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Application of perturbation theory to the vibration–rotational energies of diatomic molecules

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Abstract. To determine the vibration–rotational energies of diatomic molecules, the hypervirial perturbation theory is proved to be simpler and more convenient than other approaches. The expansion of these energies in terms of a small parameter related to the spectral parameters is independent of the unperturbed model chosen. We illustrate this point by the selection of the harmonic oscillator and the Morse oscillator as two possible unperturbed models. We apply the hypervirial perturbative method to a modified Morse oscillator, recently proposed to analyse the spectra of diatomic molecules, for which we obtain the energy coefficients in terms of the parameters of the potential-energy function.

1. Introduction

Since Morse (1929) introduced his function for the potential energy of a diatomic vibrator, which was the first potential energy for which the consequence was bound states of finite number, much attention has been devoted to not only the valuable properties of the simple Morse function but also modifications of the function to make it more closely commensurate with the spectral properties of actual diatomic molecules (within the Born–Oppenheimer separation of electronic and nuclear motions). The vibration–rotational terms (or energies of the discrete vibration–rotational states) that are the eigenvalues of two such modified functions with the associated centrifugal terms are our concern in this work. Dunham (1932) originated one form that became known as the perturbed Morse oscillator (PMO). The latter became a useful model for the accurate analysis of rotational–vibrational spectra of diatomic molecules when Huffaker and Dwivedi (1975) showed how to calculate exact perturbation corrections to the energies and eigenfunctions. This feature of PMO facilitated the study of the expansion of the vibration–rotational energies in powers of the corresponding quantum numbers (Huffaker 1976a, b, 1978, 1980) and the calculation of Franck–Condon factors (Dwivedi and Huffaker 1977, Huffaker and Dwivedi 1978). Huffaker and Dwivedi (1975) showed how to treat the quantum-mechanical perturbation of PMO by means of factorization of the differential equation (Infeld and Hull 1951); Huffaker (1976a, b, 1978) later extended the calculation of perturbation corrections to the coefficients Y_{kl} by means of the BKW method. The other form that we consider is a modification complementary to that made by Rydberg (1931), later extended by Sorbie and Murrell (1975), in which the exponential term is given as factor a truncated power series. Coxon and Hajigeorgiou (1990) have instead placed the truncated power series in the

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exponent. Each such modification bestows significant advantages over the original prototypical function, necessarily at the expense of some complication, although for many purposes even the simple Morse oscillator leads to intractably complicated analytic expressions for such quantities as matrix elements, Franck–Condon factors, etc.

Although factorization is a powerful method by which to apply perturbation theory to PMO, the resulting equations are sufficiently intricate to hinder the calculation of corrections of the large order required by the extent and precision of modern spectra. This reason justifies the development of alternative methods. Requena *et al* (1980) proposed the use of hypervirial relations and the Hellmann–Feynman theorem to obtain recurrence relations for the perturbation corrections to the energy and expectation values of properly chosen exponential functions. As these recurrence relations proved insufficient to obtain all the perturbation corrections, they resorted to the expansion of the exponential functions in power series of the coordinate. Fernández and Castro (1982a, b) showed that this approximation was unnecessary and obtained the unknown term by means of an additional relation based on the Hellmann–Feynman theorem. Although in both cases the authors developed equations for the calculation of all the perturbation corrections, they did not demonstrate the efficiency of their methods by means of calculations of large order for a realistic PMO. In particular, the algorithm of Fernández and Castro (1982a, b) for the calculation of exact perturbation corrections seemed unsuitable for such purposes because of the presence of the derivative of the energy with respect to one parameter.

Makarewicz (1991) used standard Rayleigh–Schrödinger perturbation theory to treat the PMO. He determined the necessary matrix elements by means of recurrence relations originating in the hypervirial theorems and expressed the results as double power series of an appropriate parameter and the vibrational quantum number. To overcome the problem of the incompleteness of the set of bound-state eigenfunctions of the Morse oscillator Makarewicz truncated the series in a convenient way. Although he did not justify this truncation rigorously, his results showed that it was successful; the equations appear so complicated, however, that even numerical calculation must be laborious.

Our purpose is to present two alternative calculations, with perturbations of large order, of the eigenvalues of PMO which are much simpler than the approach of Makarewicz (1991). Both are based on the combination of the hypervirial relations, the Hellmann–Feynman theorem and Rayleigh–Schrödinger perturbation theory proposed by Swenson and Danforth (1972) and subsequently used extensively (for reviews see Fernández and Castro 1987, Arteca *et al* 1990). We choose the unperturbed model to be the harmonic oscillator in section 2 and the Morse oscillator in section 3 so as to obtain perturbation expansions in terms of the parameter proposed by Makarewicz (1991). We compare both series and draw conclusions about the application of perturbation theory to the vibration-rotational spectroscopy of diatomic molecules. We apply the method analogously to another modification of the Morse oscillator as a further example of its utility.

2. Harmonic oscillator as unperturbed model

According to the Born–Oppenheimer approximation one obtains the vibration-rotational energies of a diatomic molecule from the eigenvalues of the rotating oscillator

$$-\hbar^2/(2\mu)\,\mathrm{d}^2/\mathrm{d}R^2+U(R) \tag{1}$$

in which R is the internuclear distance, μ is the reduced mass and $U(r)$ is the effective potential energy

$$U(R)=V(R)+\hbar^2J(J+1)/(2\mu R^2). \tag{2}$$

Throughout this paper we consider $^1\Sigma$ electronic states. In the latter equation $V(R)$ is the potential-energy function and J is the rotational quantum number. For the sake of simplicity and purposes of comparison, we expand $U(R)$ about its minimum at R_0. This point reduces to R_e, the equilibrium distance and minimum of $V(R)$, when $J=0$. We define a dimensionless coordinate $x=a(R-R_0)/\lambda$ in which a is a conveniently chosen reciprocal distance (Huffaker and Dwivedi 1978, Makarewicz 1991) and λ is the perturbation parameter explicitly defined below.

We expand $U(R)$ in a power series of x

$$U(R)=U_0+\sum_{j=2}^{\infty} U_j(\lambda/a)^j x^j \qquad U_j=(j!)^{-1}\,\mathrm{d}^jU/\mathrm{d}R^j|_{R=R_0} \tag{3}$$

and define $D=U_2/a^2$ and $q^2=\hbar^2a^2/(8\mu D)$. Here q is the expansion variable used by Makarewicz (1991) which is related to Huffaker's (1976a, b) parameter σ according to $q=1/(2\sigma)$. The unperturbed Hamiltonian takes a conveniently simple form when $\lambda^2=2q$ and the resulting dimensionless perturbed Hamiltonian is useful for the application of perturbation theory:

$$\mathscr{H}=(\lambda^2D)^{-1}(H-U_0)=-\mathrm{d}^2/\mathrm{d}x^2+x^2+\sum_{j=1}^{\infty} u_j\lambda^jx^{j+2} \tag{4}$$

in which $u_j=(a^jU_2)^{-1}U_{j+2}$. The eigenvalues $\mathscr{E}$ of $\mathscr{H}$ are related to the energies E by $E=2qD\mathscr{E}$.

When $\lambda=0$, the Hamiltonian $\mathscr{H}$ reduces to that of a harmonic oscillator having unit mass and force coefficient. We apply perturbation theory to obtain the vibration-rotational energies as a series of λ to non-negative powers. Let $\mathscr{E}_p$ be the coefficients of such an expansion for $\mathscr{E}$. As $\mathscr{H}(-\lambda,-x)=\mathscr{H}(\lambda,x)$ and as the eigenvalues are invariant to a change of variables, then $\mathscr{E}(-\lambda)=\mathscr{E}(\lambda)$. All coefficients of odd order in the expansion for the energy consequently vanish and

$$E/D=\sum_{p=0}^{\infty} 2^{p+1}\mathscr{E}_{2p}q^{p+1}. \tag{5}$$

This result is in a sense a semiclassical expansion because q is proportional to $\hbar$; this fact explains that quantum-mechanical perturbation theory and the BKW method give the same expression for the vibration-rotational energies. Another conclusion that we draw from the equations above is that any analytic representation of the potential-energy function $V(R)$ (to which we have yet to give a particular form) yields essentially the same q power series. For instance, Huffaker (1976) pointed out that by means of the appropriate transformation of potential-energy parameters his expressions for the PMO reduced to those derived by Dunham (1932) by application of the BKW method to an anharmonic oscillator obtained by expansion of the potential-energy function in powers of $R-R_e$.

To obtain the energy coefficients $\mathscr{E}_{2p}$ we use the hypervirial perturbative method (Fernández and Ogilvie 1990). One can thereby obtain all perturbation corrections to both $\mathscr{E}$ and the expectation values $X^{(N)}=\langle x^N\rangle$ from the following recurrence relations

$$X_p^{(N+1)}=\frac{1}{2N+2}\left(\tfrac{1}{2}N(N-1)(N-2)X_p^{(N-3)}+2N\sum_{k=0}^{p}\mathscr{E}_k X_{p-k}^{(N-1)}\right.$$
$$\left.-\sum_{j=1}^{p}(2N+j+2)u_j X_{p-j}^{(N+j+1)}\right) \qquad (6)$$

$$\mathscr{E}_p=\frac{1}{p}\sum_{j=1}^{p} j u_j X_{p-j}^{(j+2)} \qquad p>0 \qquad (7)$$

with the starting point $X_p^{(0)}=\delta_{p0}$ which arises from the normalization condition. Equation (6) is obtained from hypervirial relations and equation (7) from a particular form of the Hellmann–Feynman theorem. The calculation proceeds hierarchically and the nested loops $p=0,1,\ldots,P$, $N=0,1,\ldots,P-p+2$ are sufficient to obtain $\mathscr{E}_p$ upto $p=P$. As the eigenfunctions Ψ of the rotating oscillator are non-degenerate, the argument used previously for the energies leads us to the conclusion that $|\Psi|^2(-\lambda,-x)=|\Psi|^2(\lambda,x)$ from which $X^{(N)}(-\lambda)=(-1)^N X^{(N)}$ follows. Therefore $X_p^{(N)}$ vanishes when $N+p$ is odd. We indicated this result previously (Fernández and Ogilvie 1990) but did not prove it.

The recurrence relations (6) and (7) are much easier to use than the numerous equations and successive expansions proposed by Makarewicz (1991). Furthermore, the present calculation is straightforward and yields the correct expansion in powers of q without questionable truncations. If one is interested in the calculation of only the energies, the present method is preferable to that used by Huffaker and Dwivedi (1975) which requires the expansion of matrix elements and energy denominators as series in σ to negative powers (Huffaker and Dwivedi 1975, Huffaker 1976a, b). The recurrence relations (6) and (7) are more convenient than the BKW method (Dunham 1932) and are suitable for both analytic and numerical computation, the former facilitated by available processors for symbolic computation (Fernández and Ogilvie 1990, Ogilvie 1991a, b). As an instance of a numerical calculation, and to show the rate of convergence of the perturbation series, we show in table 1 results for two cases studied by Makarewicz (1991). We deliberately chose the examples with the largest

Table 1. Vibration-rotational energy of the state with $J=0$ and $v=10$ calculated by means of the truncated PMO reported by Huffaker (1976b); P denotes the largest perturbation order ($\mathscr{E}_{2P}$) included in the series (5).

P	E (CO)/cm^{-1}	P	E (HCl)/cm^{-1}
0	22 783.093 61	0	31 406.083 33
1	21 317.986 81	2	25 842.441 08
2	21 330.690 72	4	25 726.780 26
3	21 330.965 62	6	25 722.426 23
4	21 330.591 97	8	25 723.293 22
5	21 330.630 07	10	25 723.346 84
6	21 330.629 67	12	25 723.324 05
7	21 330.629 47	14	25 723.322 69
8	21 330.629 46	16	25 723.323 46
9	21 330.629 46	18	25 723.323 50
10	21 330.629 46	20	25 723.323 47
		22	25 723.323 47

vibrational quantum numbers for which the convergence of the perturbation series is least rapid. The convergence can be accelerated in many ways (Arteca *et al* 1990) but our purpose here is not primarily to achieve highly accurate numerical results. We present in table 2 the coefficients, obtained by means of the symbolic processor Maple, of q, q^2, q^3 and q^4 for the PMO

$$U(R)=D\left(y^2+\sum_{j=3} b_j y^j\right) \qquad y=1-\exp[-a(R-R_0)]. \tag{8}$$

In order to obtain simpler expressions we set $b_3=0$ as this term can be eliminated by an appropriate choice of the unperturbed Morse oscillator (Dunham 1932, Huffaker 1976a, b, 1978, 1980, Huffaker and Dwivedi 1978, Dwivedi and Huffaker 1977).

Table 2. Coefficients of the first four powers of q obtained by means of the method in section 2 for the case $b_3=0$.

Coefficient of q

$$2D\mathscr{E}_0$$

Coefficient of q^2

$$D[\tfrac{3}{2}b_4+(\tfrac{3}{2}b_4-1)\mathscr{E}_0^2]$$

Coefficient of q^3

$$(D/2)[(25b_6-3b_4-\tfrac{67}{4}b_4^2-15b_5)\mathscr{E}_0+(5b_6-b_4-\tfrac{17}{4}b_4^2+5b_5)\mathscr{E}_0^3]$$

Coefficient of q^4

$$\begin{aligned}(D/4)[(&-165b_4b_6/4-15b_5/2-165b_4b_5/4-15b_6/2+35b_8/2+65b_4^2/8-315b_5^2/8\\ &+35b_7/2+375b_4^3/16)\mathscr{E}_0^4+(237b_4^2/4+715b_4b_5/2+245b_8-75b_6+1707b_4^3/8\\ &-1085b_5^2/4-885b_4b_6/2-175b_7+45b_5)\mathscr{E}_0^2-27b_5/2+245b_6/2-1107b_5^2/8-875b_4^2/8\\ &-945b_4b_6/4-525b_7/2+315b_8/2+1743b_4b_5/4+1539b_4^3/16]\end{aligned}$$

3. Morse oscillator as unperturbed model

The expansion of the energies in q (Makarewicz 1991) or $1/\sigma$ (Huffaker 1976a, b) to various powers is generally used to keep track of the orders of magnitude of the contributions to the coefficients Y_{kl} (Dunham 1932). Neither factorization (Huffaker and Dwivedi 1975) nor standard Rayleigh–Schrödinger perturbation theory (Makarewicz 1991) gives such series directly; for this reason further expansion of some quantities in either approach is required. The method described in the preceding section yields the desired expansion straightforwardly. Whether one can obtain directly the corresponding expansion when the Morse oscillator is the unperturbed model is addressed in what follows.

Again we consider the rotating oscillator (1) with the effective potential-energy function (8) but here we introduce a perturbation parameter λ in order to collect the perturbation terms in a particular way

$$U(R)=D\left(y^2+\sum_{j=1}^{\infty} b_{j+2}\lambda^j y^{j+2}\right). \tag{9}$$

This parameter is set equal to unity at the end of the calculation. We can also place λ in front of the sum and treat it in its entirety as a single perturbation to the Morse oscillator; this strategy was followed by Fernández and Castro (1982a, b). To show the flexibility of the hypervirial perturbative method we consider the order of each term in the sum to be arbitrarily larger than that of the preceding one; this approach is useful when the coefficients decrease as the order increases. Different rearrangements of the perturbation may lead to different rates of convergence; we do not here amplify this point as our primary concern is to demonstrate the equivalence of different representations of the potential-energy function when the energies are expanded in powers of the same parameter.

In this case we define the dimensionless Hamiltonian operator

$$\mathscr{H} = H/D = -4q^2(\mathrm{d}^2/\mathrm{d}x^2) + \mathscr{U} \tag{10}$$

in which $x = a(R - R_0)$ and $\mathscr{U} = U/D$. The eigenvalues $\mathscr{E}$ of $\mathscr{H}$ are related to the vibration-rotational energies E by $\mathscr{E} = E/D$. As previously reported (Fernández and Castro 1982a, b), the hypervirial relations and the Hellmann–Feynman theorem,

$$\partial\mathscr{E}/\partial\lambda = \sum_{j=1}^{\infty} j b_{j+2} \lambda^{j-1} Y^{(j+2)} \tag{11}$$

in which $Y^{(j)}$ denotes the expectation value of y^j, are insufficient for a complete calculation according to perturbation theory. To overcome this difficulty one makes further use of the Hellmann–Feynman theorem:

$$\partial\mathscr{E}/\partial q = -8q\langle \mathrm{d}^2/\mathrm{d}x^2\rangle = 2(\mathscr{E} - \langle\mathscr{U}\rangle)/q. \tag{12}$$

Straightforward use of the hypervirial relations and perturbation theory (Fernández and Castro 1982a, b) leads to the following recurrence relation for the perturbation corrections to the eigenvalues $\mathscr{E}$ and to the expectation values Y:

$$Y_p^{(1)} = \mathscr{E}_p - (q/2)(\partial\mathscr{E}_p/\partial q) + (1/2)\sum_{k=1}^{p} b_{k+2}[kY_{p-k}^{(k+2)} - (k+2)Y_{p-k}^{(k+1)}] \tag{13a}$$

$$\begin{aligned} Y_p^{(N+2)} = \frac{1}{2N+2}\Bigg(&2q^2[N^3 Y_p^{(N)} - N(3N^2-3N+1)Y_p^{(N-1)} \\ &+ 3N(N-1)^2 Y_p^{(N-2)} - N(N-1)(N-2)Y_p^{(N-3)}] \\ &+ 2(N+1)Y_p^{(N+1)} + 2N\sum_{k=0}^{p}\mathscr{E}_k(Y_{p-k}^{(N)} - Y_{p-k}^{(N-1)}) \\ &+ \sum_{k=1}^{p}(2N+k+2)b_{k+2}(Y_{p-k}^{(N+k+1)} - Y_{p-k}^{(N+k+2)})\Bigg) \end{aligned} \tag{13b}$$

$$\mathscr{E}_p = \frac{1}{p}\sum_{j=1}^{p} j b_{j+2} Y_{p-j}^{(j+2)}. \tag{13c}$$

We derived the first equation here from the second with $N = 0$ and the expansion of equation (12) in a series of λ to non-negative powers. The calculation of the perturbation corrections is straightforward and proceeds hierarchically as in the previous case starting from the normalization condition $Y_p^{(0)} = \delta_{p0}$. The equations in this set are also much simpler than those proposed by Huffaker and Dwivedi (1975) and Makarewicz (1991). The presence of the derivative $\partial\mathscr{E}_p/\partial q$ offers no serious difficulty as it is easily handled by means of any symbolic processor. However, if one requires accurate and

Table 3. Vibration-rotational energy for the state with $J = 0$ and $v = 10$ calculated by means of the truncated PMO reported by Huffaker (1976b); P denotes the largest order of perturbation included in the series given by the method in section 3.

P	E (CO)/cm^{-1}	E (HCl)/cm^{-1}
0	21 233.989 47	24 877.631 07
2	21 314.162 07	25 485.590 04
3	21 322.415 82	25 667.848 97
4	21 329.064 54	25 742.772 92
5	21 330.033 57	25 732.609 92
6	21 330.726 04	25 725.241 04
7	21 330.684 66	25 722.833 87
8	21 330.636 16	25 722.760 39
9	21 330.631 76	25 723.041 44
10	21 330.629 29	25 723.330 65
11	21 330.629 17	25 723.380 24
12	21 330.629 39	25 723.339 04
13	21 330.629 43	25 723.329 50
14	21 330.629 47	25 723.321 28
15	21 330.629 47	25 723.319 99
16	31 330.629 47	25 723.323 40
17		25 723.323 62
18		25 723.323 51
19		25 723.323 65
20		25 723.323 45

rapid numerical calculations of large order one can expand all the quantities in equations (13) in series of q to non-negative powers so as to obtain the coefficients from the resulting recurrence relations. This further development is unnecessary for the present purposes. In table 3 we demonstrate the rate of convergence of the series $E = D(\mathscr{E}_0 + \mathscr{E}_1 + \ldots + \mathscr{E}_m + \ldots)$ for the same PMO examples considered before. The calculation was done by means of a simple program in Maple. We used the same processor to perform analytically the calculation to verify that the coefficients of q to the first three powers in the expression of the energy agree with the results in table 2 as expected from the reasoning of the previous section. The choice of the unperturbed model is clearly immaterial if one is interested in merely the expansion of the energies in polynomials in q or σ^{-1}.

4. Modified Morse oscillator

Coxon and Hajigeorgiou (1990) proposed a modification of the Morse oscillator equivalent to

$$V(R) = D_e\{1 - \exp[-u(x)]\}^2 \tag{14a}$$

in which $x = (R - R_e)/R_e$ and

$$u(x) = \sum_{j=1}^{\infty} u_j x^j \tag{14b}$$

as a starting point for the inverse perturbative approach. In their analysis of the vibration-rotational spectra of isotopic variants of HCl, these authors used the potential-energy function determined in this way to predict the wavenumbers of spectral lines of $T^{35}Cl$ and $T^{37}Cl$. Here we prove that the method in section 2 is useful to derive expressions for the coefficients Y_{kl} (Dunham 1932) in terms of the parameters of the potential-energy function above. For simplicity we expand the vibration-rotational energies as

$$E = \omega_e \sum_{p=0}^{\infty} \mathscr{E}_{2p}\gamma^p + B_e J(J+1) = \sum_k \sum_l Y_{kl}(v+1/2)^k [J(J+1)]^l \tag{15}$$

in which $\gamma = (2B_e/\omega_e)^{1/2}$, B_e and ω_e are the spectral parameters related to the equilibrium internuclear distance and force coefficient, and v and J are the vibrational and rotational quantum numbers, respectively. We obtain the coefficients of the expansion (15) by means of the hypervirial perturbative method (Fernández and Ogilvie 1990) which leads to the following recurrence relations for the perturbation corrections to E and to $Z^{(N)} = \langle \xi^N \rangle$, $\xi = (R - R_e)/(\gamma^{1/2} R_e)$:

$$\begin{aligned} Z_p^{(N+1)} = \frac{1}{N+1}\Big(& \tfrac{1}{4}N(N-1)(N-2)Z_p^{(N-3)} + 2N\mathscr{E}_0 Z_p^{(N-1)} \\ & + \sum_{i=1}^{p} [2N\mathscr{E}_i Z_{p-i}^{(N-1)} - (N+i/2+1)a_i Z_{p-i}^{(N+i+1)} \\ & - (-1)^i (i+1)(2N+i) J_B Z_{p-i}^{(N+i-1)}]\Big) \end{aligned} \tag{16}$$

$$\mathscr{E}_p = \frac{1}{p} \sum_{i=1}^{p} \mathrm{i}[\tfrac{1}{2}a_i Z_{p-i}^{(i+2)} + J_B(-1)^i(\mathrm{i}+1)Z_{p-i}^{(i)}] \qquad p > 0. \tag{17}$$

Here $\mathscr{E}_0 = (v+1/2)$ and $J_B = B_e J(J+1)/\omega_e$. As before the energy coefficients $\mathscr{E}_{2k+1}$ vanish for all $k = 0, 1, \ldots$. As the procedure is similar to those discussed in the previous two sections we need not amplify it here.

The expansion about the minimum of $U(R)$ leads to a perturbation series with better convergence properties than the one used here that originates in the expansion around the minimum of $V(R)$. However, for the purpose of fitting the series to the experimental spectra we prefer the latter because it is simpler. In table 4 we list contributions to selected coefficients Y_{kl} in terms of the parameters of the potential-energy function (14). We can generate many more by means of the recurrence relations (17) and the symbolic processor Maple and use them in a least-squares fitting of spectral lines. The advantage of the use of analytic expressions is that the subsequent numerical fitting is more rapid and that rounding errors are diminished.

Table 4. Leading contributions to various coefficients Y_{kl} for the modified Morse oscillator of section 4.

$$\begin{aligned} Y_{10} &= \omega_e \\ Y_{20} &= B_e(-u_1^2 + 3u_2 - 6u_2^2/u_1^2 + 3u_3/u_1) \\ Y_{30} &= (B_e^2/\omega_e)(-64u_2u_3/u_1 + 11u_1u_3/2 + 20u_4 + 10u_5/u_1 - 12u_3^2/u_1^2 - 68u_2^4/u_1^4 \\ &\quad + 138u_2^2u_3/u_1^3 - 60u_2u_4/u_1^2 + 28u_2^3/u_1^2 + 7u_2^2 - 11u_1^2u_2/3) \\ Y_{01} &= B_e \\ Y_{02} &= -4B_e^3/\omega_e^2 \\ Y_{11} &= (B_e^2/\omega_e)(-6u_1 + 12u_2/u_1 + 6) \\ Y_{21} &= (B_e^3/\omega_e^2)(30 - 252u_2u_3/u_1^2 + 120u_2/u_1 + 66u_3 + 15u_2u_1 + 60u_4/u_1 + 69u_1^2/2 \\ &\quad - 126u_2 - 84u_2^2/u_1 + 204u_2^3/u_1^3 - 60u_1 - 36u_3/u_1 + 162u_2^2/u_1^2 - 7u_1^3) \end{aligned}$$

5. Discussion and conclusion

We have presented two different applications of perturbation theory to the model of the rotating oscillator for diatomic molecules which are simpler than both the factorization method proposed by Huffaker and Dwivedi (1975) and the standard Rayleigh–Schrödinger perturbation theory that Makarewicz (1991) employed. The approach developed by Fernández and Ogilvie (1990) outlined in section 2 is certainly simpler and more rapid than the one in section 3; the convergence velocities of both series appear to be comparable. The main disadvantage of these perturbation theories without wavefunction is that they allow the calculation of no physical observable other than the energies and expectation values of chosen operators. In contrast, the factorization method (Huffaker and Dwivedi 1975) is suitable for the calculation of matrix elements and Franck–Condon factors (Dwivedi and Huffaker 1977, Huffaker and Dwivedi 1978).

The second point made plain here is that one obtains the same power series in the argument q (or σ^{-1}) regardless of the unperturbed model. Such expansions have become a standard way to analyse spectral data; increasingly further terms are required as the precision of experimental data increases. For this reason there is much interest in the improvement of the pertinent algorithms. Our method (Fernández and Ogilvie 1990) is suitable for the introduction of adiabatic and non-adiabatic effects (Ogilvie 1991a, b) because of the simplicity of the recurrence relations. Although all the analytic representations of the potential-energy function yield essentially the same q-power series for the energies, their ranges of validity as functions of $R - R_e$ differ. A commonly used strategy is the substitution of the desired representation of the potential-energy function (Simons *et al* 1973, Thakkar 1975, Ogilvie 1974, 1981) for the series in $R - R_e$ (Dunham 1932) that one produces easily by means of the approach in section 2.

The defect of the simple Morse oscillator and any modifications so far proposed is that all these functions applied to the potential energy of real molecules possess an incorrect asymptotic behaviour as R becomes large, or as the potential energy approaches the dissociation limit at large R. The correct behaviour is that of an inverse power of R, i.e. R^{-n}; the applicable power n depends on the nature of the dissociation products (Le Roy 1973). For this reason any use of these Morse functions prototypical or modified must be limited, if one is to reproduce accurately the observed frequencies of the spectral transitions, to the region of energy much less than that at the dissociation limit.

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