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

by

Jong H. Choi and Darwin W. Smith
Department of Chemistry
and
Quantum Theory Project
University of Florida
Gainesville, 32603

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.[1] Our notation is consistent with his; a convenient form of the lower bound to an eigenvalue being[2]

$$\mathcal{E}_1' = \langle \varphi | \mathcal{H}_0 | \bar{\varphi} \rangle + \underline{\alpha}^+ \underline{A}^{-1} \underline{\alpha}. \tag{1.1}$$

author

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

$$V = K U. \tag{1.2}$$

For this case we obtain

$$\mathcal{E}_1' = \langle \varphi | \mathcal{H}_0 | \bar{\varphi} \rangle + \underline{\beta}^+ \underline{B}^{-1} \underline{\beta}, \tag{1.3}$$

where

$$\underline{B} = \langle \underline{g} | U/K - U T_0 U | \underline{g} \rangle, \text{ and} \tag{1.4}$$

$$\underline{\beta} = \langle \underline{g} | U | \bar{\varphi} \rangle. \tag{1.5}$$

If φ is an eigenfunction of $\mathcal{H}_o$, then

$$\overline{\varphi} = \varphi. \tag{1.6}$$

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

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

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

$$M = (m_1 m_2)/(m_1 + m_2). \tag{2.2}$$

Let

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

and

$$(2MR^2W)/\hbar^2 = E^\circ, \tag{2.4}$$

where Ω is the Hamiltonian in dimensionless units and E° is the

corresponding energy. Then (2.1) reads simply

$$-\Omega(\theta,\phi)\,\psi^{\circ}_{\ell,m}(\theta,\phi) = E^{\circ}_{\ell}\,\psi^{\circ}_{\ell,m}(\theta,\phi), \tag{2.5}$$

or

$$-\Omega(\theta,\phi)\,\psi^{\circ}_{\ell,m}(\theta,\phi) = \ell(\ell+1)\,\psi^{\circ}_{\ell,m}(\theta,\phi). \tag{2.6}$$

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

$$\mathcal{H}\psi = E\psi, \tag{2.7}$$

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

and $$K = (2\mu F M R^2)/\hbar^2. \tag{2.8}$$

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

$$\mathcal{H}_0 = -\Omega - K, \tag{2.9}$$

$$V = K(1+\cos\theta), \tag{2.10}$$

and

$$U = 1 + \cos\theta . \tag{2.11}$$

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

$$\mathcal{H} = \mathcal{H}_0 + KU \tag{2.12}$$

with

$$U > 0 . \tag{2.13}$$

For this case the Schrödinger equation reads

$$[\, -\Omega(\theta,\phi) + K\cos\theta\,]\,\psi(\theta,\phi) = E\,\psi(\theta,\phi) . \tag{2.14}$$

This equation is easily seen to be separable with respect to the variables θ and ϕ, so we can write the eigenfunction in the product form

$$\psi(\theta,\phi) = Z(\theta)\cdot\Phi(\phi), \tag{2.15}$$

with[3] $\Phi(\phi) = (1/\sqrt{2\pi})\, e^{\pm im\phi}$ where $m = 0, 1, 2, \cdots$

$$Z(\theta) = \sum_{i=0}^{\infty} C_i\, P^m_{i+m}(\cos\theta) . \tag{2.16}$$

where $P_\ell^m(\theta)$ is an associated Lengendre 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 φ in (1.1) is arbitrary; however, in order to make the first order iteration of (1.1) convergent, the condition[4]

$$\langle T\mathcal{H}\varphi \mid T\mathcal{H}\varphi \rangle < \langle \varphi \mid \varphi \rangle \tag{2.17}$$

must be satisfied. The left side of this inequality approaches zero as K approaches zero for a fixed reference function only if φ is an eigenfunction of $\mathcal{H}_0$; therefore it seems reasonable to make this choice for φ provided K is small. Thus in the subspace m, we have for the ℓ th excited state,

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

where N_ℓ^m is the normalization factor for the associated Lengendre polynomial $p_\ell^m(\cos\theta)$ given by

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

Lower bounds $\mathcal{E}_1'$ for the energy levels can be calculated by use of (1.3) through (1.5) with $\mathcal{E}$ in T_0 obtained from a variation calculation. A simple but useful choice for the arbitrary linear manifold $\underset{\sim}{g} = (g_1, g_2, \cdots g_i \cdots g_n)$ is given by

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

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

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

Using the recurrence relation

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

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

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

and

$$\langle \varphi \mid \varphi \rangle = \langle Y_\ell^m \mid (\Omega - K) \mid Y_\ell^m \rangle = \ell(\ell+1) - K. \tag{2.24}$$

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

$$\varepsilon_1' = \ell(\ell+1) - K , \tag{2.25}$$

which is trivial.

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

$$B_{ij} = \langle g_i \mid (U/K) - U\, T_o\, U \mid g_j \rangle . \tag{2.26}$$

Let
$$F_i = T_o\, U\, g_i \tag{2.27}$$

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

where

$$p = 1 - |\varphi\rangle\langle\varphi| = 1 - |Y^m_\ell\rangle\langle Y^m_\ell| .$$

Using (2.22), we obtain

$$F_i = \sum_{k=i-1}^{i+1} D_k\, Y^m_{m+k-1} , \tag{2.29}$$

with

$$D_{i-1} = \frac{1}{\{\mathcal{E} - (i+m-2)(i+m-1) + K\}} \left\{ \frac{(i-1)(i-2m-1)}{(2i+2m-1)(2i+2m-3)} \right\}^{\frac{1}{2}}$$
$$= 0, \quad \ldots \quad (\text{if } \ell = i+m-2) ; \tag{2.30}$$

$$D_i = \frac{1}{\{\mathcal{E} - (i+m-1)(i+m) + K\}}$$
$$= 0, \quad \ldots \quad (\text{if } \ell = i+m) ; \tag{2.31}$$

$$D_{i+1} = \frac{1}{\{\mathcal{E} - (i+m)(i+m+1)\}} \left\{ \frac{i(i+2m)}{(2i+2m-1)(2i+2m+1)} \right\}^{\frac{1}{2}}$$
$$= 0, \quad \ldots \quad (\text{if } \ell = i+m) . \tag{2.32}$$

Note that the reason D_i vanishes for certain values of i is that F_i is orthogonal to Y_ℓ^m.

Introducing (2.27) into (2.26),

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

Then, the non-vanishing matrix elements of B_{ki} are

$$B_{i+2,i} = \left\{\frac{-1}{\{\varepsilon-(i+m)(i+m+1)+K\}\ (2i+2m+1)}\right\}\left[\frac{i(i+1)(i+2m)(i+2m+1)}{(2i+2m-1)(2i+2m+3)}\right]^{\frac{1}{2}} ;$$

$$B_{i+1,i} = \left[\frac{1}{K} - \left\{\frac{1}{\varepsilon-(i+m)(i+m+1)+K}\right\} - \left\{\frac{1}{E-(i+m-1)(i+m)+K}\right\}\right]\left[\frac{i(i+2m)}{(2i+2m+1)(2i+2m-1)}\right]^{\frac{1}{2}} ;$$

$$B_{i,i} = \frac{1}{K} - \left[\frac{i(i+2m)}{\{\varepsilon-(i+m)(i+m+1)+K\}\ (2i+2m-1)(2i+2m+1)}\right] - \left[\frac{1}{E-(i+m-1)(i+m)+K}\right]$$
$$- \left[\frac{(i-1)(i-1+2m)}{\{\varepsilon-(i+m-2)(i+m-1)+K\}\ (2i+2m-1)(2i+2m-3)}\right] ;$$

$$B_{i-1,i} = \left[\frac{1}{K} - \left\{\frac{1}{\varepsilon-(i+m-1)(i+m)+K}\right\} - \left\{\frac{1}{E-(i+m-2)(i+m-1)+K}\right\}\right]\left[\frac{(i-1)(i+2m-1)}{(2i+2m-1)(2i+2m-3)}\right]^{\frac{1}{2}} ;$$

$$B_{i-2,i} = \left\{\frac{-1}{\{\varepsilon-(i+m-2)(i+m-1)+K\}\ (2i+2m-3)}\right\}\left[\frac{(i-1)(i-2)(i+2m-1)(i+2m-2)}{(2i+2m-1)(2i+2m-5)}\right]^{\frac{1}{2}} .$$

(2.34)

Equations (2.23), (2.24) and (2.34) give us the necessary matrix elements for calculation of lower bounds expressed by (1.3). It is easily seen that

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

If we change the Hamiltonian in (2.8) to

$$\mathcal{H} = -\Omega - K\cos\theta \tag{2.35}$$

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[5] (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,[6] 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 ℓ 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_{m+1}, ... $P^m_{m+N_U-1}$), and N_L is the number of basis functions (P^m_m, P^m_{m+1}, ... $P^m_{m+N_L-1}$) in the linear manifold $\underset{\sim}{g}$.

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[7], 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[5] 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 Aronszajn 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 $\underset{\sim}{g}$ 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

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

In order to obtain better lower bounds, therefore, the linear manifold $\underset{\sim}{g}$ has to be chosen in such a way that there are non-vanishing elements of β_i; namely $\beta_{\ell-m}$, $\beta_{\ell-m+1}$, and $\beta_{\ell-m+2}$ (in our case). 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 the 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, = 0, K = 0.5, where it is only 13 significant figures.

for the Stark effect in a rigid rotator.

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

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

Table I. (Third section)

	m = 5,		K = 1.0
ℓ	N_U	N_L	E_U and E_L [a]
5	5		29.99359063883720
		5	29.99359063883718
6	6		41.99761861361275
		6	41.99761861361275
7	7		55.99923213730367
		7	55.99923213730366
8	8		71.99992678740871
		8	71.99992678740869
9	9		90.00023337531917
		9	90.00023337531912
10	10		110.0003640283063
		10	110.0003640283062
11	11		132.0004112436340
		10	132.0004112436339
12	12		156.000418054229O
		12	156.000418054228S
13	13		182.0004054534825
		13	182.0004054534824
14	14		210.0003840228910
		14	210.0003840228908
15	15		240.0003591944730
		15	240.0003591944728
16	16		272.0003337620168
		16	272.0003337620166
17	17		306.0003091323675
		17	306.0003091323674
18	18		342.0002859711714
		18	342.0002859711713
19	19		380.0002645455813
		19	380.0002645455812
20	20		420.0002449100770
		20	420.0002449100769
21	20		462.0002270087367
		20	462.0002270087364
22	20		506.0002107319706
		20	506.0002107319655
23	20		552.0001962023146
		20	552.0001959463010
24	20		60.00049841862676
		20	60.00001226802245

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		110.0000114416483
				1-9[a]	109.9000000000000*[b]
				10	109.9477443614383
				13	110.0000114416482
0	0.5	10	15		110.0002860416819
				1-9	109.5000000000000*
				10	109.7412282838218
				13	110.0002860416817
				15	110.0002860416818
1.	0.7	16	20		272.0002233160454
				1-14	271.3000000000000*
				15	271.6219989276613
				18	272.0002233160452
2	1.0	12	15		156.0007432191651
				1-9	155.0000000000000*
				10	155.4101468398408
				13	156.0007432191644
				15	156.0007432191651
3	0.7	10	12		110.0004230273525
				1-6	109.3000000000000*
				8	110.0003141668453
				10	110.0004230273523
5	1.0	20	20		420.0002449100770
				1-14	419.0000000000000*
				15	419.3717170996393
				18	420.0002449100768
				20	420.0002449100769

[a]The notation 1-9 indicates that the value of N ranges from one through nine.

[b]Asterisks indicate persistent lower bound.