

NSG-572

Lower Bounds to Energy Eigenvalues for the Stark Effect  
in a Rigid Rotator\*

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I. INTRODUCTION

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In this paper, the lower bounds to the energy eigenvalues for the rigid rotator in an electric field (the Stark effect) are calculated using the method of Löwdin, reported in these proceedings.<sup>1</sup> Our notation is consistent with his; a convenient form of the lower bound to an eigenvalue being<sup>2</sup>

$$E_i' = \langle \varphi | H_0 | \bar{\varphi} \rangle + \alpha_m^+ A_m^{-1} \alpha_m. \quad (1.1)$$

*author*

In a problem where  $V$  is a positive perturbation with a constant coefficient  $K$  as a strength parameter, one can write

$$V = K U. \quad (1.2)$$

For this case we obtain

$$E_i' = \langle \varphi | H_0 | \bar{\varphi} \rangle + \beta_m^+ B_m^{-1} \beta_m, \quad (1.3)$$

where

$$B_m = \langle g_m | U/K - U T_0 U | g_m \rangle, \text{ and} \quad (1.4)$$

$$\beta_m = \langle g_m | U | \bar{\varphi} \rangle. \quad (1.5)$$

If  $\varphi$  is an eigenfunction of  $\mathcal{H}_0$ , then

$$\overline{\varphi} = \varphi. \quad (1.6)$$

## II. STARK EFFECT IN THE RIGID ROTATOR

The wave equation for the rigid rotator consisting of two mass points  $m_1$  and  $m_2$ , which are separated by fixed distance  $R$ , is

$$\frac{\hbar^2}{2MR^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi^\circ(\theta, \phi) + W \psi^\circ(\theta, \phi) = 0, \quad (2.1)$$

where  $W$  is the rotational energy and  $M$  is the reduced mass of  $m_1$  and  $m_2$ , i.e.,

$$M = (m_1 m_2) / (m_1 + m_2). \quad (2.2)$$

Let

$$-\Omega(\theta, \phi) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}, \quad (2.3)$$

and

$$(2MR^2W) / \hbar^2 = E^\circ, \quad (2.4)$$

where  $\Omega$  is the Hamiltonian in dimensionless units and  $E^\circ$  is the

corresponding energy. Then (2.1) reads simply

$$\Omega(\theta, \phi) \Psi_{\ell, m}^{\circ}(\theta, \phi) = E_{\ell}^{\circ} \Psi_{\ell, m}^{\circ}(\theta, \phi), \quad (2.5)$$

or

$$\Omega(\theta, \phi) \Psi_{\ell, m}^{\circ}(\theta, \phi) = \ell(\ell+1) \Psi_{\ell, m}^{\circ}(\theta, \phi). \quad (2.6)$$

The rigid rotator of dipole moment  $\mu$  in a uniform electric field  $F$  is characterized by the wave equation of the form

$$\mathcal{H}\psi = E\psi, \quad (2.7)$$

with

$$\mathcal{H} = \Omega + K \cos \theta,$$

and

$$K = (2\mu F M R^2) / \hbar^2. \quad (2.8)$$

In order that the perturbation  $V$  in (1.2) shall be positive definite, we shall write

$$\mathcal{H}_0 = \Omega - K, \quad (2.9)$$

$$V = K(1 + \cos \theta), \quad (2.10)$$

and

$$U = 1 + \cos \theta. \quad (2.11)$$

Then this division of  $\mathcal{H}$  into an unperturbed and a perturbed part gives

$$\mathcal{H} = \mathcal{H}_0 + K U \quad (2.12)$$

with

$$U > 0. \quad (2.13)$$

For this case the Schrödinger equation reads

$$[ -\Omega(\theta, \phi) + K \cos \theta ] \Psi(\theta, \phi) = E \Psi(\theta, \phi). \quad (2.14)$$

This equation is easily seen to be separable with respect to the variables  $\theta$  and  $\phi$ , so we can write the eigenfunction in the product form

$$\Psi(\theta, \phi) = Z(\theta) \cdot \Phi(\phi), \quad (2.15)$$

with<sup>3</sup>

$$\Phi(\phi) = (1/\sqrt{2\pi}) e^{\pm im\phi} \quad \text{where } m = 0, 1, 2, \dots$$

$$Z(\theta) = \sum_{i=0}^{\infty} C_i P_{i+m}^m(\cos \theta). \quad (2.16)$$

where  $P_{\ell}^m(\theta)$  is an associated Legendre polynomial.

Since the space with which we are concerned can be subdivided according to the value of  $m$ , we can treat the problem separately for each subspace. The normalized reference function  $\varphi$  in (1.1) is arbitrary; however, in order to make the first order iteration of (1.1) convergent, the condition<sup>4</sup>

$$\langle \mathcal{T} \mathcal{H} \varphi | \mathcal{T} \mathcal{H} \varphi \rangle < \langle \varphi | \varphi \rangle \quad (2.17)$$

must be satisfied. The left side of this inequality approaches zero as  $K$  approaches zero for a fixed reference function only if  $\varphi$  is an eigenfunction of  $\mathcal{H}_e$ ; therefore it seems reasonable to make this choice for  $\varphi$  provided  $K$  is small. Thus in the subspace  $m$ , we have for the  $\ell$ th excited state,

$$\varphi = Y_{\ell}^m(\cos \theta) = N_{\ell}^m P_{\ell}^m(\cos \theta), \quad (2.18)$$

where  $N_{\ell}^m$  is the normalization factor for the associated Legendre polynomial  $P_{\ell}^m(\cos \theta)$  given by

$$N_{\ell}^m = \left[ \frac{(\ell - m)! (2 + \ell)}{(\ell + m)! 2} \right]^{\frac{1}{2}} \quad (2.19)$$

Lower bounds  $\mathcal{E}'_i$  for the energy levels can be calculated by use of (1.3) through (1.5) with  $\mathcal{E}$  in  $\mathcal{T}_e$  obtained from a variation calculation. A simple but useful choice for the arbitrary linear manifold

$\mathcal{G} = (g_1, g_2, \dots, g_i, \dots, g_n)$  is given by

$$g_i = Y_{m+i-1}^m(\cos \theta). \quad (2.20)$$

Since  $U = 1 + \cos \theta$ ,

$$\beta_i = \langle g_i | U | Y_\ell^m \rangle = \langle Y_{m+1-i}^m | (1 + \cos \theta) | Y_\ell^m \rangle. \quad (2.21)$$

Using the recurrence relation

$$(\cos \theta) P_\ell^m = (2\ell + 1) \left[ (\ell + 1 - m) P_{\ell+1}^m + (\ell + m) P_{\ell-1}^m \right], \quad (2.22)$$

we obtain

$$\beta_i = \left[ \frac{(\ell + 1 - m)(\ell + 1 + m)}{(2\ell + 1)(2\ell + 3)} \right]^{\frac{1}{2}} \delta_{m+i-1, \ell+1} + \delta_{m+i-1, \ell} + \left[ \frac{(\ell + m)(\ell - m)}{(2\ell + 1)(2\ell - 1)} \right]^{\frac{1}{2}} \delta_{m+i-1, \ell-1};$$

therefore

$$\begin{aligned} \beta_i &= \left[ \frac{(\ell + 1 - m)(\ell + 1 + m)}{(2\ell + 1)(2\ell + 3)} \right]^{\frac{1}{2}} && \text{for } i = \ell + 2 - m, \\ \beta_i &= 1 && \text{for } i = \ell + 1 - m, \\ \beta_i &= \left[ \frac{(\ell + m)(\ell - m)}{(2\ell + 1)(2\ell - 1)} \right]^{\frac{1}{2}} && \text{for } i = \ell - m, \\ \beta_i &= 0 && \text{otherwise,} \end{aligned} \quad (2.23)$$

and

$$\langle \varphi | \varphi \rangle = \langle Y_\ell^m | (-\Omega - K) | Y_\ell^m \rangle = \ell(\ell + 1) - K. \quad (2.24)$$

In order to have at least one non-zero element for  $\beta_i$ , as we can see from (2.23),  $n$  must be at least as large as  $(\ell - m)$ ; otherwise

$$\mathcal{E}'_i = \ell(\ell + 1) - K, \quad (2.25)$$

which is trivial.

For the calculation of matrix elements of  $\underline{B}$ , we consider

$$B_{ij} = \langle \xi_i | (U/K) - U T_0 U | \xi_j \rangle. \quad (2.26)$$

Let  $F_i = T_0 U \xi_i$  (2.27)

$$= \frac{p}{(\mathcal{E} - H)} (1 + \cos\theta) Y_{m+i-1}^m \quad (2.28)$$

where

$$p = 1 - |\varphi \times \varphi| = 1 - |Y_{\ell}^m \rangle \langle Y_{\ell}^m| .$$

Using (2.22), we obtain

$$F_i = \sum_{k=i-1}^{i+1} D_k Y_{m+k-1}^m, \quad (2.29)$$

with

$$D_{i-1} = \frac{1}{\{\mathcal{E} - (i+m-2)(i+m-1) + K\}} \left\{ \frac{(i-1)(i-2m-1)}{(2i+2m-1)(2i+2m-3)} \right\}^{\frac{1}{2}}$$

$$= 0, \quad \dots \quad (\text{if } \ell = i+m-2) ; \quad (2.30)$$

$$D_i = \frac{1}{\{\mathcal{E} - (i+m-1)(i+m) + K\}}$$

$$= 0, \quad \dots \quad (\text{if } \ell = i+m) ; \quad (2.31)$$

$$D_{i+1} = \frac{1}{\{\mathcal{E} - (i+m)(i+m+1)\}} \left\{ \frac{i(i+2m)}{(2i+2m-1)(2i+2m+1)} \right\}^{\frac{1}{2}}$$

$$= 0, \quad \dots \quad (\text{if } \ell = i+m) . \quad (2.32)$$



Note that the reason  $D_i$  vanishes for certain values of  $i$  is that  $F_i$  is orthogonal to  $Y_{\ell}^m$ .

Introducing (2.27) into (2.26),

$$B_{k,i} = \langle g_k | (U/K) | g_i \rangle - \langle g_k | U | F_i \rangle \quad (2.33)$$

Then, the non-vanishing matrix elements of  $B_{\ell}$  are

$$\begin{aligned} B_{i+2,i} &= \left[ \frac{-1}{\{E-(i+m)(i+m+1)+K\} (2i+2m+1)} \right] \left[ \frac{i(i+1)(i+2m)(i+2m+1)}{(2i+2m-1)(2i+2m+3)} \right]^{\frac{1}{2}} ; \\ B_{i+1,i} &= \left[ \frac{1}{K} - \left\{ \frac{1}{\{E-(i+m)(i+m+1)+K\}} - \left\{ \frac{1}{\{E-(i+m-1)(i+m)+K\}} \right\} \right] \left[ \frac{i(i+2m)}{(2i+2m+1)(2i+2m-1)} \right]^{\frac{1}{2}} ; \\ B_{i,i} &= \frac{1}{K} - \left[ \frac{i(i+2m)}{\{E-(i+m)(i+m+1)+K\} (2i+2m-1)(2i+2m+1)} \right] - \left[ \frac{1}{\{E-(i+m-1)(i+m)+K\}} \right] \\ &\quad - \left[ \frac{(i-1)(i-1+2m)}{\{E-(i+m-2)(i+m-1)+K\} (2i+2m-1)(2i+2m-3)} \right] ; \\ B_{i-1,i} &= \left[ \frac{1}{K} - \left\{ \frac{1}{\{E-(i+m-1)(i+m)+K\}} - \left\{ \frac{1}{\{E-(i+m-2)(i+m-1)+K\}} \right\} \right] \left[ \frac{(i-1)(i+2m-1)}{(2i+2m-1)(2i+2m-3)} \right]^{\frac{1}{2}} ; \\ B_{i-2,i} &= \left[ \frac{-1}{\{E-(i+m-2)(i+m-1)+K\} (2i+2m-3)} \right] \left[ \frac{(i-1)(i-2)(i+2m-1)(i+2m-2)}{(2i+2m-1)(2i+2m-5)} \right]^{\frac{1}{2}} . \end{aligned} \quad (2.34)$$

Equations (2.33), (2.34) and (2.34) give us the necessary matrix elements for calculation of lower bounds expressed by (1.3). It is easily seen that

$$B_{i+2,i} = B_{i,i+2} \quad \text{and} \quad B_{i+1,i} = B_{i,i+1} .$$

If we change the Hamiltonian in (2.8) to

$$\mathcal{H} = \Omega - K \cos \theta \quad (2.35)$$

we would expect the same result since we only reversed the uniform electric field. The algebraic identity of these two cases has been demonstrated as a partial check on the algebra.

### III. UPPER AND LOWER BOUNDS FOR THE RIGID ROTATOR--NUMERICAL RESULTS

The entire calculation was done on the IBM 709 at the University of Florida Computing Center. Upper Bound energies were first obtained by the Rayleigh-Ritz variational method using subroutine Givens<sup>5</sup> (single precision). In order to clarify the cases where the upper bound and lower bound were so close that it was difficult to say which was lower, the upper bounds were refined using a double-precision iteration method,<sup>6</sup> and the remainder of the calculation was carried out in double precision also.

Except for the level  $m = 0$ , all the other levels are degenerate. However, the Hamiltonian  $\mathcal{H}$  commutes with  $L_z$  and therefore one can separately solve the energy eigenvalue problem for each subspace  $S_m$  for a given value  $m$  of  $L_z$ . Calculations for the first six subspaces ( $S_0$  to  $S_5$ ) have been carried out for the twenty lowest eigenvalues in each subspace with the perturbation coefficient  $K$  ranging from 0.1 to 1.0.

In Table I, upper bounds  $E_U = \mathcal{E}$  and lower bounds  $E_L = \mathcal{E}'$  of energy eigenvalues are given to sixteen significant digits for typical choices of  $K$  and  $m$ . The eigenvalues are labeled by the  $\ell$  of the unperturbed state.

$N_U$  is the number of basis functions used for finding upper bounds (these functions are the associated Legendre polynomials  $P_m^m, P_{m+1}^m, \dots, P_{m+N_U-1}^m$ ), and  $N_L$  is the number of basis functions ( $P_m^m, P_{m+1}^m, \dots, P_{m+N_L-1}^m$ ) in the linear manifold  $\underline{g}$ .

This method of evaluating lower bounds, using the bracketing property of (1.1), requires good upper bounds, and the upper bounds are improved by increasing the number of basis functions  $N_U$  used in the variational calculation. The results in Table I indicate that fairly good upper bounds are generally obtained by taking  $N_U = \ell + 5$ . In order to obtain good lower bounds, we have to have a well-chosen basis for the Aronzajn space<sup>7</sup>, and we can see from the results indicated in Table I that in the present case the dimension of the Aronzajn space  $N_L$  is sufficient to give good lower bounds provided  $N_L = \ell + 5$ . Upper and lower bounds agree to fourteen significant digits<sup>8</sup> in those cases where  $N_U = N_L = \ell + 5$ . For the highest energy levels listed, for example  $m = 1, \ell = 20, N_U = 20, N_L = 20$ , the agreement is poorer, but is improved somewhat by increasing  $N_L$ . The limitation here seems to be due to the poorness of the upper bound rather than the dimension of the Aronzajn space.

To see in more detail the effect of  $N_L$  for a fixed value of  $N_U$ , several examples are given in Table II. It is seen from (2.23) that, when the linear manifold  $\underline{g}$  is chosen as indicated in (2.20), for  $N_L$  less than  $(\ell - m)$ , the lower bound  $E_U$  is a persistent lower bound, given by

$$E_L = \ell(\ell+1) - K$$

In order to obtain better lower bounds, therefore, the linear manifold  $\underline{g}$  has to be chosen in such a way that there are non-vanishing elements of  $\beta_i$ ; namely  $\beta_{\ell-m}, \beta_{\ell-m+1}$ , and  $\beta_{\ell-m+2}$  <sup>in our case,</sup>  $\lambda$  Increasing  $N_U$  in Table II beyond the values indicated did not improve the lower bound.

REFERENCES

\*Supported in part by the National Science Foundation and in part by research grant NsG-512 from the National Aeronautics and Space Administration.

1. P. O. Löwdin, J. Chem. Phys., 00, 0000 (1965). (This issue.)
2. Reference 1, equation (43).
3. Except for the case  $m = 0$ , we have doubly degenerate eigenstates, so we will consider only <sup>the</sup> absolute value of  $m$ .
4. Equation (15) in Reference 1.
5. "Eigenvalues and Eigenvectors by Given's Method", Quantum Chemistry Program Exchange, QCPE 12C (1963).
6. C. E. Reid, "Eigenvalues by Löwdin's Partitioning Method", Double Precision, QCPE 14C (1963).
7. P. O. Löwdin, Quantum Theory Project, University of Florida, Report No. 64, 1964 (unpublished).
8. Except for one case,  $m = 0$ ,  $\epsilon = 0$ ,  $K = 0.5$ , where it is only 13 significant figures.

for the Stark effect in a rigid rotator.

$l$	$m = 0,$		$K = 0.5$
	$N_U$	$N_L$	$E_U$ and $E_L^a$
0	5	5	-0.410507934822997 -0.410507934823054
1	6	6	2.024369028254599 2.024369028254599
2	7	7	6.005966607238925 6.005966607238923
3	8	8	12.00277848867649 12.00277848867648
4	9	9	20.00016234906589 20.00016234906587
5	10	10	30.00106840547832 30.00106840547831
6	11	11	42.00075758568145 42.00075758568144
7	12	12	56.00056561485280 56.00056561485278
8	13	13	72.00043859831220 72.00043859831218
9	14	14	90.00003501409683 90.00003501409682
10	15	15	110.0002860416819 110.0002860416819
11	16	16	132.0002380955195 132.0002380955193
12	17	17	156.0002012884138 156.0002012884136
13	18	18	182.0001724138988 182.0001724138987
14	19	19	210.0001493429597 210.0001493429596
15	20	20	240.0001306165556 240.0001306165555
16	20	20	272.0001152074046 272.0001152074045
17	20	20	306.0001023751246 306.0001023751242
18	20	20 23	342.0000916098325 <i>b</i> 342.0000915749897 342.0000915751040
19	20	20 24	380.0016458419702 380.0000722250626 380.0000822706509

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<i>l</i>	$N_U$	$N_L$	$E_U$ and $E_L^a$
1	5	5	1.950333905229181 1.950333905229141
2	6	6	6.011577927242672 6.011577927242670
3	7	7	12.00832614435840 12.00832614435839
4	8	8	20.00551933162358 20.00551933162356
5	9	9	30.00384626739139 30.00384626739137
6	10	10	42.00281392300602 42.00281392300600
7	11	11	56.00214127777589 56.00214127777586
8	12	12	72.00168130591093 72.00168130591091
9	13	13	90.00135388552912 90.00135388552910
10	14	14	110.0011129663826 110.0011129663825
11	15	15	132.0009307395922 132.0009307395921
12	16	16	156.0007896715423 156.0007896715422
13	17	17	182.0006782886897 182.0006782886897
14	18	18	210.0005888386502 210.0005888386500
15	19	19	240.0005159358681 240.0005159358679
16	18	18	272.0004557472937 272.0004557472681
17	20	20	306.0004054860207 306.0004054860206
18	20	20 22	342.0003630874514 342.0003630874365 342.0003630874366
19	20	20 23	380.0003274705419 380.0003269927098 380.0003269958156
20	20	20 24	420.0062377999262 420.0002179895039 420.0002942543069

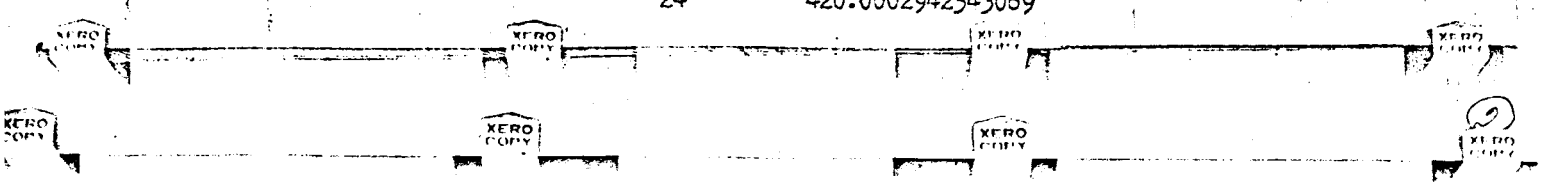


Table I. (Third section)

$l$	$m = 5,$		$K = 1.0$
	$N_U$	$N_L$	$E_U$ and $E_L^a$
5	5	5	29.99359063883720 29.99359063883718
6	6	6	41.99761861361275 41.99761861361275
7	7	7	55.99923213730367 55.99923213730366
8	8	8	71.99992678740871 71.99992678740869
9	9	9	90.00023337531917 90.00023337531912
10	10	10	110.0003640283063 110.0003640283062
11	11	10	132.0004112436340 132.0004112436339
12	12	12	156.0004180542290 156.0004180542288
13	13	13	182.0004054534825 182.0004054534824
14	14	14	210.0003840228910 210.0003840228908
15	15	15	240.0003591944730 240.0003591944728
16	16	16	272.0003337620168 272.0003337620166
17	17	17	306.0003091323675 306.0003091323674
18	18	18	342.0002859711714 342.0002859711713
19	19	19	380.0002645455813 380.0002645455812
20	20	20	420.0002449100770 420.0002449100769
21	20	20	462.0002270087367 462.0002270087364
22	20	20	506.0002107319706 506.0002107319655
23	20	20	552.0001962023146 552.0001959463010
24	20	20	60.00049841862676 60.00001226802245

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Table II. Effect of  $N_U$  on  $E_U$  in the convergence to the eigenvalue.

m	K	$l$	$N_U$	N	$E_U$ and E
0	0.1	10	15	1-9 <sup>a</sup>	110.0000114416483
				10	109.90000000000000* <sup>b</sup>
				13	109.9477443614383
					110.0000114416482
0	0.5	10	15	1-9	110.0002860416819
				10	109.50000000000000*
				13	109.7412282838218
				15	110.0002860416817
1.	0.7	16	20	1-14	272.0002233160454
				15	271.30000000000000*
				18	271.6219989276613
					272.0002233160452
2	1.0	12	15	1-9	156.0007432191651
				10	155.00000000000000*
				13	155.4101468398408
				15	156.0007432191644
3	0.7	10	12	1-6	110.0004230273525
				8	109.30000000000000*
				10	110.0003141668453
					110.0004230273523
5	1.0	20	20	1-14	420.0002449100770
				15	419.00000000000000*
				18	419.3717170996393
				20	420.0002449100768
				20	420.0002449100769

<sup>a</sup>The notation 1-9 indicates that the value of N ranges from one through nine.

<sup>b</sup>Asterisks indicate persistent lower bound.