

# Analytic matrix elements of the dipole moment and Herman–Wallis coefficients

F.M. Fernández<sup>1</sup> and J.F. Ogilvie

*Academia Sinica, Institute of Atomic and Molecular Sciences, P. O. Box 23-166,  
Taipei 10764, Taiwan*

Received 2 July 1992; revised 11 May 1993

Perturbation theory proves to be a powerful approach to obtain in analytic form both vibration-rotational energies and matrix elements of the dipole moment of diatomic molecules in terms of the expansion parameter  $\gamma = 2B_e/\omega_e$ ,  $B_e$  and  $\omega_e$  being, respectively, the equilibrium rotational and harmonic vibrational spectral parameters. A systematic and efficient algorithm has been developed to execute such calculations with sufficient accuracy for most physical applications when the potential-energy function is accurately represented in the Dunham form. The method also provides analytic expressions of the Herman–Wallis coefficients  $C'_v$  and  $D'_v$  for the vibration-rotational overtone bands  $v' \leftarrow v$  for diatomic molecules in  $^1\Sigma$  electronic states.

## 1. Introduction

The approach that Herman and Wallis [1] proposed to investigate the influence of the vibration–rotational interaction on the intensities of lines in vibration-rotational bands of diatomic molecules has become a standard way to determine the coefficients  $M_j$  of the expansion of the molecular dipole moment about the equilibrium separation in terms of the reduced variable  $x = (R - R_e)/R_e$ ; here  $R$  is the instantaneous internuclear separation and  $R_e$  is the equilibrium distance. The application of this method requires the calculation of matrix elements of  $x$  to non-negative powers between vibration-rotational states with an accuracy comparable to the corresponding experimental measurements. These matrix elements can be calculated either by numerical integration of the Schrödinger equation with a properly chosen potential-energy function [2–5] or analytically [1,6–30]. Although numerical methods may be necessary for very high vibrational states, they are no more accurate than analytic expressions in current practical applications for states of relatively small vibrational energy [8,22,31]. Among other advantages, analytic

<sup>1</sup> Permanent address: QUINOR, Facultad de Ciencias Exactas, Universidad Nacional de la Plata, Calle 47 y 115, Casilla de Correo 962, 1900 La Plata, Argentina.

expressions allow a more transparent interpretation of the experimental data and a simpler analysis of the relative magnitudes of the various contributions to the line intensities. Despite an evident increase in the complexity of analytic expressions for matrix elements and other quantum-mechanical quantities with increasing values of the vibrational quantum number  $v$ , the actual application of these expressions is computationally more rapid and more efficient than numerical solutions of differential equations that must be repeated for each particular value of the quantum numbers  $v$  and  $J$  (the latter for angular momentum), and even for each combination of  $vJ$  and  $v'J'$ ; therefore in our work we have concentrated primarily on analytic expressions. In order to generate sufficiently accurate analytic matrix elements one must base them on a correspondingly accurate analytic potential-energy function. Earlier use of the Morse oscillator showed that this function allowed no systematic improvement of the results and led to intractably complicated expressions [6]. Hence in most of the work to interpret quantitatively vibration-rotational spectra, use has been made of the Dunham potential-energy function (or functions of equivalent forms) that allows the systematic derivation of analytic matrix elements in terms of the small parameter  $\gamma = \lambda^2 = 2B_e/\omega_e$ ,  $B_e$  and  $\omega_e$  being, respectively, the equilibrium rotational and harmonic vibrational spectral parameters. Perturbation theory provides a natural means to obtain an expansion in the form of a power series in terms of a small parameter [1,7–17]. As this approach is (inaccurately) believed to be tedious and difficult to extend to large orders, other procedures have been proposed. According to one procedure one expresses the vibration-rotational wavefunction as  $\Psi_{vJ}(x) = g_{vJ}(x) \exp[-\frac{1}{2}\int y(x)dx]$  and expands both functions  $g_{vJ}$  and  $y$  in series of  $x$  to non-negative powers [18–27]. The hypervirial theorems that lead to recurrence relations among the desired matrix elements provide an alternative approach [28–30]; one solves iteratively these recurrence relations starting from the results for the harmonic oscillator. However, because these recurrence relations prove insufficient to obtain all the matrix elements one has to resort either to the method already mentioned or to the use of appropriate sum rules [21,26,29,30]. Of all these methods, the one based on explicit construction of the eigenfunctions has produced, in part by means of symbolic processors, the most extensive collection of matrix elements and Herman–Wallis factors [19–27].

For an approach to calculate general analytic vibration-rotational matrix elements to be acceptable, at least three conditions must be fulfilled: the procedure should be flexible enough to allow a systematic improvement of the accuracy of the results according to the increasing accuracy and extent of the experimental data; it should be readily tractable by means of symbolic processors to allow extensive calculations, and it should be entirely automatic in the sense that no interactive manipulation, likely to lead to human mistakes, should be required. Some methods to which we have alluded are appropriate for manual calculation and interactive use of symbolic processors but seem less easily adaptable to automatic computation according to a general and currently implementable algorithm. A weak feature

of previous applications of perturbation theory is the use of standard textbook formulae which are unsuitable for algebraic programming [7–15]. Even the application of contact transformations has proved to be of limited avail due to the extremely complicated expressions that arise [16,17]. An alternative approach based on perturbed ladder operators and expansion of the potential-energy function in terms of Hermite polynomials has been used to calculate expectation values but not off-diagonal matrix elements [32]. The powerful method consisting of the iterative construction of the eigenfunctions has in the past required either tedious manual calculations or interactive use of symbolic processors [18–27]. Despite such disadvantages, successive application of those techniques during the past forty years has enabled the calculation of all the Herman–Wallis coefficients  $C_v^{v'}$  and  $D_v^{v'}$  with  $0 \leq (v' - v) \leq 7$  required for the interpretation of the then available experimental data.

Calculating the required rotationless matrix elements and Herman–Wallis factors by means of direct numerical integration of the Schrödinger equation with an RKR potential energy, Carlisle et al. [5] used the numerical results to determine the coefficients of the assumed dipole-moment function from the newly measured intensities of some overtone bands of HBr up to  $v = 8$ . Such an RKR potential energy suffers from limited accuracy because only the zero-order BKW integrals are at present calculable. To perform the same calculation entirely in accordance with an analytic approach, one must first derive the expressions for the Herman–Wallis coefficients  $C_0^8$  and  $D_0^8$  because they are so far unreported. These expressions, and the succeeding ones for even higher overtone and “hot” bands, are most readily obtained by means of an algorithm satisfying the three properties specified above. We describe here such a calculation based on perturbation theory that allows in principle the calculation of any vibration-rotational matrix element and Herman–Wallis factor in a most efficient, systematic and automatic way.

In order both to make the paper self-contained and to introduce a consistent scheme of notation we first review briefly the method of Herman and Wallis [1]. Formulating the Rayleigh–Schrödinger perturbation theory in the most convenient way for the use of symbolic processors we demonstrate that when the vibration-rotational energies and matrix elements are expanded in series of  $\lambda$  to non-negative powers some contributions vanish; by avoiding their superfluous calculation one makes economical use of both memory space in a computer and duration of computation. The implementation of these principles according to an efficient algorithm has yielded analytic expressions for the Herman–Wallis coefficients  $C_v^{v'}$  and  $D_v^{v'}$ .

## 2. Basis of the formulation

According to the quantum theory of radiation, the intensity of the spectral line

associated with the vibration-rotational transition between two states denoted by  $v'J' \leftarrow vJ$  is proportional to

$$\sum_{M_J} \sum_{M_{J'}} |\langle \Psi_{vJ} Y_{JM_J} | \mathbf{M} | \Psi_{v'J'} Y_{J'M_{J'}} \rangle|^2, \quad (1)$$

in which  $\Psi_{vJ}$  and  $Y_{JM_J}$  are, respectively, the radial and angular parts of the vibration-rotational wavefunction with vibrational quantum number  $v = 0, 1, \dots$  and rotational quantum numbers  $J = 0, 1, \dots$  and  $M_J = -J, -J + 1, \dots, J$ . Because every component of the dipole-moment vector operator  $\mathbf{M}$  factors as a common radial part  $M(x)$  multiplied by an angular part giving its orientation in space equation (1) simplifies to [1]

$$|\langle \Psi_{vJ} | M(x) | \Psi_{v'J'} \rangle|^2 [J\delta_{J-1,J'} + (J+1)\delta_{J+1,J'}]. \quad (2)$$

In the neighbourhood of the equilibrium internuclear separation, we approximate the dipole-moment function  $M(x)$  with reasonable accuracy by

$$M(x) = \sum_{j=0} M_j x^j. \quad (3)$$

Therefore, if the dipole moments matrix elements  $\langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle$  were available one could determine the coefficients  $M_j$  from the set of equations

$$\langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle = \sum_{j=0}^{v_m} M_j \langle \Psi_{0,0} | x^j | \Psi_{v',0} \rangle, \quad v' = 0, 1, \dots, v_m, \quad (4)$$

in which  $v_m$  denotes the quantum number of the highest overtone band measured. Because the line intensities depend on the square of the dipole-moment matrix elements, the sign of the term on the left side of eq. (4) is thus unknown. One can determine it from the Herman–Wallis factors  $F_v^{v'}(m_{\pm})$  defined according to

$$|\langle \Psi_{0,J} | M(x) | \Psi_{v'J'} \rangle|^2 = F_0^{v'}(m_{\pm}) |\langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle|^2, \quad (5)$$

in which  $v = 0$  for the cases of greatest interest. In this expression  $m_{\pm} = [J_{\pm}(J_{\pm} + 1) - J(J + 1)]/2$  with  $J' = J_{\pm} = J \pm 1$  so that  $J(J + 1) = m_{\pm}(m_{\pm} - 1)$  and  $J_{\pm}(J_{\pm} + 1) = m_{\pm}(m_{\pm} + 1)$  [31]. Since  $m_+$  and  $m_-$  satisfy identical equations for simplicity we write  $m$  for  $m_{\pm}$  from now on. The Herman–Wallis factors are commonly fitted to a polynomial function of  $m$ :  $F_0^{v'}(m) = 1 + C_0^{v'} m + D_0^{v'} m^2 + \dots$ , in which  $C_0^{v'}$  and  $D_0^{v'}$  denote the Herman–Wallis coefficients. From the squares of the individual dipole-moment matrix elements derived from the experimental line strengths one obtains by means of a fitting procedure the rotationless matrix elements and the Herman–Wallis coefficients. Comparing the experimental and theoretical Herman–Wallis coefficients enables one to determine uniquely (subject to experimental error) a set of dipole-moment coefficients  $M_j$ . In order to obtain the theoretical Herman–Wallis coefficients one has to calculate the matrix elements

$\langle \Psi_{0,J} | M(x) | \Psi_{v',J'} \rangle$  according to an accurate representation of the potential energy. We proceed here with the convenient representation proposed by Dunham [33]:

$$V(R) = a_0 x^2 \left( 1 + \sum_{j=1} a_j x^j \right). \tag{6}$$

### 3. Perturbation theory and matrix elements

The standard form of the Rayleigh–Schrödinger perturbation theory generally described in textbooks on quantum mechanics leads to closed-form expressions for the energies and eigenfunctions (and thereby for matrix elements and Herman–Wallis factors [7–15]) which are useful for manual calculation but unsuitable for machine computation with a symbolic processor. A step intermediate in the development of those final closed-form expressions proves more convenient. As the practical utility of perturbation theory has been overlooked by even some users we deem it essential to develop in detail the appropriate formulae that we believe make this approach more convenient than others to obtain analytic expressions for vibration-rotational matrix elements.

If the Hamiltonian operator  $H$  can be expanded in a series of an appropriate parameter  $\lambda$  to non-negative powers,

$$H = \sum_{p=0} H_p \lambda^p, \tag{7}$$

in such a way that the eigenfunctions and eigenvalues of  $H_0$  are known

$$H_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}, \tag{8}$$

then one can expand the perturbed eigenvalues and eigenfunctions according to

$$E_n = \sum_{p=0} E_n^{(p)} \lambda^p, \quad \Psi_n = \sum_{p=0} \Psi_n^{(p)} \lambda^p, \tag{9}$$

and obtain the coefficients of these expansions from the physically acceptable solutions of

$$[H_0 - E_n^{(0)}] \Psi_n^{(p)} = \sum_{s=1}^p [E_n^{(s)} - H_s] \Psi_n^{(p-s)}, \quad p = 1, 2, \dots \tag{10}$$

We assume that  $\Psi_n$  is normalized to unity for all values of  $\lambda$  so that  $\Psi_n^{(0)}$  is also normalized to unity. If we apply  $\langle \Psi_n^{(0)} |$  from the left we obtain an expression for the perturbation correction to the energy of order  $p$  in terms of expressions of lesser order:

$$E_n^{(p)} = \langle \Psi_n^{(0)} | H_p | \Psi_n^{(0)} \rangle + \sum_{s=1}^{p-1} \left[ \langle \Psi_n^{(0)} | H_s | \Psi_n^{(p-s)} \rangle - E_n^{(s)} \langle \Psi_n^{(0)} | \Psi_n^{(p-s)} \rangle \right]. \tag{11}$$

On the other hand, if we apply  $\langle \Psi_j^{(0)} |$  with  $j \neq n$  we derive an expression for the corrections to the eigenfunction

$$\langle \Psi_j^{(0)} | \Psi_n^{(p)} \rangle = \left[ E_j^{(0)} - E_n^{(0)} \right]^{-1} \sum_{s=1}^p \left[ E_n^{(s)} \langle \Psi_j^{(0)} | \Psi_n^{(p-s)} \rangle - \langle \Psi_j^{(0)} | H_s | \Psi_n^{(p-s)} \rangle \right]. \quad (12)$$

From the perturbation expansion of  $\langle \Psi_n | \Psi_n \rangle = 1$  we obtain an additional equation for the perturbation corrections to the eigenfunction

$$\langle \Psi_n^{(0)} | \Psi_n^{(p)} \rangle = -\frac{1}{2} \sum_{s=1}^{p-1} \langle \Psi_n^{(s)} | \Psi_n^{(p-s)} \rangle, \quad p > 1; \quad \langle \Psi_n^{(0)} | \Psi_n^{(1)} \rangle = 0. \quad (13)$$

For the present application of perturbation theory it is convenient to expand the perturbation corrections to the eigenfunctions as linear combinations of the unperturbed eigenfunctions

$$\Psi_n^{(p)} = \sum_j c_{jn}^{(p)} \Psi_j^{(0)}. \quad (14)$$

The coefficients of these expansions are obtained from recurrence relations that we discuss in detail below in relation to the present problem.

In the case of a diatomic molecule in a  $^1\Sigma$  electronic state, and within the Born–Oppenheimer approximation, the vibration-rotational energies  $E_{vJ}$  and eigenfunctions  $\Psi_{vJ}$  are solutions of the Schrödinger equation for the rotating oscillator of reduced mass  $\mu$ :

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) + \frac{\hbar^2}{2\mu} \frac{J(J+1)}{R^2}. \quad (15)$$

The physically acceptable eigenfunctions of this operator vanish at  $R = 0$  and when  $R \rightarrow \infty$ . In order to rewrite the Schrödinger equation in a convenient form for the application of perturbation theory we define the new variable  $q = x/\lambda$ , with  $\lambda = \gamma^{1/2} = (2B_e/\omega_e)^{1/2}$ , and expand the centrifugal term in eq. (15) in a series of  $q$  to non-negative powers. Using the Dunham form (6) for  $V(R)$  and the relation  $a_0 = \omega_e^2/(4B_e)$  we obtain the following expression for the dimensionless operator  $H = (hc\omega_e)^{-1}[\mathcal{H} - hcB_eJ(J+1)]$ :

$$H = -\frac{1}{2} \frac{d^2}{dq^2} + \frac{1}{2} q^2 + \frac{1}{2} \sum_{j=1} [a_j q^{j+2} + (-1)^j (j+1) \lambda^2 J(J+1) q^j] \lambda^j, \quad (16)$$

to which we apply the perturbation method described above with the Hamiltonian operator for a dimensionless harmonic oscillator,

$$H_0 = -\frac{1}{2} \frac{d^2}{dq^2} + \frac{1}{2} q^2, \quad (17)$$

and

$$H_s = \frac{1}{2} [a_s q^{s+2} + (-1)^s (s-1)\theta(s)J(J+1)q^{s-2}]. \tag{18}$$

For compactness we have introduced the function  $\theta(s)$  which is equal to zero if  $s \leq 2$  and equal to 1 otherwise.

Before proceeding we deem it worthwhile to recount briefly the problem of the boundary conditions because it seems to be poorly understood. When we change variables from  $R$  to  $q$  the coordinate origin  $R = 0$  is mapped into  $q = -1/\lambda$ ; therefore within the realm of perturbation theory, which implies an expansion of all quantities about  $\lambda = 0$ , the point  $R = 0$  is mapped into  $q \rightarrow -\infty$ . For this reason the unperturbed model is the familiar harmonic oscillator with  $-\infty < q < \infty$ . The approximate perturbed eigenfunction fails to vanish at  $R = 0$  but at this point it has the form  $p(\lambda) \exp[-1/(2\lambda^2)]$ , in which  $p(\lambda)$  is a polynomial of  $\lambda$  with a leading term that is expected to decrease in magnitude as the perturbation order increases. In other words, once one adopts perturbation theory as the approximate method to treat the problem just mentioned one has to choose the boundary conditions for the harmonic oscillator in one dimension, but in so doing one makes no additional approximation.

To simplify the notation we designate the eigenfunctions of the harmonic oscillator by  $|n\rangle, n = 0, 1, \dots$ , because they do not depend on  $J$ . Straightforward application of the perturbation theory described above to the rotating anharmonic oscillator in eq. (16) leads to the following equations for the perturbation corrections to the energies and expansion coefficients for the wavefunctions:

$$E_n^{(p)} = \frac{1}{2} \sum_{s=1}^p \left[ a_s \sum_{k=k_{11}}^{k_{12}} \langle n|q^{s+2}|k\rangle c_{kn}^{(p-s)} + (-1)^s (s-1)\theta(s)J(J+1) \sum_{k=k_{21}}^{k_{22}} \langle n|q^{s-2}|k\rangle c_{kn}^{(p-s)} \right] - \sum_{s=1}^{p-1} E_n^{(s)} c_{nn}^{(p-s)}, \tag{19}$$

$$c_{jn}^{(p)} = (j-n)^{-1} \sum_{s=1}^p \left\{ E_n^{(s)} c_{jn}^{(p-s)} - \frac{1}{2} \left[ a_s \sum_{k=k_{31}}^{k_{32}} \langle j|q^{s+2}|k\rangle c_{kn}^{(p-s)} + (-1)^s (s-1)\theta(s)J(J+1) \sum_{k=k_{41}}^{k_{42}} \langle j|q^{s-2}|k\rangle c_{kn}^{(p-s)} \right] \right\}, \quad p > 0, \tag{20}$$

$$c_{nn}^{(p)} = -\frac{1}{2} \sum_{s=1}^{p-1} \sum_{j=j_1}^{j_2} c_{jn}^{(s)} c_{jn}^{(p-s)}. \tag{21}$$

The lower and upper limits of these sums are

$$\begin{aligned}
k_{11} &= \max \{0, n - s - 2, n - 3(p - s)\}, & k_{12} &= \min \{n + s + 2, n + 3(p - s)\}, \\
k_{21} &= \max \{0, n - s, n - 3(p - s)\}, & k_{22} &= \min \{n + s, n + 3(p - s)\}, \\
k_{31} &= \max \{0, j - s - 2, n - 3(p - s)\}, & k_{32} &= \min \{j + s + 2, n + 3(p - s)\}, \\
k_{41} &= \max \{0, j - s + 2, n - 3(p - s)\}, & k_{42} &= \min \{j + s - 2, n + 3(p - s)\}, \\
j_1 &= \max \{0, n - 3s, n - 3(p - s)\} & \text{and} & j_2 = \min \{n + 3s, n + 3(p - s)\},
\end{aligned}$$

containing the indicated maxima and minima. From these recurrence relations one obtains all the expansion coefficients hierarchically starting from  $c_{jn}^{(0)} = \delta_{jn}$ . The perturbation corrections to the energies are irrelevant here as they are calculated more efficiently by means of the hypervirial perturbative method [34]. The calculation of the matrix elements of  $q$  to non-negative powers in the basis set of the harmonic oscillator is straightforward; as several formulae are given in standard textbooks on quantum mechanics we need not amplify it here. It suffices to state that because of the leading anharmonic term  $a_1 q^3$  in the potential-energy function and because  $\langle n | q^i | k \rangle = 0$  if  $|n - k| > i$  then  $c_{jn}^{(p)} = 0$  if  $|n - j| > 3p$ .

One can easily obtain closed-form expressions for the perturbation corrections to the eigenvalues and eigenfunctions from eqs. (19)–(21) in terms of the harmonic oscillator eigenvalues and eigenfunctions in the way shown in most textbooks on quantum mechanics. This procedure, followed by most authors in their calculations of Herman–Wallis factors [1, 7–15], soon becomes tedious because of the increasing complexity of the intermediate and final explicit expressions. Here, on the other hand, we solve eqs. (19)–(21) hierarchically for  $p = 1, 2, \dots$  up to the greatest desired perturbation order by means of a symbolic processor so that the whole problem reduces to the relatively trivial task of programming these equations in a convenient way. The procedure is clearly indicated by the equations themselves: for every perturbation order  $p$  one obtains  $E_n^{(p)}$  and  $c_{jn}^{(p)}$  in terms of corrections of lesser order obtained in previous steps.

We showed above that the theoretical determination of the transition moments reduces to the calculation of matrix elements of the form  $\langle \Psi_{vJ} | q^i | \Psi_{v'J'} \rangle$ . The latter quantities are directly expressed in terms both of the coefficients  $c_{jn}$  just obtained and of matrix elements between harmonic-oscillator eigenfunctions according to

$$\begin{aligned}
\langle \Psi_{vJ} | q^i | \Psi_{v'J'} \rangle &= \sum_{p=0} \lambda^p \sum_{s=0}^p \langle \Psi_{vJ}^{(s)} | q^i | \Psi_{v'J'}^{(p-s)} \rangle \\
&= \sum_{p=0} \lambda^p \sum_{s=0}^p \sum_{j=j_1}^{j_2} \sum_{k=k_1}^{k_2} c_{jv}^{(s)}(J) c_{kv'}^{(p-s)}(J') \langle j | q^i | k \rangle, \quad (22)
\end{aligned}$$

in which  $j_1 = \max \{0, v - 3s\}$ ,  $j_2 = v + 3s$ ,  $k_1 = \max \{0, v' - 3(p - s), j - i\}$ , and  $k_2 = \min \{v' + 3(p - s), j + i\}$ . By repeated application of this formula one easily derives analytic expressions for the matrix elements of the dipole moment:



$$\langle \Psi_{vJ} | M(x) | \Psi_{v'J'} \rangle = \sum_{i=0} M_i \lambda^i \langle \Psi_{vJ} | q^i | \Psi_{v'J'} \rangle, \tag{23}$$

consistent with all the required powers of  $\lambda$ .

The expanded form of the Hamiltonian operator given in eq. (16) exhibits interesting symmetry properties that are useful not only to verify the results but also to make the calculation more efficient. This operator is invariant under the transformation  $(\lambda, q) \rightarrow (-\lambda, -q)$  so that  $\Psi_{vJ}(-\lambda, -q) = \pm \Psi_{vJ}(\lambda, q)$ . Therefore it follows from this equality and from  $\Psi_{vJ}(0, -q) = (-1)^v \Psi_{vJ}(0, q)$  that  $\Psi_{vJ}(-\lambda, -q) = (-1)^v \Psi_{vJ}(\lambda, q)$  for all values of  $\lambda$ . Expansion of both sides of the latter equation in series of  $\lambda$  to non-negative powers demonstrates that  $\Psi_{vJ}^{(p)}(-q) = (-1)^{p+v} \Psi_{vJ}^{(p)}(q)$  so that  $c_{kv}^{(p)}(J) = 0$  if  $v + k + p$  is odd. Arguing analogously one easily proves that the perturbation correction of order  $p$  to  $\langle \Psi_{vJ} | q^j | \Psi_{v'J'} \rangle$  vanishes when  $v + v' + j + p$  is odd. This result was previously noticed but not proved rigorously [30]; moreover, this perturbation correction vanishes when  $j < |(v' - v)| - p$  with  $p < |v' - v|$  [30]. This result, which follows partly from the symmetry argument just given and partly from the number of terms in the vibration-rotational eigenstates, is confirmed by our calculations. By means of all these simplifications each vibration-rotational matrix element of the dipole moment becomes reduced to a leading term plus corrections of which only the first is significant for practical applications:

$$\begin{aligned} \langle \Psi_{0,J} | M(x) | \Psi_{v'J'} \rangle &= \lambda^{v'+2} \sum_{j=0}^{v'+2} M_j \langle \Psi_{0,J} | q^j | \Psi_{v'J'} \rangle^{(v'+2-j)} \\ &+ \lambda^{v'+4} \sum_{j=0}^{v'+4} M_j \langle \Psi_{0,J} | q^j | \Psi_{v'J'} \rangle^{(v'+4-j)} + \mathcal{O}(\lambda^{v'+6}). \end{aligned} \tag{24}$$

#### 4. Herman–Wallis coefficients

Following Herman and Wallis [1] we express the dipole-moment matrix elements

$$\langle \Psi_{0,J} | M(x) | \Psi_{v'J'} \rangle = \langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle + G_{v'}(m), \tag{25}$$

in which  $G_{v'}(m)$  is a polynomial function of the running index  $m$  that is generally truncated up to second order

$$G_{v'}(m) = \alpha_{v'} m + \beta_{v'} m^2 + \mathcal{O}(m^3). \tag{26}$$

Under this approximation, which is sufficiently accurate for the analysis of present experimental data, the ratio of vibration-rotational matrix element to pure vibrational matrix element, i.e. the Herman–Wallis factor, becomes

$$F_0^{v'}(m) = \frac{|\langle \Psi_{0,J} | M(x) | \Psi_{v',J'} \rangle|^2}{|\langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle|^2} = 1 + \frac{2\alpha_{v'}m}{|\langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle|} + \frac{(\alpha_{v'}^2 + 2\beta_{v'})m^2}{|\langle \Psi_{0,0} | M(x) | \Psi_{v',0} \rangle|^2} + \mathcal{O}(m^3). \quad (27)$$

The coefficients  $\alpha_{v'}$  and  $\beta_{v'}$  are easily calculated from the equations derived in the previous section which are suitable for programming with a symbolic processor such as Maple or Reduce. By this means we have generated the expressions for  $\alpha_8$  and  $\beta_8$  thus extending the previous calculations [23,24,27]. We do not present them here because they are too long and extremely cumbersome. However, they are available upon request. The coefficients  $\alpha_{v'}$  and  $\beta_{v'}$  that we here introduce simplify the presentation of the results and are simply related to the coefficients  $C_0^{v'}$  and  $D_0^{v'}$  customarily used; the relations are obvious according to the definition in eq. (27). At every step of the calculation we have truncated all intermediate expressions to the order  $m^3$  in order to obtain just the desired Herman–Wallis coefficients and to keep the memory requirements to a minimum; we could easily extend the calculation to coefficients of  $m$  to higher powers if necessary.

## 5. Discussion and conclusion

The perturbation method developed in this paper proves useful to calculate both matrix elements of the dipole moment and Herman–Wallis factors because it involves simple recurrence relations that are easily programmable by means of standard symbolic processors. The calculation proceeds hierarchically through the perturbation equations in a way which is familiar in perturbation theory so as to yield at each step all terms consistent with the corresponding power of  $\lambda$ . This consistency is important because of cancellation of terms. To test our method we have repeated the calculation of all previously published results for  $C_0^{v'}$  and  $D_0^{v'}$ ; by means of our newly developed algorithm we confirm thereby the correctness of those results [23,24,27]. Likewise we have not only verified the vibrational matrix elements previously reported [36] but also extended them in the order of the potential-energy coefficients  $a_j$ , the power of  $x$  (or  $\lambda q$  in eq. (22)) and the vibrational quantum number  $v$ . Because our method eliminates the need to use symbolic processors interactively, the calculation of Herman–Wallis coefficients for higher overtones and “hot” bands has been made automatic. These results obtained by means of perturbation theory are expected to be accurate enough provided that the values of  $v$  and  $|v' - v|$  are not particularly large [10–15].

The calculation of Herman–Wallis factors for Raman transitions of  $^1\Sigma$ -state diatomic molecules by means of the algorithm just described is straightforward, the only modification being the requirement of the proper relations between  $J(J+1)$ ,  $J'(J'+1)$  and  $m$  [31]. In also this case the analytic expressions generated

according to perturbation theory prove to be of accuracy comparable to those of numerical calculations [31,35].

After a new and accurate determination of the potential-energy function of HBr, taking into account all the adiabatic and nonadiabatic effects as in recent determinations for other diatomic molecular species [37,38] we shall proceed to a full critical and statistical analysis of all available data for the intensities of vibration-rotational transitions and the Stark effect on pure rotational transitions of HBr in order to determine accurately the dipole-moment function, just as we have done previously for HCl [39]. For this purpose the analytic expressions for the Herman–Wallis coefficients  $C_0^8$  and  $D_0^8$  will be essential.

## Acknowledgements

We thank the National Science Council of the Republic of China for support of this research. F.M.F. thanks the National Science Council for appointment as visiting associate research professor at the Institute of Atomic and Molecular Sciences.

## References

- [1] R. Herman and R.F. Wallis, *J. Chem. Phys.* 23 (1955) 637.
- [2] L.A. Young and W.J. Eachus, *J. Chem. Phys.* 44 (1966) 4195.
- [3] F.G. Smith, *J. Quant. Spectrosc. Radiat. Transfer* 13 (1973) 717.
- [4] M.F. Weisbach and C. Chackerian, *J. Chem. Phys.* 59 (1974) 4272.
- [5] C.B. Carlisle, H. Riris, L.G. Wang, G.R. Janik, T.F. Gallagher, A. Lopez Piñeiro and R.H. Tipping, *J. Mol. Spectrosc.* 130 (1988) 395.
- [6] R. Herman and R.J. Rubin, *Astrophys. J.* 121 (1955) 533.
- [7] R.A. Toth, R.H. Hunt and E.K. Plyler, *J. Mol. Spectrosc.* 23 (1969) 74.
- [8] R.A. Toth, R.H. Hunt and E.K. Plyler, *J. Mol. Spectrosc.* 23 (1969) 85.
- [9] R.A. Toth, R.H. Hunt and E.K. Plyler, *J. Mol. Spectrosc.* 36 (1970) 110.
- [10] J.P. Bouanich and C. Brodbeck, *J. Quant. Spectrosc. Radiat. Transfer* 14 (1974) 1199.
- [11] J.P. Bouanich and C. Brodbeck, *J. Quant. Spectrosc. Radiat. Transfer* 15 (1975) 873.
- [12] J.P. Bouanich and C. Brodbeck, *J. Quant. Spectrosc. Radiat. Transfer* 16 (1976) 153.
- [13] J.P. Bouanich, *J. Quant. Spectrosc. Radiat. Transfer* 16 (1976) 1119.
- [14] J.P. Bouanich, *J. Quant. Spectrosc. Radiat. Transfer* 17 (1977) 639.
- [15] J.P. Bouanich, *J. Quant. Spectrosc. Radiat. Transfer* 20 (1978) 419.
- [16] Y.S. Makushkin and V.G. Tyuterev, *Opt. Spectrosc.* 37 (1974) 31.
- [17] H. Hanson, H.H. Nielsen, W.H. Shaffer and J. Waggoner, *J. Chem. Phys.* 27 (1957) 40.
- [18] R.M. Herman, R.H. Tipping and S. Short, *J. Chem. Phys.* 53 (1970) 595.
- [19] R.H. Tipping and R.M. Herman, *J. Mol. Spectrosc.* 36 (1970) 404.
- [20] R.H. Tipping and A. Forbes, *J. Mol. Spectrosc.* 39 (1971) 65.
- [21] R.H. Tipping and J.F. Ogilvie, *J. Mol. Struct.* 35 (1976) 1.
- [22] R.H. Tipping, *J. Mol. Spectrosc.* 61 (1976) 272.
- [23] R.H. Tipping and J.F. Ogilvie, *J. Mol. Spectrosc.* 96 (1982) 442.
- [24] J.F. Ogilvie and R.H. Tipping, *Int. Rev. Phys. Chem.* 3 (1983) 3.

- [25] J.F. Ogilvie, W.R. Rodwell and R.H. Tipping, *J. Chem. Phys.* 73 (1980) 5221.
- [26] P. Bernage and P. Niay, *J. Quant. Spectrosc. Radiat. Transfer* 18 (1977) 315.
- [27] J.F. Ogilvie and R.H. Tipping, *J. Quant. Spectrosc. Radiat. Transfer* 33 (1985) 145.
- [28] R.H. Tipping, *J. Chem. Phys.* 59 (1973) 6433.
- [29] R.H. Tipping, *J. Chem. Phys.* 59 (1973) 6443.
- [30] P. Niay, C. Coquant and P. Bernage, *Can. J. Phys.* 57 (1979) 572.
- [31] R.H. Tipping and J.F. Ogilvie, *J. Raman Spectrosc.* 15 (1984) 38.
- [32] G. Hadinger, Y.S. Tergiman and G. Hadinger, *J. Chem. Phys.* 87 (1987) 2143.
- [33] J.L. Dunham, *Phys. Rev.* 41 (1932) 721.
- [34] F.M. Fernández and J.F. Ogilvie, *Phys. Rev. A* 42 (1990) 4001.
- [35] M. Cheung, D.M. Bishop, D.L. Drapcho and G.M. Rosenblatt, *Chem. Phys. Lett.* 80 (1981) 445.
- [36] J.P. Bouanich, J.F. Ogilvie and R.H. Tipping, *Comput. Phys. Commun.* 39 (1986) 439.
- [37] J.F. Ogilvie, *J. Mol. Spectrosc.* 148 (1991) 243.
- [38] J.F. Ogilvie, *J. Phys. B* 27 (1994) 47.
- [39] J.F. Ogilvie, *Comput. Chem.* 15 (1991) 59.