm}^{**}	0.505 444 417 95	–0.517 522 534 661	0.330 320 615 19 882

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

$$S_0 = \phi_v^{(0)}$$

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

$$S_2 = S_1 + \phi_v^{(2)} m^2$$

$$S_3 = S_2 + \phi_v^{(3)} m^3$$

$$S_4 = S_3 + \phi_v^{(4)} m^4$$

$$S_5 = S_4 + \phi_v^{(5)} m^5$$

for m= –3, x = 0.03 Å, 0.06 Å, 0.09 Å and for the vibrational levels v = 0, 5, 10. The comparison of S_5 to Ψ_{vm} 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 S_i to Ψ_{vm} 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 $vJ \leftrightarrow v'J'$ (infrared, Raman, …), the corresponding eigenfunctions and eigenvalues are expressed for the two considered states in terms of the same transition number m as:

$$E_{vm} = \sum_{i=0} E_v^{(i)} m^i \quad E_{v'm} = \sum_{i=0} E_{v'}^{(i)} m^i$$

$$\Psi_{vm} = \sum_{i=0} \phi_v^{(i)} m^i \quad \Psi_{v'm} = \sum_{i=0} \phi_{v'}^{(i)} m^i$$

where the coefficients $E_v^{(i)}$ and $\phi_v^{(i)}$ are given by analytical expressions (Eqs.(16), (32) and (39)). This approach is governed by three coefficients a_0, a_1 and a_2 (Eqs. (3d)). The type of a transition is defined by the value of j in a_0 and a_2 ($j = \pm 1$ in infrared and $j = \pm 2$ 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.

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