Application of the hypervirial perturbation theory to the vibrational-rotational spectroscopy of diatomic molecules

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(Received 7 February 1990)

We have developed a simple and systematic method to calculate analytic perturbation corrections of large order to the vibrational-rotational energies and matrix elements between vibrational-rotational states of diatomic molecules. The method, which is based on a powerful combination of perturbation theory and the hypervirial and Hellmann-Feynman theorems, is suitable to derive analytic expressions for both expectation values of observables and transition moments. As an illustrative example we discuss the isotopic effect on the vibrational-rotational energies. We show that, according to the Kratzer potential-energy function, perturbation theory renders a good approximation to the vibrational-rotational energies of diatomic molecules.

I. INTRODUCTION

Dunham proposed the theory[1] that is commonly used for the analysis of the vibrational-rotational spectra of diatomic molecules.[2] The vibrational-rotational energies $E(v,J)$ of a diatomic molecule in a $^1\Sigma$ electronic state are represented according to the expression

$$E(v,J)/(hc) = \sum_k \sum_l Y_{kl}(v+\tfrac{1}{2})^k[J(J+1)]^l . \tag{1}$$

The fit of the frequencies of the experimental lines to the differences of these energies determines the spectral parameters, the term coefficients Y_{kl}.[1,2] The latter fitting parameters acquire physical significance through their relationship to the internuclear potential energy. For small displacements from the equilibrium distance R_e this internuclear potential-energy function $V(R)$ is expanded in a power series of $x = (R-R_e)/R_e$:

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

Dunham[1] solved the Schrödinger equation with this potential energy by means of the WKB method to obtain algebraic relationships between the coefficients a_j and Y_{kl}. By this means, the form of the potential energy about its minimum is readily determined from appropriate spectroscopic measurements.

Kilpatrick[3] later derived the same relationships through quantum-mechanical perturbation theory. Bouanich[4] extended these results to calculate contributions to the eighth- and tenth-order perturbation corrections to the vibrational-rotational energies by numerical programming whereas Bryukhanov et al.[5] obtained the 12th-order corrections by methods of computer algebra.

Perturbation calculations of large order are useful provided that the perturbation series are not strongly divergent for those values of the perturbation parameter that are necessary for the physical application. Bender and

Wu[6] and Simon[7] proved that the perturbation expansion for relatively simple models of an anharmonic oscillator is divergent for all values of the perturbation parameter. A rigorous mathematical study of the convergence properties of the perturbation series for the vibrational-rotational energies of diatomic molecules is impracticable because the potential-energy function is imperfectly determined. As a first approximation one can estimate such properties by means of more-or-less realistic analytic models for potential energy. Sprandel and Kern[8] conducted a numerical test of the convergence of the perturbation series for the vibrational-rotational energies of several molecules. They found that when all the anharmonic terms were taken into account as a single perturbation term the series was divergent. On the other hand, when each anharmonic term was identified with a successively greater order of perturbation the series exhibited remarkable convergence properties. These authors failed to recognize that the success of the latter method was due to their use of the Morse function for potential energy to generate the coefficients a_j. According to this model all perturbation corrections to the energy of order greater than 2 vanish when the second method is used. They overlooked this fact because in their numerical solution of the differential equations from perturbation theory they obtained spurious contributions to the larger orders. Because such contributions, which originate in approximations to derivatives and boundary conditions, are almost negligible if the calculation is accurate enough, the resulting series appears to be convergent. That the perturbation terms of order greater than 2 vanish in the case of the Morse oscillator, as a consequence of the particular form of this model function, has been overlooked also by other authors[9,10] and has been only recently explained properly.[11]

Although the accuracy and generality of certain numerical techniques may be superior to those of perturbation theory, spectroscopists commonly continue to find it useful to fit the vibrational-rotational spectrum to Eq. (1)

and then to calculate the coefficients of the expansion (2) from the relatively simple analytical expressions that relate the coefficients a_j and Y_{kl}.[1,2] As one can derive these and other analytic expressions from perturbation theory, this approach proves useful in spectroscopic applications. The purpose of this paper is twofold. In Secs. II and III we show that perturbation theory can be efficiently applied to the study of vibrational-rotational properties of diatomic molecules if one takes into account the hypervirial and Hellmann-Feynman theorems. In Sec. II we derive recurrence relations for the perturbation corrections to both the energies and the expectation values of the coordinate x to various powers. We show also how to calculate expectation values of properties which depend on the coordinate and which can be expanded in a Taylor series about the equilibrium distance. We consider, as a particular example, the calculation of the isotopic effect on the vibrational-rotational energies. In Sec. III we discuss a systematic calculation of off-diagonal matrix elements. The method is especially designed to exploit available software for computer algebra, hence allowing one to derive analytic expressions of large order. In Sec. IV we study the convergence properties of the Rayleigh-Schrödinger perturbation series for the time-independent Schrödinger equation with the Kratzer function for potential energy which can be solved exactly. Further comments and conclusions are presented in Sec. V.

II. PERTURBATION THEORY WITHOUT WAVE FUNCTIONS

One advantage of the application of Rayleigh-Schrödinger perturbation theory to the vibrational-rotational spectroscopy of diatomic molecules is that it yields analytic approximate expressions for physical observables. The vibrational-rotational energies derived in this way are suitable for obtaining the potential-energy coefficients from spectral data. However, direct application of Rayleigh-Schrödinger perturbation theory is rather tedious even if a contact transformation[12] is used. In the case of diatomic molecules, analytic perturbation calculation of large order is straightforward if one takes into account the hypervirial and Hellmann-Feynman theorems. The method, commonly termed perturbation theory without wave functions or the hypervirial perturbation method, has been applied to many quantum-mechanical models,[13] but it appears to have been overlooked as a useful tool in spectroscopic theory. For this reason we derive here the main equations and show how to apply this technique to obtain vibrational-rotational energies, expectation values, and matrix elements.

We consider the time-independent one-dimensional Schrödinger equation $H|j\rangle = \varepsilon(j)|j\rangle$, with Hamiltonian $H = -d^2/dq^2 + U(q)$, and normalized eigenfunctions $|j\rangle$. Here q is a dimensionless coordinate ranging from $-\infty$ to ∞. For any sufficiently differentiable function $f(q)$ we have

$$[H,[H,f]]+2[H,f''] = -f^{IV}+2f'U'+4f''(U-H) ,$$
$$(3)$$

in which $[A,B] = AB - BA$ is the commutator between the operators A and B, and the superscripts denote derivatives with respect to q. We take matrix elements between two arbitrary states k and j on both sides of Eq. (3) and rearrange the resulting equation as

$$[\epsilon(k)-\epsilon(j)]^2\langle k|f|j\rangle$$
$$= -\langle k|f^{IV}|j\rangle -2[\epsilon(k)+\epsilon(j)]\langle k|f''|j\rangle$$
$$+2\langle k|f'U'|j\rangle+4\langle k|f''U|j\rangle .$$
$$(4)$$

We apply this formalism to the vibrational-rotational motion of a diatomic molecule because the radial part of the time-independent Schrödinger equation is expressed as an eigenvalue problem with one degree of freedom. The radial part of the wave functions is an eigenfunction of

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+V(R)+\frac{\hbar^2}{2\mu}J(J+1)R^{-2} ,$$
$$(5)$$

in which all the symbols have their conventional meaning. In order to cast H into a suitable form we expand $V(R)$ according to Eq. (2) and introduce the change of variables $q = x/\lambda$, $\lambda = (2B_e/\omega_e)^{1/2} = \gamma^{1/2}$. Then we expand R^{-2} in a Taylor series about $q = 0$ so that the Hamiltonian operator (5) can be rewritten

$$H' = \frac{2H}{hc\omega_e}-2J_B = -\frac{d^2}{dq^2}+U(q) ,$$
$$(6a)$$

$$U(q) = q^2+\sum_{j=1}^{\infty}\lambda^j[a_jq^{j+2}+J_B(-1)^j(j+1)q^j] ,$$
$$(6b)$$

in which we introduce $J_B = 2B_eJ(J+1)/\omega_e$ in order to simplify the resulting equations and to obtain more J-dependent terms with the same order of perturbation theory.

It is clear that the general equation (4) applies to the operator H'. The vibrational-rotational energies can be expressed in terms of the eigenvalues $\epsilon(v,J)$ of H' as

$$E(v,J)/(hc) = \tfrac{1}{2}\omega_e\epsilon(v,J)+B_eJ(J+1) .$$
$$(7)$$

For the sake of simplicity we consider first the diagonal form of the hypervirial theorems which enables one to obtain the perturbation corrections to the energy and expectation values; off-diagonal matrix elements are treated in Sec. III.

If we choose $f = q^{N+1}/(N+1)$, define $Q^{(N)} = \langle v,J|q^N|v,J\rangle$ and $\epsilon = \epsilon(v,J)$, then the master equation (4) can be rewritten as

$$Q^{(N+1)} = (2N+2)^{-1} \left[\tfrac{1}{2} N(N-1)(N-2)Q^{(N-3)} + 2N\epsilon Q^{(N-1)} \right.$$

$$\left. - \sum_{j=1}^{\infty} [a_j(2N+j+2)Q^{(N+j+1)} + J_B(-1)^j(j+1)(2N+j)Q^{(N+j-1)}] \right] . \tag{8}$$

The Hellmann-Feynman theorem provides an additional equation:

$$\frac{\partial \epsilon}{\partial \lambda} = \sum_{j=1}^{\infty} j\lambda^{j-1}[a_j Q^{(j+2)} + J_B(-1)^j(j+1)Q^{(j)}] . \tag{9}$$

We expand the energy and the expectation values in power series of λ:

$$\epsilon = 2\epsilon_0 + \sum_{p=1}^{\infty} \epsilon_p \lambda^p, \quad \epsilon_0 = v + \tfrac{1}{2}, \quad Q^{(N)} = \sum_{p=0}^{\infty} Q_p^{(N)} \lambda^p . \tag{10}$$

In the next step we substitute Eq. (10) into Eqs. (8) and (9), and collect the coefficients of λ to like powers. By this means one obtains a recurrence relation for the coefficients $Q_p^{(N)}$ which in the present case is conveniently split into two equations:

$$\epsilon_p = \frac{1}{p} \sum_{j=1}^{p} j[a_j Q_{p-j}^{(j+2)} + J_B(-1)^j(j+1)Q_{p-j}^{(j)}], \quad p>0 . \tag{11a}$$

$$Q_p^{(N+1)} = (2N+2)^{-1} \left[\tfrac{1}{2} N(N-1)(N-2)Q_p^{(N-3)} + 4N\epsilon_0 Q_p^{(N-1)} \right.$$

$$\left. + \sum_{j=1}^{p} [2N\epsilon_j Q_{p-j}^{(N-1)} - a_j(2N+j+2)Q_{p-j}^{(N+j+1)} - J_B(-1)^j(j+1)(2N+j)Q_{p-j}^{(N+j-1)}] \right] ,$$

$$p = 1,2,\ldots, \quad N = 0,\ldots . \tag{11b}$$

Because the eigenfunctions of H' are normalized to unity we have $Q_p^{(0)} = \delta_{p0}$.

All perturbation corrections to the energy and moments of the coordinate, $Q^{(N)} = \langle q^N \rangle$, are obtained from Eqs. (11) hierarchically starting from $p=0$. These equations have been programmed to exploit current software for computer algebra. For instance, we have used REDUCE to obtain analytic expressions for the first 16 perturbation corrections in the case of purely vibrational motion $(J=0)$ and the first ten including rotational terms, confirming and extending previous results.[2-5] In addition to the well-known result $\epsilon_p = 0$, $p=1,3,5,\ldots,$[2-5] our calculation shows that $Q_p^{(N)} = 0$ if $N+p = 1,3,5,\ldots$. Expressions of large order are too complicated to be displayed here; for this reason we only show below the first nonzero perturbation corrections to the energy and expectation values:

$$\epsilon_2 = \tfrac{3}{2}(\tfrac{1}{4}+\epsilon_0^2)a_2 - \tfrac{1}{8}(\tfrac{7}{4}+15\epsilon_0^2)a_1^2 + 3J_B\epsilon_0(1+a_1) - J_B^2 , \tag{12}$$

$$Q_1^{(1)} = J_B - \tfrac{3}{2}a_1\epsilon_0 , \tag{13a}$$

$$Q_3^{(1)} = (\tfrac{23}{16} + \tfrac{39}{4}\epsilon_0^2)a_1 a_2 - \tfrac{15}{4}(\tfrac{1}{4}+\epsilon_0^2)a_3$$

$$- \tfrac{3}{8}(\tfrac{7}{4}+15\epsilon_0^2)a_1^3 + J_B\epsilon_0(6+\tfrac{27}{4}a_1 + \tfrac{27}{4}a_1^2 - 6a_2)$$

$$- J_B^2(3+\tfrac{3}{2}a_1) , \tag{13b}$$

$$Q_0^{(2)} = \epsilon_0 , \tag{14a}$$

$$Q_2^{(2)} = (\tfrac{7}{16} + \tfrac{15}{4}\epsilon_0^2 - \tfrac{3}{2}(\tfrac{1}{4}+\epsilon_0^2)a_2$$

$$- \tfrac{3}{2}J_B\epsilon_0(1+3a_1) + J_B^2 , \tag{14b}$$

$$Q_1^{(3)} = 3J_B\epsilon_0 - (\tfrac{7}{16} + \tfrac{15}{4}\epsilon_0^2)a_1 , \tag{15}$$

$$Q_0^{(4)} = \tfrac{3}{2}(\tfrac{1}{4}+\epsilon_0^2) . \tag{16}$$

The vibrational-rotational energies are expressed

$$E(v,J)/(hc) = \omega_e \epsilon_0 + B_e J(J+1)$$

$$+ \tfrac{1}{2}\omega_e \sum_{p=1}^{\infty} \epsilon_{2p}(v,J)\lambda^{2p} , \tag{17}$$

and the expectation values of powers of x take the form

$$\langle v,J|x^N|x,J \rangle = \lambda^N Q^{(N)} = \sum_{p=0}^{\infty} Q_p^{(N)}\lambda^{p+N} . \tag{18}$$

Notice that both expansions have powers of $\lambda^2 = 2B_e/\omega_e$ because the corrections of odd order vanish.

The method just developed has many useful applications in addition to the calculation of the coefficients a_j from spectral data. For instance, it is suitable for the evaluation of the expectation value of any property $\mathcal{P}$ that can be expanded in a power series of x: $\mathcal{P} = \mathcal{P}_0 + \mathcal{P}_1 x + \mathcal{P}_2 x^2 + \cdots .$[14] One can easily verify that the general expression is

$$\langle v,J|\mathcal{P}|v,J \rangle = \sum_{p=0}^{\infty} \lambda^{2p} \sum_{j=0}^{2p} \mathcal{P}_j Q_{2p-j}^{(j)} , \tag{19}$$

which up to fourth order in λ becomes

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$$\langle v,J|\mathcal{P}|v,J\rangle = \mathcal{P}_0 + (\mathcal{P}_1 Q_1^{(1)} + \mathcal{P}_2 Q_0^{(2)})\lambda^2$$
$$+ (\mathcal{P}_1 Q_3^{(1)} + \mathcal{P}_2 Q_2^{(2)} + \mathcal{P}_3 Q_1^{(3)})\lambda^4 + \cdots .$$

$$(20)$$

The combination of this equation and (13)–(16) yields an analytic expression, accurate to second order in γ, for any physical property which can be expanded in a Taylor series about the equilibrium distance. One can readily derive more accurate analytic expressions by means of the recurrence relations (11) and the general equation (19).

As another application of the present method we calculate the isotopic effect; i.e., the change of the energies due to a change of the reduced atomic mass μ of the diatomic molecule.[15] We obtain a simple expression for this effect by means of the Hellmann-Feynman and virial theorems. Because the kinetic energy operator T is inversely proportional to the reduced atomic mass μ of the molecule we have $\partial E/\partial\mu = -\langle T\rangle/\mu$, which together with the virial theorem $2\langle T\rangle = \langle RdV/dR\rangle$ yields

$$\frac{\partial E(v,J)}{\partial\mu} = -\frac{1}{2\mu}\left\langle v,J\left|R\frac{dV}{dR}\right|v,J\right\rangle .$$

$$(21)$$

We write this equation in a more convenient form in terms of the expectation values $Q^{(N)}$ by taking into account that $R = R_e(1+\lambda q)$ and expanding $V(R)$ as in Eq. (2). We then expand the resulting equation

$$\frac{\partial E}{\partial\mu} = -\frac{\omega_e}{4\mu}\left[\frac{2}{\lambda}Q^{(1)}(3a_1+2)Q^{(2)}\right.$$
$$\left. + \sum_{j=1}^{\infty}[(j+3)a_{j+1}+(j+2)a_j]Q^{(j+2)}\lambda^j\right] ,$$

$$(22)$$

in series of λ to non-negative powers so as to obtain an expression in terms of perturbation corrections that can be calculated through the recurrence relations (11):

$$\frac{\partial E}{\partial\mu} = -\frac{\omega_e}{4\mu}\sum_{p=0}^{\infty}\left[2Q_{p+1}^{(1)}+(3a_1+3)Q_p^{(2)}\right.$$
$$+\sum_{j=1}^{p}[(j+3)a_{j+1}$$
$$\left. +(j+2)a_j]Q_{p-j}^{(j+2)}\right]\lambda^p .$$

$$(23)$$

For the sake of simplicity we omit the labels v and J on E and $Q^{(N)}$ in the latter two equations. The resulting analytic expression for the isotopic effect accurate to first order in γ is:

$$\frac{\partial E}{\partial\mu} = -\frac{\omega_e}{4\mu}\{2Q_1^{(1)}+(3a_1+2)Q_0^{(2)}$$
$$+[2Q_1^{(1)}+(3a_1+2)Q_2^{(2)}$$
$$+(4a_2+3a_1)Q_1^{(3)}+(5a_3+4a_2)Q_0^{(4)}]$$
$$\times\lambda^2+\cdots\} .$$

$$(24)$$

All terms appearing in this equation are given above in Eqs. (13)–(16).

III. OFF-DIAGONAL MATRIX ELEMENTS

In order to make simpler the presentation of the method and its applications we discuss separately matrix elements diagonal and off-diagonal in v. One can obtain a recurrence relation for all matrix elements from the master equation (4) simply by introducing the effective potential (6b), setting $f = q^N$, and substituting v,J for j and v',J for k. The resulting equation

$$\{[\epsilon(v',J)-\epsilon(v,J)]^2-4N^2\}\langle v,J|q^N|v',J\rangle = -N(N-1)(N-2)(N-3)\langle v,J|q^{N-4}|v',J\rangle$$
$$-2[\epsilon(v',J)+\epsilon(v,J)]N(N-1)\langle v,J|q^{N-2}|v',J\rangle$$
$$+2N\sum_{k=1}^{\infty}\lambda^k[a_k(2N+k)\langle v,J|q^{N+k}|v',J\rangle$$
$$+J_B(-1)^k(k+1)(2N+k-2)\langle v,J|q^{N+k-2}|v',J\rangle]$$

$$(25)$$

appears complicated because of the many subscripts and superscripts that one has used. However, by noting that it is unnecessary to refer explicitly to the quantum numbers v, v', and J because they do not change during the calculation, we simplify the form of the perturbation equations to write

$$\epsilon(v',J)-\epsilon(v,J) = \sum_{p=0}^{\infty}\omega_p\lambda^p, \quad \epsilon(v',J)+\epsilon(v,J) = \sum_{p=0}^{\infty}\Omega_p\lambda^p ,$$

$$(26a)$$

$$[\epsilon(v',J)-\epsilon(v,J)]^2 = \sum_{p=0}^{\infty}\omega_p^{(2)}\lambda^p, \quad \omega_p^{(2)} = \sum_{s=0}^{p}\omega_s\omega_{p-s} ,$$

$$(26b)$$

$$\langle v,J|q^N|v',J\rangle = \sum_{p=0}^{\infty}Q_p'^{(N)}\lambda^p .$$

$$(26c)$$

Thus we obtain the recurrence relations for the perturbation corrections as in Sec. II. However, a careful inspection of the resulting equations shows that one has to treat separately two different situations. Because $\omega_0^2-4N^2=4[(v'-v)^2-N^2]$ may vanish it is convenient to define $n = |v'-v|$, or $v'=v\pm n$. Therefore we have

$$Q_p'^{(n)}=[2\Omega_0(n+1)(n+2)]^{-1}\bigg[-n(n^2-1)(n+2)Q_p'^{(n-2)}$$

$$+\sum_{k=1}^{p}[2(n+2)(2n+k+4)a_kQ_p'^{(n+k+2)}_{-k}-\omega_k^{(2)}Q_p'^{(n+2)}_{-k}$$

$$+2(n+2)(-1)^k(k+1)(2n+k+2)J_BQ_p'^{(n+k)}_{-k}-2(n+1)(n+2)\Omega_kQ_p'^{(n)}_{-k}]\bigg] \quad (27a)$$

when $N=n$, and

$$Q_p'^{(N)}=(4n^2-4N^2)^{-1}\bigg[-N(N-1)N-2)(N-3)Q_p'^{(N-4)}-2N(N-1)\Omega_0Q_p'^{(N-2)}$$

$$+\sum_{k=1}^{p}[2N(2N+k)a_kQ_p'^{(N+k)}_{-k}-\omega_k^{(2)}Q_p'^{(N)}_{-k}$$

$$+2N(-1)^k(k+1)(2N+k-2)J_BQ_p'^{(N+k+2)}_{-k}-2N(N-1)\Omega_kQ_p'^{(N-2)}_{-k}]\bigg] \quad (27b)$$

otherwise. If we add the Hellman-Feynman theorem to these two equations we obtain a system of recurrence relations from which the perturbation corrections to all the matrix elements and to the energy can be calculated. However, actually to enable this calculation to be performed analytically to large order by means of computer algebra, the machine requires a large memory. An alternative procedure is to evaluate first the perturbation corrections to the energy and diagonal matrix elements as discussed in Sec. II and then to use the former together with Eqs. (27) to generate the perturbation corrections to the off-diagonal matrix elements.

There are other methods that enable one to derive perturbation corrections to the off-diagonal matrix elements of the coordinate to various powers.[2,16] However, when both states have the same rotational quantum number J, the present approach leads to more general results which apply to arbitrary vibrational quantum numbers v and $v'=v\pm n$. To illustrate this assertion we show below the first-order correction of some off-diagonal matrix elements:

$$\langle v,J|q^n|v\pm n,J\rangle_1=0, \quad n=1,2,\ldots, \quad (28a)$$

$$\langle v,J|q|v\pm n,J\rangle_1=[2(n^2-1)]^{-1}$$

$$\times(3a_1\langle v,J|q^2|v\pm n,J\rangle_0$$

$$-2J_B\delta_{v,v\pm n}), \quad n\neq1, \quad (28b)$$

$$\langle v,J|q^2|v\pm n,J\rangle_1=(n^2-4)^{-1}(5a_1\langle v,J|q^3|v\pm n,J\rangle_0$$

$$-6J_B\langle v,J|q|v\pm n,J\rangle_0), $$

$$n\neq2. \quad (28c)$$

in which the subscript denotes the them of correction.

The hypervirial theorems are insufficient to determine the nonvanishing off-diagonal matrix elements when $\lambda=0$. However, one can readily obtain them by using well-known properties of the harmonic-oscillator eigenfunctions. A simple recurrence relation for such matrix elements is

$$\langle v,J|q^N|v',J\rangle_0=\left[\frac{v+1}{2}\right]^{1/2}\langle v+1,J|q^{N-1}|v',J\rangle_0$$

$$+\left[\frac{v}{2}\right]^{1/2}\langle v-1,J|q^{N-1}|v',J\rangle_0,$$

$$N=1,2,\ldots, \quad (29a)$$

$$\langle v,J|v',J\rangle_0=\delta_{vv'}. \quad (29b)$$

One can use the off-diagonal matrix elements derived in this way to calculate physical properties such as transition moments.[2]

The application of hypervirial theorems and perturbation theory to the calculation of off-diagonal matrix elements was first proposed by Clarke,[17] who considered simpler anharmonic oscillators. This author studied the recurrence relations in detail, drawing interesting conclusions on the structure of the perturbation coefficients.

IV. CONVERGENCE OF THE PERTURBATION EXPANSIONS

In order to carry out either analytic or numerical investigations of the convergence properties of the perturbation expansion for the vibrational-rotational energy of diatomic molecules one has to resort to an appropriate model for the potential energy. When proceeding thus, one should bear in mind that, even if one considers the most realistic analytic potential-energy function available, the conclusions drawn from it are not of general validity. However, these conclusions may provide insight into the subject and lead to improved perturbation theories. As we discussed in the Introduction, the Morse oscillator is useless for such purposes because all perturbation corrections in powers of λ of order larger than 2 vanish identically.[11] One can readily verify this fact simply by substituting the coefficients a_j corresponding to the Morse potential-energy function into the recurrence relations (11). One also finds that the perturbation series for the matrix elements are infinite.

In what follows we discuss the Kratzer potential energy which, although it is not considered to be as realistic

as the Morse function, is more useful for our present purposes for two reasons. First, in the sense that it has terms of infinite number, the perturbation series for the energy in λ to non-negative powers is not trivial; one can therefore study its convergence properties. Second, the time-independent Schrödinger equation can be exactly solved leading to an analytic expression for the vibrational-rotational energies. This fact enables one to obtain the convergence radius of the perturbation series in closed form.

The Kratzer potential-energy function is expressed

$$V(R) = D(1 - R_e/R)^2 , \qquad (30)$$

in which D is the equilibrium binding energy. The dimensionless energies are

$$\epsilon(v,J) = E(v,J)/(D\lambda^2)$$

$$= \frac{(2v+1)\Delta + \lambda^2[(v+\tfrac{1}{2})^2 + (J+\tfrac{1}{2})^2]}{[\lambda^2(v+\tfrac{1}{2}) + \Delta]^2} \qquad (31)$$

in which $\Delta = [1 + \lambda^4(J+\tfrac{1}{2})^2]^{1/2}$, and $\lambda = [\hbar^2/(2\mu DR_e^2)]^{1/4}$ is the perturbation parameter.

The analysis of the convergence of the perturbation expansion in λ to non-negative powers is simpler if we do not substitute J_B for $\lambda^2 J(J+1)$ as we did previously. According to Eq. (31) $\epsilon(v,J)$ has singularities of two types on the complex λ plane: poles $\lambda_p^4 = [(v+\tfrac{1}{2})^2 - (J+\tfrac{1}{2})^2]^{-1}$ and branch points $\lambda_b^4 = -(J+\tfrac{1}{2})^{-2}$. The perturbation series converges provided $\lambda < \min(|\lambda_p|, |\lambda_b|)$. We find that $|\lambda_b| < |\lambda_p|$ if $(v+\tfrac{1}{2})^2 < 2(J+\tfrac{1}{2})^2$ and $|\lambda_p| < |\lambda_b|$ otherwise. The conditions for convergence of the perturbation series become

$$(J+\tfrac{1}{2}) < \lambda^{-2} \qquad (32)$$

in the former case, and

$$(v+\tfrac{1}{2}) < \lambda^{-2} \qquad (33)$$

otherwise. Because for any neutral molecule in its ground electronic state the largest value of λ is 0.166, which applies to H_2, we conclude that if the vibrational motion is governed by the Kratzer potential energy the perturbation series of all diatomic molecules is convergent provided that v and J have values less than 35. We refrain from claiming that this conclusion applies without restriction to real molecules. However, it is our purpose to show that there is no apparent reason to be-

lieve that perturbation theory in powers of λ is a poor method to apply to the vibrational-rotational motion of diatomic molecules.

V. FURTHER COMMENTS AND CONCLUSIONS

We have developed a simple and systematic method to calculate analytic perturbation corrections of large order to both the vibrational-rotational energies of diatomic molecules and matrix elements between vibrational-rotational states. The procedure leads to recurrence relations that can be readily programmed using standard software for computer algebra. By this means the range of matrix elements of x to various powers has been extended considerably beyond what was previously achieved using explicitly either a basis set of harmonic-oscillator functions or approximate anharmonic-oscillator functions.[2,16,18] One should emphasize that the programming of the formulas presented in this work is far more concise and efficient than the formalism used in previous calculations, especially of off-diagonal matrix elements. One can also express many physical properties of the diatomic molecules in terms of the perturbation corrections just described.

The method is flexible enough to include further effects on the vibrational-rotational states of diatomic molecules not considered above. For instance, one can readily add adiabatic and nonadiabatic corrections which are necessary to improve the agreement with experimental data.[2,19]

We have also discussed the convergence properties of the perturbation series for the particular case of the Kratzer potential-energy function. According to this simplified model, perturbation theory may be accurate enough for most spectroscopic purposes. However, we are aware that the results obtained here are not conclusive and that further investigation is required. If in some cases the perturbation expansion fails to converge rapidly enough or is suspected to be divergent one could try appropriate summation techniques[20] to improve the convergent properties and, thereby, the accuracy of the spectral parameters derived from the vibrational-rotational spectrum. One can also apply different approaches commonly used in other fields of physics, such as the N^{-1} expansion which can also be implemented in combination with perturbation theory without wave functions.[21]

The principal disadvantage of the perturbation theory without wave functions developed here is that it applies to problems with only one degree of freedom. In other cases one can resort to an alternative procedure based on the moments of the wave function which may eventually find useful application in the vibrational-rotational spectroscopy of polyatomic molecules.[22]

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