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Calculation of rotational energies of molecules in electric and magnetic fields by perturbation theory

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Perturbation theory is shown to be one of the most powerful tools in calculating rotational eigenenergies of molecules in electric and magnetic fields, provided that the rigid-rotator approximation holds. The energy shifts for the Stark effect in symmetric-top molecules and for the hydrogen molecular ion in a magnetic field are accurately calculated in the whole range of field intensities.

I. INTRODUCTION

Recently, there has been a great interest in obtaining the energy shifts for the Stark effect in diatomic and symmetric-top molecules by perturbation theory (PT).[1–8] Though the rigid-rotator approximation invoked in those calculations is somewhat rough, results are supposed to be useful in the interpretation of molecular-beam resonance and electrical level crossing experiments,[9] in the calculation of permanent dipole moment and polarizability anisotropies,[1,2,9,10] and even in the study of the dynamic Stark effect in symmetric-top molecules.[11,12] A PT calculation has also proved to be suitable in a theoretical study of the hydrogen molecular ion in a uniform magnetic field[13] which has been motivated by recent experiments on semiconductors.

When dealing with PT, two problems always arise: the calculation of the perturbation corrections and the summation of the Taylor expansions. Since the usual Rayleigh-Schrödinger PT leads to too-cumbersome expressions,[1–3] appropriate techniques have been recently developed in order to obtain large-order corrections.[4–8,14]

The second difficulty is due to the well-known fact that most problems of physical interest lead to divergent power series. Fortunately, the perturbation series for the models we consider in this paper are found to have finite convergence radii. But even in such favorable cases a difficulty still remains, since a perturbation expansion has to include a very large number of terms in order to yield accurate enough results when the perturbation parameter approaches the convergence radius closely. Moreover, the convergence radius is sometimes so small that the physical value of the perturbation parameter lies beyond it. These obstacles in PT calculations made other approximate methods preferable.

The purpose of this paper is to show that PT is a powerful tool in calculating rotational energies of molecules in electric or magnetic fields, provided that the rigid-rotator approximation holds. In Sec. II we develop quite general hypervirial relationships which will prove to be useful in Secs. III and IV when obtaining the perturbation series for the small- and large-field cases, respectively. In Sec. V we show how to rearrange a power series so that both its convergence rate and convergence radius are largely increased. Results are discussed in Sec. VI, where the perturbation series for the small- and large-field cases are shown to match smoothly in the intermediate region, thereby yielding very accurate and reliable energies in the whole range of field strengths. Besides, the method developed in Sec. V will prove to improve markedly the matching as well as the results that can be obtained from only one of the above-mentioned perturbation expansions.

II. GENERAL HYPERVIRIAL RELATIONSHIPS

In order to obtain the energy perturbation corrections in both the small- and large-field cases we will use a generalized Swenson and Danforth procedure[15,16] which from now on will be called the hypervirial perturbative method (HPM)[17–19] and that we will briefly discuss to make the paper self-contained. In this section we develop quite general hypervirial relationships that, together with the Hellmann-Feynman theorem, are the main ingredient of the HPM.

All of the quantum-mechanical models studied in this paper can be represented by the following general eigenvalue equation:

$$L\psi(x)=ER(x)\psi(x)\ , \quad a\leq x\leq b \tag{1}$$

L being a self-adjoint operator,[20] with

$$L=\frac{d}{dx}P(x)\frac{d}{dx}+Q(x)\ . \tag{2}$$

By a straightforward manipulation it is very easy to show that

$$[L,f(d/dx)]=(1/P)(2Pf'-fP')(L-Q)+[L,Y]+(PY')'-fQ'\ , \tag{3}$$

where $f\equiv f(x)$ is any differentiable function ($f'\equiv df/dx$, etc.) and $[A,B]=AB-BA$ is the commutator of the operators A and B. The function $Y(x)$ is a solution of

$$Y'(x)=\tfrac{1}{2}[(fP'/P)'-f'']\ . \tag{4}$$

When $P[\psi(f\psi')'-f\psi'^2]$ vanishes at the points a and b, it immediately follows from Eq. (3) that

$$\langle (fP'-2Pf')(Q-ER)/PR \rangle + \langle (PY')'/R \rangle + \langle (ER-Q)'f/R \rangle = 0 \,, \tag{5}$$

where

$$\langle A \rangle = \int_a^b \psi A \psi R \, dx \tag{6}$$

holds for the expectation value of the operator A provided ψ is real and normalized to unity:

$$\int_a^b \psi^2(x) R(x) dx = 1 \,. \tag{7}$$

Let us now suppose that Q also depends upon a real parameter λ [i.e., $Q \equiv Q(\lambda,x)$]. In such a case, the rate of change of the eigenvalue E with λ is given by the well-known Hellmann-Feynman theorem:

$$\partial E/\partial\lambda = \langle (\partial Q/\partial\lambda) \rangle \,. \tag{8}$$

Both the hypervirial relationships (5) and the Hellmann-Feynman theorem (8) will prove to be useful in calculating the energy perturbation corrections in Secs. III and IV.

III. SMALL-FIELD CASE

As said before, in this paper we study only linear and symmetric-top molecules under the rigid-rotator (and, of course, under the Born-Oppenheimer) approximation. Therefore, it is sufficient to consider the latter and more general problem that includes the former, as will be briefly discussed below.

The stationary Schrödinger equation describing the rotational motion of a rigid symmetric-top molecule that bears the influence of a potential $U(\lambda,\theta)$ is[3]

$$[-\sin^{-1}\theta (d/d\theta)\sin\theta (d/d\theta) + (M^2+K^2)\sin^{-2}\theta - 2KM\cot\theta\sin^{-1} + U(\lambda,\theta)]\psi(\theta) = W\psi(\theta) \,, \tag{9a}$$

$$M,K = 0, \pm 1, \pm 2, \ldots, \pm J, \quad J = 0,1,2,\ldots \,, \tag{9b}$$

where θ is the angle between the z and molecular symmetry axes, W is the adimensional energy, and J,K,M are the quantum numbers related to the total angular momentum and its projections onto the above-mentioned axes, respectively. The total wave function can be written as $\Psi(\phi,\chi,\theta) = \exp[i(M\phi + K\chi)]\psi(\theta)$, where as usual ϕ and χ are the remaining Euler angles.[3] When $K=0$, Eq. (9) becomes the Schrödinger equation for the hindered rotational motion of a rigid diatomic molecule.

When $U(\lambda,\theta) = \lambda V(\theta)$, $V(\theta)$ being a periodic, bounded function of θ, Kato's theorem[21] states that the perturbation expansions

$$W = \sum_{i=0}^{\infty} W_i \lambda^i, \quad W_0 = J^* = J(J+1), \quad \psi = \sum_{i=0}^{\infty} \psi_i \lambda^i \,, \tag{10}$$

have a finite, non-null convergence radius.

In order to simplify notation, we will write W and ψ instead of W_{JKM} and ψ_{JKM} throughout this paper, except in those cases where it may be misleading.

It will be sufficient for us to consider only the quite general potential function

$$U(\lambda,\theta) = \sum_{j=1}^{\infty} c_j \lambda^j \cos^j\theta \,, \tag{11}$$

where the perturbation parameter λ (related to the field intensity) and the coefficients c_j depend on the problem studied. For example, the shifts of the rotational energy levels of a polar, symmetric-top molecule in a uniform electric field of intensity ϵ are given by Eq. (9) with (throughout this paper, field directions are supposed to coincide with the z axis)[3]

$$U(\lambda,\theta) = c_1\lambda\cos\theta + c_2\lambda^2\cos^2\theta \,, \tag{12a}$$

$$c_1 = -1, \quad c_2 = (4I_B\mu^2)^{-1}\hbar^2(\alpha_{xx} - \alpha_{zz}) \,, \quad \lambda = 2\mu\epsilon I_B/\hbar \,, \tag{12b}$$

$$W = 2I_B E/\hbar^2 + (I_C - I_B)K^2/I_C + (4I_B\mu^2)^{-1}\hbar^2\alpha_{xx}\lambda^2 \,, \tag{12c}$$

where E is the energy, μ is the molecular dipole moment, I_C is the moment of inertia about the symmetry axis, I_B is the remaining (twofold degenerate) principal moment of inertia, and α_{zz} and $\alpha_{xx} = \alpha_{yy}$ are the components of the diagonal polarizability tensor.

To deal with the rotational motion of the hydrogen molecular ion H_2^+, in a magnetic field, we can also use Eq. (9) with $K=0$. Larsen[13] showed that the interaction potential for this problem is given approximately by

$$U(\theta) = mr_e^2(A_R + B_R\sin^2\theta)\sin^2\theta \,, \tag{13a}$$

where m is the reduced mass of the system, r_e is the equilibrium value of the internuclear separation, and A_R, B_R ($|A_R| > |B_R|$) are constants depending on an adimensional form of the magnetic field intensity.[13] In this case the rotational energy E is related to W by

$$W = mr_e^2 E \,. \tag{13b}$$

Obviously, Eq. (13a) can be easily rewritten as in Eq. (11), with $c_j = 0$ if $j > 4$, by a proper definition of λ and c_j.

We now show how to apply PT to the general model given in Eqs. (9) and (11). To begin with, we notice that Eq. (9) is a particular case of Eqs. (1) and (2) with

$$x \equiv \theta, \quad P(\theta) = R(\theta) = \sin\theta, \quad (a,b) \equiv (0,\pi) \,, \tag{14a}$$

$$Q(\lambda,\theta) = (M^2+K^2)/\sin\theta - 2KM\cot\theta + U(\lambda,\theta)\sin\theta \,. \tag{14b}$$

Therefore, the general hypervirial relationship (5) must hold in the present case. If we choose f in Eq. (5) to be any function in the set $\{f_s(\theta)\}$,

$$f_s(\theta) = \sin\theta\cos^s\theta, \quad s = 0,1,2,\ldots \tag{15}$$

we will straightforwardly obtain the following recursion relationship:

$$[2(s+1)W-s(s^2/2+3s/2+1)]G^{(s+1)}+s[s^2-2W+2(M^2+K^2)]G^{(s-1)}$$
$$-(s/2)(s-1)(s-2)G^{(s-3)}-2KM(2s+1)G^{(s)}-\sum_{i=1}^{\infty}ic_i\lambda^i[G^{(s+i+1)}-G^{(s+i-1)}]$$
$$-2\sum_{i=1}^{\infty}[(s+1)c_i\lambda^iG^{(s+i+1)}-sc_i\lambda^iG^{(s+i-1)}]=0\ , \tag{16a}$$

among the expectation values

$$G^{(s)}=\langle\cos^s\theta\rangle,\ s=0,1,\ldots\ . \tag{16b}$$

We then apply PT by expanding W and every $G^{(s)}$ in powers of λ [cf. Eq. (10)]:

$$W=\sum_{i=0}^{\infty}W_i\lambda^i,\ \ G^{(s)}=\sum_{i=0}^{\infty}G_i^{(s)}\lambda^i\ . \tag{17}$$

Though in this way we do not get the wave function explicitly, we obtain all of the expectation values $G^{(s)}$ that are closely related to many physical properties of the system.

If we expand W and each $G^{(s)}$ in Eq. (16) in powers of λ and make use of the Hellmann-Feynman theorem [cf. Eq. (8)],

$$\partial W/\partial\lambda=\sum_{i=1}^{\infty}ic_iG^{(i)}\lambda^{i-1},$$
$$tW_t=\sum_{j=0}^{t-1}(j+1)c_{j+1}G_{j-t-1}^{(j+1)}\ , \tag{18}$$

to eliminate each W_i in the resulting equation, we obtain, after equating to zero the coefficient of λ^t, the following recursion relationship:

$$[2(s+1)J^*-s(\tfrac{1}{2}s^2+\tfrac{3}{2}s+1]G_t^{(s+1)}+2(s+1)\sum_{i=1}^{t}\sum_{j=0}^{i-1}\frac{j+1}{i}c_{j+1}G_{i-j-1}^{(j+1)}G_{t-i}^{(s+1)}$$
$$+s[s^2-2J^*+2(M^2+K^2)]G_t^{(s-1)}-2s\sum_{i=1}^{t}\sum_{j=0}^{i-1}\frac{j+1}{i}c_{j+1}G_{i-j-1}^{(j+1)}G_{t-i}^{(s-1)}-\tfrac{1}{2}s(s-1)(s-2)G_t^{(s-3)}$$
$$-2KM(2s+1)G_t^{(s)}+\sum_{j=0}^{t-1}[(2s+j+1)c_{j+1}G_{t-j-1}^{(s+j)}+(2s+j+3)c_{j+1}G_{t-j-1}^{(s+j+2)}]=0\ . \tag{19}$$

Any perturbation correction $W_i,G_j^{(s)}$ can be obtained from Eqs. (18) and (19) through a recursive calculation starting off with the normalization condition [cf. Eqs. (7) and (14a)] $G_t^{(0)}=\delta_{t0}$. Of course, $G_t^{(s)}=0$ if $t<0$.

In two previous papers[8,14] we have used the HPM to obtain approximate analytical expressions for the energy levels of problems (12) and (13) in terms of the quantum number J, K, and M. Since Eq. (19) is very easy to solve with a computer, we have also obtained the eigenvalues very accurately.[8,14] However, due to the fact that the Taylor series (17) have a finite convergence radius and that they must be truncated to carry out any calculation, results obtained in this way are reliable only when λ is small enough. In the next sections we will show how to get PT energies valid in the entire range of λ values.

IV. LARGE-FIELD CASE

The aim of this section is to supplement the λ power series obtained in Sec. III, which is reliable only when λ is small enough, with another one valid for large enough λ values. If both perturbation expansions were found to match smoothly in the intermediate region, we would then have quite accurate results in the whole range of field intensities.

If we neglect polarization effects, the interaction potential (12) becomes

$$U(\lambda,\theta)=-\lambda\cos\theta\ . \tag{20}$$

This simple model proved to be useful when dealing with the static[3] and dynamic[11,12] Stark effect and we will use it as an illustrative example here.

As the field strength increases, the hindered rotation becomes an oscillation about $\theta=0$, which is where $U(\lambda,\theta)$ attains its minimum value. The larger λ, the larger the force constant of the oscillation and the smaller the amplitude of the motion. It is then possible to apply PT and to expand the energy and the wave function in powers of $\lambda^{-1/2}$.[22-24] Obviously, these perturbation series become increasingly accurate as $\lambda\to\infty$ and thus they are an appropriate supplement for those series in Sec. III. Moreover, the large-field expansions proved to be useful by themselves in calculating physical properties of molecular systems in strong electric[9,11,12] and magnetic fields.[13]

In order to apply PT when $\lambda\to\infty$, we must first rewrite the stationary Schrödinger equation (9) as

$$[-d^2/d\theta^2+(M^2+K^2-\tfrac{1}{4})/\sin^2\theta$$
$$-2KM\cot\theta/\sin\theta-U(\lambda,\theta)-W-\tfrac{1}{4}]\Phi=0\ , \tag{21}$$

where $\Phi=\sin^{1/2}\theta\psi$. We then define $x=\theta^2/\sigma$, $\sigma=(2/\lambda)^{1/2}$, and expand $\sin\theta$ and $\cos\theta$ in powers of θ having[8,24]

$$\left[x\frac{d^2}{dx^2}+\tfrac{1}{2}\frac{d}{dx}-\frac{\alpha}{x}-\frac{x}{4}+\frac{\sigma}{16}-\sum_{s=0}^{\infty}(\gamma A_s'-KMD_s/2)\sigma^{s+1}x^s+\tfrac{1}{2}\sum_{s=0}^{\infty}L_s\sigma^{s+1}x^{s+2}\right]\Phi=\mathscr{W}\Phi\ , \tag{22a}$$

where

$$\alpha=[4(M-K)^2-1]/16,\quad \gamma=[4(M^2+K^2)-1]/16\ ,\qquad \mathscr{W}=-\sigma(W+\lambda)/4\ , \tag{22b}$$

$$A_s'=2C_s+\sum_{i=0}^{s-1}C_iC_{s-i-1},\quad A_0'=2C_0\ ,\qquad C_s=2(2^{2s+1}-1)\,|\,B_{2s+2}\,|\,/(2s+2)!\ , \tag{22c}$$

$$D_s=(-1)^{s+1}/(2s+2)!+\sum_{j=0}^{s}(-1)^jA_{s-j}'/(2j)!\ ,\qquad L_s=(-1)^s/(2s+4)!\ , \tag{22d}$$

and B_{2s} are the Bernoulli numbers. By multiplying Eq. (22) by $x^{-1/2}$ we obtain a self-adjoint equation which is easily shown to be a particular case of Eqs. (1) and (2) with $(a,b)=(-\infty,\infty)$, $P(x)=x^{1/2}$, $R(x)=x^{-1/2}$, and $Q(x)$ the remaining polynomial.

After applying the procedure of Sec. III we obtain[8]

$$\tfrac{1}{8}(N-1)[2\alpha-(2N-1)(2N-3)]X_k^{(N-2)}+\tfrac{1}{2}NX_k^{(N)}+(2N-1)\mathscr{W}_0X_k^{(N-1)}-(2N-1)X_{k-1}^{(N-1)}/16$$
$$+\sum_{s=0}^{k-1}(2N+s-1)(\gamma A_s'-KMD_s/2)X_{k-s-1}^{(N+s-1)}-\tfrac{1}{2}\sum_{s=0}^{k-1}(2N+s+1)L_sX_{k-s-1}^{(N+s+1)}+(2N-1)\sum_{s=1}^{k}\mathscr{W}_sX_{k-s}^{(N-1)}=0\ , \tag{23}$$

where

$$X^{(N)}=\langle x^N\rangle=\sum_{j=0}^{\infty}X_j^{(N)}\sigma^j\ ,\quad X_j^{(0)}=\delta_{j0},\quad N=0,1,\ldots\ , \tag{24a}$$

$$\mathscr{W}=\sum_{j=0}^{\infty}\mathscr{W}_s\sigma^s,\quad \mathscr{W}_0=-\tfrac{1}{2}(2J-|M+K|+1)\ . \tag{24b}$$

To carry out any calculation we must relate both sets of perturbation corrections $\{\mathscr{W}_i\}$ and $\{X_j^{(N)}\}$. This is done via the Hellman-Feynman theorem which results in[8]

$$k\mathscr{W}_k=\tfrac{1}{16}\delta_{0,k-1}-\sum_{s=0}^{k-1}(s+1)(\gamma A_s'-KMD_s/2)X_{k-s-1}^{(s)}+\tfrac{1}{2}\sum_{s=0}^{k-1}(s+1)L_sX_{k-s-1}^{(s+2)}\ . \tag{25}$$

Using Eqs. (23)—(25) we have obtained an analytical third-order perturbation expression for the energy W [up to $\mathscr{O}(\lambda^{-3/2})$] valid for sufficiently large λ values.[8] In this paper we obtain more accurate results by solving these equations numerically with a computer. Though we do not know whether the power series (24b) is convergent, we may still be sure about the accuracy of our calculation whenever the λ and $\lambda^{-1/2}$ power series match smoothly.

The procedure just sketched applies easily to any model with a potential $U(\lambda,\theta)$ provided the depth of the potential well tends to infinity as $\lambda\to\infty$. In fact, we have successfully treated the problem posed by the hydrogen molecular ion in a uniform magnetic field.[14]

V. RENORMALIZED PERTURBATION SERIES

As will be seen in Sec. VI the λ power series converges quickly enough and matches the large-λ expansion smoothly. We can, however, increase the accuracy of the computed energy by rearranging both power series properly. Although we are not able to prove rigorously that our renormalized series really converge, we can show, by a numerical calculation, that such a rearrangement results in a remarkable improvement.

In this section we will show a new way of renormalizing perturbation series which has recently proved to be successful in dealing with the asymptotic expansions for the eigenvalues of the anharmonic oscillator and confining potential models.[25] This procedure is closely related with the functional method[26–28] that is really known to sum several divergent power series.

Let $F(g,\lambda)$ be a real, unknown function of the real variables g and λ $(0\le g,\lambda<\infty)$ so that the first $N+1$ coefficients F_i in the Taylor expansion

$$F(1,\lambda)=\sum_{i=0}^{\infty}F_i\lambda^i \tag{26}$$

are known. Suppose we are interested in calculating $F(1,\lambda)$ as accurately as possible in the whole range of λ values even though the convergence radius of (26) may be small or even null.

We can rewrite (26) in a more convenient way provided $F(g,\lambda)$ satisifies

$$F(g,\lambda)=g^aF(1,\lambda g^b)\ , \tag{27}$$

where a and b are real numbers and $b<0$. Our method consists of defining

$$\bar{F}(Z,\beta)=F(Z(1-\beta),\beta)\ , \tag{28}$$

where both Z and β are real numbers, too. It immediately follows from Eqs. (27) and (28) that

$$\bar{F}(Z,\beta)=Z^{a}(1-\beta)^{a}F(1,\lambda)\ , \tag{29}$$

where

$$\lambda=Z^{b}\beta(1-\beta)^{b}\ . \tag{30}$$

Since $b<0$, this last equation maps $0\leq\lambda<\infty$ onto $0\leq\beta<1$.

Equations (26), (29), and (30) enable us to expand $\bar{F}(Z,\beta)$ in powers of β:

$$\bar{F}(Z,\beta)=\sum_{i=0}^{\infty}\bar{F}_i(Z)\beta^{i}\ . \tag{31}$$

A straightforward algebraic manipulation shows that the new Taylor coefficients $\bar{F}_i(Z)$ are related to the original ones F_i as follows:

$$\bar{F}_j(Z)=\sum_{t=0}^{j}\sum_{i=0}^{t}(-1)^{j-1}\begin{bmatrix} a \\ j-t \end{bmatrix}\begin{bmatrix} bi \\ t-i \end{bmatrix}Z^{a+bi}F_i\ , \tag{32}$$

where $\binom{u}{i}=u(u-1)\cdots(u-i+1)/i!$. We are then able to calculate $F(1,\lambda)$ approximately as

$$S_N(Z,\beta)=Z^{-a}(1-\beta)^{-a}\sum_{i=0}^{N}\bar{F}_i(Z)\beta^{i}\ . \tag{33}$$

Since β is a bounded parameter we expect that $S_N(Z,\beta)$ will approach $F(1,\lambda)$ more closely than a sum of the first $N+1$ terms in Eq. (26) does.

It only remains to obtain a proper Z value. This parameter has been introduced to improve convergence, as it can be easily shown. Let $\beta_s(Z)$ be the distance from the origin to the nearest singularity of $\bar{F}(Z,\beta)$ in the complex β plane. Therefore, the β power series, Eq. (31), converges for any $|\beta|<\beta_s(Z)$. If we were able to choose Z so that $\beta_s(Z)>1$, then $S_N(Z,\beta)$ would converge towards $F(1,\lambda)$ for any β $(0\leq\beta<1)$ and, thereby, for any λ $(0\leq\lambda<\infty)$.

Though we do not actually know $\beta_s(Z)$, we can, however, take advantage of the following argument to obtain Z. If $S_N(Z,\beta)$ converged towards $F(1,\lambda)$ (λ fixed) as $N\rightarrow\infty$, the plot $S_N(Z,\beta)$ versus Z would exhibit a plateau whose extension should increase as N increases. We thus need a good plateau criterion to determine Z. In this paper we will choose Z to be the inflection point Z_N $[(\partial^2 S_N/\partial Z^2)(Z=Z_N)=0$, λ fixed] with the smallest slope $|(\partial S_N/\partial Z)(Z=Z_N)|$.

Sometimes we do not have any scaling law like Eq. (27) but we know that $F(1,\lambda)$ obeys a large-λ expansion. In such cases we can also obtain a and b as follows. Equation (27) tells us that

$$F(1,\lambda)=\lambda^{-a/b}F(\lambda^{1/b},1)\ . \tag{34}$$

Therefore, we may argue that $F(1,\lambda)$ can be expanded in powers of $\lambda^{1/b}$ according to

$$F(1,\lambda)=\lambda^{-a/b}\sum_{i=0}^{\infty}f_i\lambda^{i/b}\ . \tag{35}$$

We are thus able to obtain a and b from a power series like (35) even though a scaling law like Eq. (27) does not hold. This is exactly what occurs in our present case, as we will see below.

If f_0 is known, in addition to the first $N+1$ coefficients F_i, we will be able to improve results by forcing S_N to behave like $F(1,\lambda)$ when $\lambda\rightarrow\infty$; that is to say

$$\lim_{\lambda\rightarrow\infty}[S_N(Z,\beta)/F(1,\lambda)]=S_N(Z,1)/f_0=1\ . \tag{36}$$

This equation leads to

$$\bar{F}_N(Z)=f_0-\sum_{i=1}^{N-1}\bar{F}_i(Z)\ . \tag{37}$$

We can thus calculate the first N coefficients $\bar{F}_j(Z)$ via Eq. (32) and then determine $\bar{F}_N(Z)$ according to Eq. (37) so that Eq. (36) is obeyed.

In what follows we will show how to apply the method just developed to the problems presented in the previous sections. Let us consider the simple model in Eq. (20) as an illustrative example. From the results in Secs. III and IV we know that W must obey

$$\begin{gathered} W+\lambda=\lambda+\sum_{i=0}^{\infty}W_i\lambda^{i}\ , \\ W+\lambda=-\lambda^{1/2}\sum_{i=0}^{\infty}2^{(i+3)/2}\mathscr{W}_i\lambda^{-i/2}\ , \end{gathered} \tag{38}$$

or

$$\begin{gathered} \lambda^{-1/2}(W+\lambda)=-\sum_{i=0}^{\infty}2^{3/2}\mathscr{W}_i\sigma^{i}\ , \\ \lambda^{-1/2}(W+\lambda)=\sigma\sum_{i=0}^{\infty}2^{(i-1)/2}W_i\sigma^{-2i}\ . \end{gathered} \tag{39}$$

Therefore, in the first case we have $a=\frac{1}{4}$, $b=-\frac{1}{2}$, and $[F(1,\lambda)=W+\lambda]$

$$\begin{gathered} F_i=W_i\ \ (i\neq1),\ \ F_1=W_1+1\ , \\ f_i=-2^{(i+3)/2}\mathscr{W}_i\ , \end{gathered} \tag{40}$$

while in the second one we must use $a=-b=2$ and $[F(1,\sigma)=\lambda^{-1/2}(W+\lambda)]$

$$F_i=-2^{3/2}\mathscr{W}_i,\ \ f_i=2^{(i-1)/2}W_i\ . \tag{41}$$

Both cases are easily treated since either set of coefficients $\{W_i\}$ or $\{\mathscr{W}_i\}$ can be obtained without any difficulty via Eqs. (19), and (23) and (25), respectively. In the Sec. VI we will show that the rearrangement of the power series just discussed improves results greatly.

VI. RESULTS AND DISCUSSION

We will now attempt to prove that PT is actually a very powerful tool in calculating rotational molecular energies. To this end, we will obtain very accurate results for all field intensities using at most 15th-order PT.

Let us begin with the model in Eq. (20). It has been numerically shown that the convergence radius of the λ power series for the Stark effect in diatomic molecules increases as the quantum numbers increase.[4] This is also

TABLE I. Rotational energy of the state $K=M=J=1$ of the model given in Eq. (20). $W^{(a)}$, 15th-order PT, small-λ case; $W^{(b)}$, 15th-order PT, large-λ case; $W^{(c)}$, numerical calculation (Ref. 9); $W^{(d)}$, Eqs. (33), (36) ($N=16$), and (40); $W^{(e)}$, Eqs. (33), (36) ($N=16$), and (41).

λ	$W^{(a)}$	$W^{(b)}$	$W^{(c)}$	$W^{(d)}$	$W^{(e)}$
1	1.465 50		1.465 50	1.465 50	1.463 57
2	0.872 9		0.873	0.872 9	0.873 0
3	0.235 5		0.236	0.235 5	0.236 8
3.5	−0.096 6	−0.1072		−0.097 0	−0.095 9
4	−0.436 3	−0.4406	−0.437	−0.436 6	−0.436 4
4.5	−0.781 6	−0.7849		−0.783 3	−0.783 3
5	−1.127 4	−1.1368	−1.136	−1.136 2	−1.136 3
5.5	−1.455 5	−1.4948			−1.494 6
10		−4.901	−4.901	−4.901 3	−4.901
14		−8.106	−8.106	−8.106 6	−8.106
18		−11.412	−11.412	−11.418	−11.412
20		−13.093	−13.092	−13.082	−13.093
100		−85.3	−85.3	−85.1	−85.3

expected to occur in all of the problems studied in this paper since analytical calculations performed earlier[8,14] suggest that the ratios W_{i+1}/W_i must decrease as the quantum numbers grow. In the present work we compare results for the state $K=M=J=1$ and $K=M=J=4$ only, but any other state may be treated in the same way.

In Tables I and II we compare our results with those obtained by Shirley[9] using continued fractions. Since this technique is nonperturbative, we will suppose that Shirley's eigenvalues are accurate up to the last decimal place reported.

In Table I ($K=M=J=1$) we notice that the small- and large-λ expansions do not cross but approach most closely about $\lambda=4.5$. We may therefore suppose that $W^{(a)}$ and $W^{(b)}$ should be used for $\lambda<4.5$ and $\lambda\geq4.5$, respectively. This yields very accurate results in the whole range of λ values.

When considering $W^{(d)}$ and $W^{(e)}$ in Table I ($\lambda=4.5$ being the matching point), one immediately concludes that the method of Sec. V improves results remarkably. In addition to this, both $W^{(d)}$ and $W^{(e)}$ are themselves accurate enough in the whole range of λ values. This fact confirms our previous assumption that the method of Sec. V actually improves convergence.

Table II shows the results for the state $K=M=J=4$. As expected, the convergence radius of the small-λ expansion is much larger than that of the state $K=M=J=1$. On the other hand, when comparing both $\lambda^{-1/2}$ power series we find that the results for the state $K=M=J=4$ are much worse (cf. $W^{(b)}$ in Tables I and II). However, if we choose $\lambda=18$ as the matching point for the state $K=M=J=4$, we obtain results that are as accurate as Shirley's.[9] Therefore, we do not need to resort to the method of Sec. V because the use of both PT series yields sufficiently accurate results in the whole range of λ values.

It is worth comparing $W^{(b)}$ ($\lambda^{-1/2}$ PT series) with $W^{(e)}$ (rearranged large-λ expansion) in Table II to see once more how greatly the method given in Sec. V increases the accuracy of the computed eigenvalues.

Let us now study the problem posed by the hydrogen molecular ion H_2^+ in a magnetic field.[13,14] Following Larsen[13] we assume $B_R=0$ in Eq. (13a) and write simply

TABLE II. Rotational energy of the state $K=M=J=4$ of the model given in Eq. (20). $W^{(a)}$, 15th-order PT, small-λ case; $W^{(b)}$, 15th-order PT, large-λ case; $W^{(c)}$, numerical calculation (Ref. 9); $W^{(e)}$, Eqs. (33), (36) ($N=16$), and (41).

λ	$W^{(a)}$	$W^{(b)}$	$W^{(c)}$	$W^{(e)}$
0.2	19.839 87		19.839 87	19.839 97
0.6	19.518 84		19.518 84	19.519 08
0.8	19.357 95		19.357 95	19.358 24
1.0	19.196 81		19.196 81	19.197 14
2.0	18.387 6		18.388	18.388 0
3.0	17.572 7		17.573	17.573 1
4.0	16.752 7		16.753	16.753 0
5.0	15.927 8		15.928	15.928 1
6.0	15.098 3		15.098	15.098 5
8.0	13.427 1	14.0	13.427	13.427 1
10.0	11.741 0	11.9	11.741	11.740 9
14.0	8.330 3	8.34	8.330	8.330 2
18.0	4.877 3	4.878	4.877	4.877 1
20.0	3.138	3.137	3.137	3.137 0

$$U(\lambda,\theta)=\lambda\cos^2\theta\ . \tag{42}$$

The small- and large-λ expansions can be easily obtained as shown in Secs. III and IV. A detailed discussion appears in Ref. 14, from which we obtain $a=\frac{1}{4}$, $b=-\frac{1}{2}$. It must be kept in mind that in this case we have to use $K=0$ since the rotation about the internuclear axis is meaningless. Figure 1 shows that the renormalized power series (circles) are valid far beyond what seems to be the convergence radius of the small-λ expansion (dashed line).

Summarizing, we have already proved that PT is very powerful in calculating rotational energies of molecular systems in electric and magnetic fields, provided that the rigid-rotator approximation holds. One may reasonably argue that, as $\lambda\rightarrow\infty$, the field strength may become too large for such an approach to remain valid. We do not discuss this point in this paper and we assume, as other authors did before,[22-24] that the rigid-rotator approximation is still useful when $\lambda\rightarrow\infty$. Though this limit may seem unphysical, it proved to be useful[9,11,12] and its consideration allowed us to improve results even in the small-field case.

The two problems that arise in any PT calculation have been already overcome in the case of rotational molecular systems. In Secs. II—V we have shown how to calculate the perturbation corrections in both the small- and large-field cases and how to sum the resulting power series for any value of the field intensity.

The results in Tables I and II show that PT may be even more accurate than some usually nonperturbative approaches like the continued fraction technique[9] and the Rayleigh-Ritz variational method.[8,14] The main advantage of PT is that knowing how the spectrum changes when the field strength is modified requires little effort after having built the perturbation polynomial. On the other hand, most nonperturbative approaches require an entire calculation for each value of the field intensity.

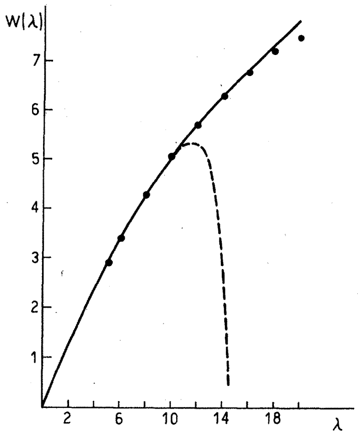

FIG. 1. Ground-state energy of the model in Eqs. (9) ($k=0$) and (42). ——, Rayleigh-Ritz variational method (Ref. 14). — — —, 14th-order PT. Small-λ case. ●, Eqs. (33), (36) ($N=15$), and (40).

Recently, two of us[29] developed a more general version of the HPM that applies to multidimensional quantum-mechanical systems having nonseparable degrees of freedom. We hope that this method, together with the resummation technique of Sec. V, will enable us to deal with the problem posed by the interaction between the rotational and vibrational motions in molecules.

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