

HYPERVIRIAL-PERTURBATIVE CALCULATION OF STARK ENERGY LEVELS OF
SYMMETRIC-TOP MOLECULES

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(Received: May 1983)

SUMMARY

Hypervirial theorems and the perturbation theory are used to obtain Stark energy levels of symmetric-top molecules. Analytical energy levels up to the third order are shown and numerical higher-order perturbation eigenvalues are compared with accurate results obtained via continued fraction techniques.

INTRODUCTION

In many areas of physical chemistry such as in Electric Resonance Spectroscopy, the knowledge of the energy levels of molecules in an electric field plays an important role. In order to evaluate spectroscopic data, exact Stark energy levels are needed for an accurate determination of molecular and nuclear parameters (such as dipole moments, polarizabilities, anisotropies, etc.) which also affect the energy levels.

The Stark energy levels of symmetric-top molecules can be obtained numerically from a continued fraction technique /1,2/ or by using the Rayleigh-Schrödinger (RS) perturbation theory /3/. This last approach allows one to obtain an analytic expression for a general rotational state, and clearly it constitutes a great advantage. When the external field is relatively strong, as may

happen in molecular beam resonance and electrical level-crossing experiments, higher-order perturbation corrections are necessary. The conventional RS perturbation theory is not useful in these cases, and consequently one has to resort to other perturbative techniques /4-6/.

The purpose of this work is to present a new method for obtaining high-order Stark effect terms for symmetric-top molecules. The procedure is based upon hypervirial theorems, and is a modification of that developed several years ago by Swenson and Danforth /7/. It was applied recently with remarkable success to analyse the Stark effect of a plane rigid rotator /8,9/ and the three-dimensional rigid rotator /10/ in both low and high intensity field cases. From now on, we will refer to this method as the hypervirial-perturbative method (HPM).

This paper is organized as follows: the HPM is briefly developed in Section II, where it is used in order to obtain a recursion formula to calculate perturbative terms of any order, in an analytical as well as numerical way. The Stark energy levels are computed analytically up to the third order and numerically till convergence, and for different values of the perturbation parameter and quantum numbers. Our recursive formula possesses the merit of being easily programmable, so that it allows us to get a sufficient number of perturbation terms for obtaining very accurate Stark energy levels even for quite strong fields. In addition, our analytic third-order energy correction is wholly new since it has not been given before.

Finally, in Section III we discuss the application of the HPM to other closely related and more complex physical problems.

STARK ENERGY LEVELS OF SYMMETRIC-TOP MOLECULES

The rotational energy levels of a rigid symmetric-top molecule in an electric field can be determined from the stationary Schrödinger equation

$$H\Psi = E\Psi, \quad (1a)$$

$$H = -\hbar^2(2I_B)^{-1}(\sin^{-1}\theta \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \sin^{-2}\theta \partial^2/\partial\phi^2)$$

$$\begin{aligned}
 & + (\cos^2\theta/\sin^2\theta + I_B/I_C)\partial^2/\partial\chi^2 - 2\cos\theta\sin^{-2}\theta \partial^2/\partial\chi\partial\phi \\
 & - \mu\mathcal{E}\cos\theta \quad , \quad (1b)
 \end{aligned}$$

where ϕ, θ, χ are the Euler angles specifying the orientation of the molecule, I_C is the moment of inertia along the symmetry axis, I_B is the other principal moment of inertia, μ is the permanent electric dipole moment, and \mathcal{E} is the electric field strength.

The Schrödinger equation (1) may be separated by letting $\Psi(\theta, \phi, \chi) = \Theta(\theta)\exp(iM\phi)\exp(iK\chi)$. By introduction of the dimensionless field strength and energy parameter

$$\lambda = 2\mu\mathcal{E}I_B/\hbar^2 \quad , \quad (2)$$

$$\epsilon = 2EI_B/\hbar^2 + (1 - I_B/I_C)K^2 \quad , \quad (3)$$

the equation for $\Theta(\theta)$ becomes

$$H\Theta = \epsilon\Theta \quad , \quad (3a)$$

$$\begin{aligned}
 H = & -\sin^{-1}\theta \frac{d}{d\theta} \sin\theta \frac{d}{d\theta} + (M^2 + K^2)\sin^{-2}\theta - 2KM\cos\theta\sin^{-2}\theta \\
 & - \lambda\cos\theta \quad . \quad (3b)
 \end{aligned}$$

For the zero field case ($\lambda=0$), this last equation may be solved in terms of hypergeometric series. The eigenvalues are found to be

$$\epsilon^{(0)} = J^* = J(J+1) \quad , \quad (4)$$

where J is the total angular momentum quantum number, M is its

component along the direction of the field, and K is its component along the molecular symmetry axis.

The Hamiltonian operator (3b) satisfies the following diagonal hypervirial relationships

$$\langle H, g^n \partial / \partial \theta \rangle = 0 , \quad (5a)$$

$$\langle H, g^n \rangle = 0 , \quad (5b)$$

where $g^n = \sin \theta \cos^n \theta$. Using the Schrödinger equation (3) and Eq. (5b) in order to get rid of all the terms containing derivative expressions in Eq.(5a), we obtain

$$\begin{aligned} & -(a_n + 3n^2)G^{n+1} + 2(n+1)\epsilon G^{n+1} + \{3n^2 + 2a_n + 2n(K^2 + M^2 - 1)\}G^{n-1} \\ & - 2n\epsilon G^{n-1} - a_n G^{n-3} - 2KM(2n+1)G^n + \lambda\{2G^{n+2} + (2n+1)(G^{n+2} - G^n)\} \\ & = 0 , \end{aligned} \quad (6)$$

where $G^n = \langle \cos^n \theta \rangle$ and $a_n = n(n-1)(n-2)/2$.

Now we expand the G^n terms and the energy parameter ϵ in λ power series, i.e.,

$$G^n = \sum_{i=0}^{\infty} G_i^n \lambda^i , \quad \epsilon = \sum_{i=0}^{\infty} \epsilon^{(i)} \lambda^i . \quad (7)$$

The energy perturbative corrections can be related to the G_i^1 terms by means of the Hellmann-Feynman theorem

$$\partial \epsilon / \partial \lambda = -G^1 , \quad s\epsilon^{(s)} = -G_{s-1}^1 . \quad (8)$$

The substitution of Eqs. (7)-(8) in Eq. (6) permits us to arrive at a recursion relationship involving only G_s^n terms:

$$\begin{aligned}
 & \{2(n+1)J^* - a_n - 3n^2\}G_s^{n+1} - 2(n+1) \sum_{i=1}^s G_{i-1}^1 G_{s-i}^{n+1}/i \\
 & + \{3n^2 + 2a_n + 2n(K^2 + M^2 - J^* - 1)\}G_s^{n-1} + 2n \sum_{i=1}^s G_{i-1}^1 G_{s-i}^{n-1}/i - a_n G_s^{n-3} \\
 & - 2(2n+1)KMG_s^n - (2n+1)G_{s-1}^n + (2n+3)G_{s-1}^{n+2} = 0 . \quad (9)
 \end{aligned}$$

Starting from the normalization condition $G_s^0 = \delta_{s0}$ and calculating with Eq.(9) order by order yields all the G_s^n terms. Then, we obtain the energy perturbative terms from Eq.(8).

The computation of $\epsilon^{(s)}$ requires the set of terms $\{G_{s-i}^i, i=1,2, \dots, s\}$ from the previous steps. The first three energy orders are

$$\epsilon^{(1)} = -KM/J^* , \quad (10)$$

$$\epsilon^{(2)} = \{2K^2M^2(5J^*+3) - 2J^{*2}\{3(M^2+K^2) - J^*\}\}\{4J^{*3}(J^*-3)\}^{-1} , \quad (11)$$

$$\begin{aligned}
 \epsilon^{(3)} = & KM\{(M^2+K^2)J^{*2}(7J^*+6) - 5J^{*4} - K^2M^2(9J^{*2}+19J^*+6)\} \\
 & / \{2J^{*5}\{4J^*-3\}(J^*-2)\} . \quad (12)
 \end{aligned}$$

The determination of trajectories in beam deflectors and state selectors requires the knowledge of the effective dipole moment $\mu_{\text{eff}} = -\partial E / \partial \mathcal{E}$. From Eqs.(2) and (3) it can be seen that our method allows one to calculate μ_{eff} in a very easy and simple manner:

$$\mu_{\text{eff}} = -\mu \partial \epsilon / \partial \lambda = \mu G^1 . \quad (13)$$

We have numerically calculated the first N perturbation coefficients $\epsilon^{(i)}$ by means of Eqs. (8) and (9) and obtained

$$\epsilon_{J,K,M}(\lambda) = \sum_{i=0}^N \epsilon_{J,K,M}^{(i)} \lambda^i, \quad (14)$$

for N large enough to achieve convergence. Results for several λ , K, M and J values are compared with Shirley's in Tables I and II. It is noteworthy that perturbative Stark effect eigenvalues are accurate enough, even for quite strong electric fields, and their accuracies increase with the total angular momentum quantum number.

TABLE I

Stark energy levels $\epsilon_{J,K,M}(\lambda)$ of symmetric-top molecules. J=1 and J=2.

λ	M = -1		M = 1		N
	Ref.1	Present	Ref.1	Present	
0.2	2.09847	2.09847	1.89852	1.89852	3
0.4	2.19380	2.19380	1.79420	1.79420	3
0.6	2.28581	2.28581	1.68716	1.68716	4
0.8	2.37437	2.37437	1.57755	1.57755	5
1.0	2.45931	2.45931	1.46550	1.46550	6
2.0	2.825	2.8246	0.873	0.8728	7
3.0	3.080	3.0804	0.236	0.2356	9

λ	M = 1		M = 2		N
	Ref.1	Present	Ref.1	Present	
0.2	5.96679	5.96679	5.93249	5.93249	3
0.4	5.93375	5.93375	5.86332	5.86332	3
0.6	5.90075	5.90075	5.79251	5.79251	4
0.8	5.86769	5.86769	5.72009	5.72009	5
1.0	5.83445	5.83445	5.64610	5.64610	6
2.0	5.662	5.6623	5.254	5.2535	7
3.0	5.473	5.4733	4.826	4.8259	9

TABLE II

Stark energy levels $\epsilon_{J,K,M}(\lambda)$ of symmetric-top molecules. $J = 3$ and $J = 4$.

		M = -3		M = 3		J = K = 3	
λ	Ref. 1	Present	Ref. 1	Present	N		
1.0	12.74369	12.74369	11.24414	11.24414	5		
2.0	13.474	13.4737	10.477	10.4774	5		
3.0	14.188	14.1884	9.701	9.7009	5		
4.0	14.886	14.8858	8.915	8.9155	6		
5.0	15.564	15.5637	8.122	8.1221	6		
		M = -4		M = 2		J = 4, K = 1	
λ	Ref. 1	Present	Ref. 1	Present	N		
1.0	20.19122	20.19122	19.90184	19.90184	5		
2.0	20.365	20.3647	19.807	19.8068	5		
3.0	20.520	20.5200	19.714	19.7142	5		
4.0	20.657	20.6572	19.623	19.6230	6		
5.0	20.776	20.7758	19.532	19.5324	6		

CONCLUSIONS

The method presented in this work is very useful to calculate high-order perturbational corrections. The recursion formula (9) permits us to obtain analytic perturbative terms with plain ease and can be programmed readily in order to compute higher-order corrections. In short, we may affirm that Eq.(9) summarizes in itself all the advantages of the HPM.

Our method is not constrained to the problem considered in this work, but, in addition, it allows us to include, without any extra trouble, the effect due to molecular polarizability. At present, we are performing the calculations for diatomic molecules and results will be published elsewhere in a forthcoming paper.

An alternative procedure to calculate perturbational corrections was given recently by Morita and Watanabe /11/. Later on, Fernández and Castro /12/ presented an extension of it with the purpose to treat degenerate states. This method, which is based on continued fractions, may be directly employed for the problem

considered in this work. However, in striking difference with regard to the HPM, it does not afford us a simple and easy to use formula equivalent to Eq.(9).

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