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Rotational energy of the hydrogen molecular ion in a magnetic field

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A general method which combines hypervirial relations with the Hellmann-Feynman theorem and perturbation theory is applied in order to calculate the rotational eigenvalues of the hydrogen molecular ion in a magnetic field. Analytical expressions as well as numerical results are presented for both low and high field strengths.

I. INTRODUCTION

Recent experiments on semiconductors motivated a theoretical study of the hydrogen molecular ion $H_2{}^+$ in a magnetic field.[1] The form of the potential function for the rotational-vibrational motion of protons under the Born-Oppenheimer approximation was determined by Larsen.[1] Under certain conditions, it is a fairly good approximation to write the total potential for the proton motion in the form

$$v(x)+V(\theta)\ , \tag{1}$$

where x represents the displacement of the nuclei from the equilibrium position r_e, and θ is the angle between the internuclear axis and the direction of the applied magnetic field.

Using a least-squares procedure, Larsen fitted the change in energy with θ, by means of the function

$$V(\theta)=(A_R+B_R\sin^2\theta)\sin^2\theta\ , \tag{2}$$

where A_R and B_R depend on the dimensionless magnetic field γ.[1]

In a first approximation we can neglect the rotation-vibration interaction. Under these conditions, the rotational energy W_{LM} is given by the Schrödinger equation

$$H_R\Psi_{LM}(\theta)=W_{LM}\Psi_{LM}(\theta)\ , \tag{3a}$$

$$H_R=-\mu^{-1}r_e^{-2}\left[\sin^{-1}\theta\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}-M^2\sin^{-2}\theta\right]+V(\theta)\ , \tag{3b}$$

where L and M are the quantum numbers associated to the total angular momentum and its z component, respectively.

In the zero-field case ($\gamma=0$), the energy eigenvalues W_{LM}^0 are well known:

$$W_{LM}^0=\mu^{-1}r_e^{-2}L^*,\quad L^*=L(L+1)\ . \tag{4}$$

In the small-γ limit, $V(\theta)$ produces energy shifts which are easily calculated by use of perturbation theory. On the other hand, for large γ Larsen[1] approximated $V(\theta)$ as $A_R\theta^2$. The function $\Psi_{LM}(\theta)$ behaves like an harmonic oscillator eigenfunction in this small amplitude approximation.

The purpose of this paper is to determine the eigenvalues associated with Eq. (3) both in the large as well as in the low magnetic-field strength limits. We will not consider any issue regarding the validity of those approximations that lead to Eq. (3), because our aim is this equation in itself. Besides, the accuracy of our calculations might probably be much higher than the aforesaid model for the $H_2{}^+$ molecule, as will be seen later.

Our interest about this problem is motivated by the fact that Eq. (3) appears frequently in several problems of physical concern. For example, rotational energies of diatomic and symmetric-top polyatomic polar molecules in an electric field can be calculated by solving an equation similar to (3).[2-16]

This paper is organized as follows. In Sec. II we develop the hypervirial relationships (HR) that satisfy second-order differential self-adjoint operators in one dimension. Sections III and IV deal with the combination of HR with perturbation theory to calculate the eigenvalues corresponding to Eq. (3) in the low ($\gamma<1$) and high ($\gamma>1$) field strength cases.

The method that relates the HR with perturbation theory [termed hypervirial perturbative method (HPM) in this paper] was first developed by Swenson and Danforth[17] and then applied by various authors to study many different problems.[18-25] Notwithstanding, the version to be given below is more general than previous ones and, consequently, it allows us to apply the method to a larger class of problems. The present generalization of the HPM is due to the fact that the HR to be used include, as particular cases, those employed before.[17–25] This point is described at length in the first part of this paper.

Finally, in Sec. V we discuss some of the results obtained in previous sections as well as other problems of current physical interest which are tractable by means of the HPM.

II. GENERAL HYPERVIRIAL RELATIONS

The stationary states of the majority of one-dimensional nonrelativistic problems in quantum mechanics can be obtained from the resolution of a second-order differential equation with the general form

$$L\Psi(x)=ER(x)\Psi(x), \quad a\le x\le b \tag{5a}$$

L being a self-adjoint operator[26]

$$L=\frac{d}{dx}P(x)\frac{d}{dx}+Q(x)\ . \tag{5b}$$

For any differentiable function $f(x)$ we know that

$$\left[L,f\frac{d}{dx}\right]=\frac{1}{P}(2Pf'-fP')(L-Q)+[L,F] + (PF')'-fQ'\ , \tag{6}$$

where

$$[A,B]=AB-BA \tag{7}$$

and

$$F'(x)=\tfrac{1}{2}[(fP'/P)'-f'']\ . \tag{8}$$

As usual, $S'=dS/dx$. When the function $P[\Psi(f\Psi')'-f\Psi'^2]$ is null in the points a,b, it follows from Eq. (6) that

$$\left\langle\frac{1}{P}(fP'-2Pf')(Q-ER)\right\rangle_1+\langle(PF')'\rangle_1 +\langle f(ER-Q)'\rangle_1=0 \tag{9}$$

with

$$\langle A\rangle_1=\int_a^b \Psi A\Psi\,dx\ . \tag{10}$$

In what follows, we will assume that Ψ is normalized with the metric $R(x)dx$, i.e.,

$$\int_a^b \Psi^2(x)R(x)dx=1 \tag{11}$$

and the definition

$$\langle A\rangle=\int_a^b \Psi A\Psi R\,dx\ , \tag{12}$$

holds for the expectation value of any linear operator A.

III. LOW-FIELD CASE

The stationary Schrödinger equation (3) may be rewritten in the general form (5) if we perform the identifications

$$\begin{gathered} x=\theta,\quad a=0,\quad b=\pi,\quad P(\theta)=-\sin\theta\ ,\\ R(\theta)=\sin\theta,\quad E=\mu r_e^2W_{LM}\ ,\\ Q(\theta)=M^2/\sin\theta+\mu r_e^2V(\theta)\sin\theta\ . \end{gathered} \tag{13}$$

Since $|A_R|>|B_R|$, we restrict ourselves just to the first term of Eq. (2), i.e.,

$$Q(\theta)=M^2/\sin\theta+\lambda\sin^3\theta,\quad \lambda=\mu r_e^2A_R\ . \tag{14}$$

This restriction is really not necessary nor fundamental, because the HPM allows us to treat both terms in Eq. (2) without any trouble. The only purpose in choosing $B_R=0$ is to simplify and shorten the presentation of the method.

Substituting (13) in (9) with

$$f(\theta)=\sin\theta\cos^n\theta\ , \tag{15}$$

we deduce the equation

$$[2(n+1)E-n(n^2/2+3n/2+1)]A^{(n+1)}+n(n^2+2M^2-2E)A^{(n-1)}-\frac{n}{2}(n-1)(n-2)A^{(n-3)} +\lambda[2(n+2)A^{(n+3)}-4(n+1)A^{(n+1)}+2nA^{(n-1)}]=0\ , \tag{16a}$$

where

$$A^{(n)}=\langle\cos^n\theta\rangle\ . \tag{16b}$$

In the present case (low field strength), λ is small enough so as to expand $A^{(n)}$ and E in a power series in λ:

$$E=\sum_{s=0}^{\infty}E^{(s)}\lambda^s,\quad E^{(0)}=L^*\ , \tag{17a}$$

$$A^{(n)}=\sum_{s=0}^{\infty}A_s^{(n)}\lambda^s,\quad A_s^{(0)}=\delta_{s0}\ . \tag{17b}$$

The Hellmann-Feynman theorem

$$\partial E/\partial\lambda = \langle \sin^2\theta \rangle = 1 - A^{(2)} \tag{18}$$

allows us to write $E^{(s)}$ in terms of $A_{s-1}^{(2)}$:

$$sE^{(s)} = \delta_{0,s-1} - A_{s-1}^{(2)} \ . \tag{19}$$

Finally, replacing (17) and (19) in (16) we get the following recursion relationship:

$$\begin{aligned}
&[2(n+1)L^* - n(n^2/2+3n/2+1)]A_s^{(n+1)} + 2(n+1)\sum_{j=1}^{s} j^{-1}(\delta_{0,j-1} - A_{j-1}^{(2)})A_{s-j}^{(n+1)} \\
&\quad + n(n^2+2M^2-2L^*)A_s^{(n-1)} - 2n\sum_{j=1}^{s} j^{-1}(\delta_{0,j-1} - A_{j-1}^{(2)})A_{s-j}^{(n-1)} - \frac{n}{2}(n-1)(n-2)A_s^{(n-3)} \\
&\qquad - 4(n+1)A_{s-1}^{(n+1)} + 2(n+2)A_{s-1}^{(n+3)} + 2nA_{s-1}^{(n-1)} = 0 \ .
\end{aligned} \tag{20}$$

This last formula enables us to calculate all perturbation corrections $E^{(s)}$ of any order. For example, in the cases $s=1$ and 2 we have

$$E^{(1)} = 2(L^* + M^2 - 1)/(4L^* - 3) \ , \tag{21a}$$

$$\begin{aligned}
E^{(2)} = [(4L^*-3)^3(30-8L^*)]^{-1}(&-16L^{*3} + 60L^{*2} - 68L^* + 96L^{*2}M^2 - 104L^*M^2 - 80L^*M^4 \\
&+ 120M^2 - 132M^4 + 12) \ .
\end{aligned} \tag{21b}$$

In Table I we present the first eigenvalues corresponding to the problems of (13) and (14) calculated by way of the HPM [$E(L,M)$] for several λ values. In every case we have included a sufficient number of perturbation corrections, N, to assure the stability of the last decimal place. We have determined the same eigenvalues by diagonalizing a large enough Hamiltonian matrix in the zeroth-order basis set $|LM\rangle$. Since it is a standard procedure[11] we do not detail it here nor do we give the matrix elements. Both calculations are coincident up to the last decimal place reported in Table I. It is found that for a given N value the exactness of the perturbative eigenvalues increases with L. On the contrary, if we want to include larger L values in the variational calculation, it is mandatory to modify the basis set. This fact constitutes a clear advantage of the perturbation method. In addition to this, the HPM gives us analytical approximate expressions for eigenvalues.

The second term of the potential function (2) may be included without any further difficulty within our computational scheme by just writing $Q(\theta)$ as follows:

$$Q(\theta) = M^2/\sin\theta + \lambda(\sin^3\theta + \alpha\sin^5\theta) \ ,$$

$$\alpha = B_R/A_R \ . \tag{22}$$

The procedure developed in this section may be applied to this actual problem without any extra modification being necessary. In addition to the λ power-series expansion (17), this case admits an expansion in λ and β $(=\lambda\alpha)$ power series through the application of the double perturbation theory.[19,20] Both methods yield identical results but the second possibility may be more appropriate when the magnitudes of λ and α are very different from each other.

TABLE I. First rotational energy levels of the hydrogen molecular ion in weak magnetic fields.

λ	$E(0,0)$	$E(1,0)$	$E(1,1)$	$E(2,0)$	$E(2,1)$	N
0.2	0.132 74	2.079 73	2.159 82	6.095 65	6.114 13	3
0.4	0.264 27	2.158 91	2.319 26	6.192 13	6.227 95	4
0.6	0.394 57	2.237 55	2.478 33	6.289 47	6.341 45	5
0.8	0.523 62	2.315 64	2.637 01	6.387 69	6.454 65	5
1.0	0.651 40	2.393 21	2.795 30	6.486 80	6.567 52	6
2.0	1.270 61	2.773 10	3.580 71	6.996 48	7.127 20	6
3.0	1.855 67	3.140 12	4.355 40	7.531 02	7.678 96	8

IV. STRONG MAGNETIC FIELDS

At the same time as the field strength increases, the molecule tends to align along the direction of the applied magnetic field, and the rotation becomes an oscillation around $\theta=0$ [where $V(\theta)$ attains its minimum value]. The larger the field strength is, the smaller the oscillatory amplitude that results. The force constant corresponding to these rotational oscillations increases with the increase of the field strength, as does the energy.

At sufficiently large magnetic fields, the zero-point rotational oscillations around $\theta=0$ have higher energy than the zero-point vibrational energy evaluated at the same field. Under these circumstances, the rotational energy can represent a significant fraction of the molecular dissociation energy.[1]

The HPM may also be applied, without any further difficulty, in the limit of high magnetic-field strengths whenever Eq. (3) is properly modified.

The change of variables $\theta=(\sigma x)^{1/2}$, with $\sigma=\lambda^{-1/2}$, allows us to expand H_R in a σ power series.[7–9] When $V(\theta)$ possesses the general form (2) with $B_R=0$, we obtain

$$\left[x\frac{d^2}{dx^2}+\frac{1}{2}\frac{d}{dx}-\frac{\phi}{x}-\frac{x}{4}\right]\chi = \left[E'-\tfrac{1}{4}\sum_{s=0}^{\infty}F_{s+2}\sigma^{s+1}x^{s+2} + \phi\sum_{s=0}^{\infty}G_s\sigma^{s+1}x^{s}-\frac{\sigma}{16}\right]\chi\ , \tag{23a}$$

where

$$\chi=(\sin\theta)^{1/2}\Psi_{LM}\ , \tag{23b}$$

$$E'=-\frac{\sigma}{4}\mu r_e^2 W_{LM}\ , \tag{23c}$$

$$F_s=-\left[2C_{s-2}+\sum_{i=0}^{s-3}C_iC_{s-i-3}\right],\quad F_2=-2C_0\ , \tag{23d}$$

$$G_s=\left[2D_s+\sum_{i=0}^{s-1}D_iD_{s-i-1}\right],\quad G_0=2D_0\ , \tag{23e}$$

$$C_s=\frac{(-1)^{s+1}}{(2s+3)!},\quad D_s=\frac{2(2^{2s+1}-1)\,|B_{2s+2}|}{(2s+2)!}\ , \tag{23f}$$

$$\phi=(4M^2-1)/16\ , \tag{23g}$$

and B_s are the Bernoulli numbers.

Multiplying (23a) by $x^{-1/2}$ we obtain a self-adjoint differential equation like that discussed formerly in Sec. II, Eq. (5), where $P(x)=x^{1/2}$, $R(x)=x^{-1/2}$, and $Q(x)$ is the remaining polynomial.

The application of the procedure sketched in Sec. III yields, in this case, the following result:

$$aX_s^{(n-2)}+\frac{N}{2}X_s^{(N)}-\frac{2N-1}{16}X_{s-1}^{(N-1)}+\sum_{j=0}^{s-1}\phi(2N+j-1)G_jX_{s-j-1}^{(N+j-1)}-\tfrac{1}{4}\sum_{j=0}^{s-1}(2N+j+1)F_{j+2}X_{s-j-1}^{(N+j+1)} +E'^{(0)}(2N-1)X_s^{(N-1)}+(2N-1)\sum_{j=1}^{s}E'^{(j)}X_{s-j}^{(N-1)}=0\ , \tag{24a}$$

where

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

$$E'=\sum_{j=0}^{\infty}E'^{(j)}\sigma^j,\quad E'^{(0)}=-\frac{n}{2}\ ,\quad n=2L-|M|+1\ , \tag{24c}$$

$$a=\tfrac{1}{8}(1-N)(2N-1)(2N-3)+2(N-1)\phi\ . \tag{24d}$$

In a fashion similar to that in Sec. III, the Hellmann-Feynman theorem

$$\frac{\partial E'}{\partial\sigma}=\tfrac{1}{16}-\phi\sum_{j=0}^{\infty}(j+1)G_j\sigma^jX^{(j)} +\tfrac{1}{4}\sum_{j=0}^{\infty}(j+1)F_{j+2}\sigma^jX^{(j+2)} \tag{25}$$

allows us to relate both sets of perturbation corrections $\{X_s^{(N)}\}$ and $\{E'^{(s)}\}$:

$$sE'^{(s)}=\tfrac{1}{16}\delta_{0,s-1}-\phi\sum_{j=0}^{s-1}(j+1)G_jX_{s-j}^{(j)} +\tfrac{1}{4}\sum_{j=0}^{s-1}(j+1)F_{j+2}X_{s-j}^{(j+2)}\ . \tag{26}$$

From Eqs. (24) and (26) we can calculate the whole set of perturbation corrections in an analytical or numerical way. After some algebraic manipulations, we obtain the following expressions for the first two energy corrections:

$$E'^{(1)}=\tfrac{1}{8}(n^2-M^2+1)\ , \tag{27a}$$

$$E'^{(2)}=n(n^2-M^2+1)/32\ . \tag{27b}$$

In Table II we give the values of the ground-state rotational energy W $(=W_{00})$ for several magnetic field strengths (γ), calculated in the zeroth-order [$W(0)$], first-order [$W(1)$], and second-order [$W(2)$] approximation levels, respectively. Units are the same as in Ref. 1 so that $W(0)$ corresponds exactly to the harmonic-oscillator energy $E_R(0,0)$ of Larsen's work.[1] We have also added the λ and $E(0,0)$ $(=\mu r_e^2 W_{00})$ values in order to make a close comparison between the results of Tables I and II.

The $W(i)$ values of Table II show plainly that the error introduced when one replaces $V(\theta)$ by $A_R\theta^2$ is larger than 1% for those field strengths of the intensity considered by Larsen.[1] However, as we pointed out before, the errors involved in the assumptions which lead to Eq. (3) might be probably much higher.

The addition of the term $B_R \sin^4\theta$ to the potential function $V(\theta)$ just modifies the polynomial $Q(x)$ slightly. Moreover, the HPM may be applied without extra difficulties in the manner indicated before. Since $|B_R| < |A_R|$, the correction terms associated to this new term in the potential function will be even smaller than those calculated in this section.

V. SUMMARY AND CONCLUSIONS

The HPM developed in this paper makes up a generalization of the original method first proposed by Swenson and Danforth[17] and applied later with some modifications[21–24] by several authors.[18–25] The greater general character of our proposal lies on the HR (9) which includes all those formerly employed as particular cases.[17–25]

In Secs. III and IV we have shown that HPM is very useful to calculate the rotational energy levels of diatomic molecules within uniform magnetic fields. This procedure can be applied to handle both the low as well as the high field strength limit, provided that the Schrödinger equation is properly written. In the first case, our results compare favorably with those obtained via the Rayleigh-Ritz variational method. In fact, if the perturbation polynomial converges for an L_0 state, it also converges for any other L state with $L > L_0$. On the contrary, it is necessary to modify the basis set in order to include higher L states in the Rayleigh-Ritz calculation.

There is a large gap between the largest λ value in Table I and the smallest one in Table II because it is necessary to perform a careful numerical calculation of higher-order perturbation terms and, perhaps, a good summation technique in order to match the results of the λ and σ power-series expansions smoothly in the intermediate λ regime. Since our goal is only to show how to generate the terms of these power series easily, we do not consider it appropriate to discuss here the aforesaid calculation.

The HPM is especially suitable and useful since knowing the approximate dependence of the energy levels on the quantum numbers because it gives us analytical expressions for all perturbation corrections. Furthermore, the recursion formulas can be easily programmed and it enables us to calculate higher-order perturbation terms at once. This fact is of great importance in those cases where sufficiently accurate rotational energies are required.

Several quite rough simplifying assumptions were needed for settling the model of the $H_2{}^+$ molecule just described. However, the great accuracy of our eigenvalues are necessary because any improvement of the model has to be followed by an improved computation of its associated eigenvalues.

Another useful feature of the HPM consists in the possibility of applying it to several other problems such as diatomic and symmetric-top molecules in the presence of uniform electric fields.[2–16] This calculation may be accomplished within the rigid rotator approximation framework or, if necessary, the polarization effects can be taken into account. In both cases the computation of the rotational

TABLE II. Ground-state rotational energy level $(L=M=0)$ of $H_2{}^+$ molecule in strong magnetic fields. $W(0)$, $W(1)$, and $W(2)$ include up to the zeroth-, first-, and second-order correction, respectively, and the energies are given in units of $\mathscr{R}$. Also $E(0,0)=\mu r_e^2 W(2)$.

γ	λ	$W(0)$	$W(1)$	$W(2)$	$E(0,0)$
1	163.84	0.0091	0.0088	0.0087	24.580
10	196	0.1321	0.1274	0.1273	26.982
100	1128.96	0.3643	0.3389	0.3388	66.193
1000	1608.01	1.7756	1.7534	1.7533	79.194

eigenenergies can be performed in the way just described in Secs. III and IV. To change the quantum-mechanical rotating system under study only implies modification of the polynomial Q, but the procedure remains the same as was discussed before. At present, we are working in this particular field and results are planned to be given elsewhere in a forthcoming paper.

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