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Exact spectrum of the two-dimensional rigid rotator in external fields. I. Stark effect

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An exact solution of the two-dimensional rigid rotator in a static uniform electric field of arbitrary strength is given. The eigenvalue spectrum is found to consist of the characteristic values of the even-index Mathieu functions of π periodicity. At low field strengths $\mathcal{E}$ the double degeneracy of the rotational states $\pm m$ is broken in order $\mathcal{E}^{2m}$. The broken degeneracy persists for arbitrary field strength. Results are compared with perturbation theory.

I. INTRODUCTION

The two- and three-dimensional rigid rotators are well-known exactly soluble quantum systems which serve as models for interpretation of molecular rotational spectra. It is of interest, therefore, to determine precisely the energy spectrum of these systems in interaction with electric and magnetic fields. For sufficiently weak fields the energy eigenvalues of the rigid rotator can be easily obtained by perturbation theory; these calculations for the three-dimensional rotator in an electric field are now routinely presented in many quantum-mechanics textbooks.[1] For strong electric fields the determination of the energy eigenvalues has necessitated either alternative approximative techniques or computer calculations. Peter and Strandberg[2] have presented a perturbation theoretic method for the three-dimensional rotator based on a harmonic oscillator approximation which converges when the electric energy is greater than the rotational energy. An approximate method utilizing continued fractions has been published by Hughes[3] and Schlier.[4] Von Meyenn[5] has made a numerical investigation of the three-dimensional rotator for the intermediate region where neither second-order perturbation theory nor the harmonic-oscillator approximations are particularly appropriate.

In this article and the following one we consider the problems of a two-dimensional rigid rotator in arbitrarily strong electric and magnetic fields, respectively. The Stark effect of the two-dimensional rotator with electric dipole moment $\vec{p}$ has previously been examined by Barriol[6] who used a continued fraction approximation and more recently by Flügge[7] who employed second-order nondegenerate perturbation theory. Flügge's justification for use of nondegenerate as opposed to degenerate perturbation theory is that the zero-field degenerate basis states (eigenstates of the single nonvanishing component of orbital angular momentum) are uncoupled by the perturbation $-\vec{p}\cdot\vec{\mathcal{E}}$, where $\vec{\mathcal{E}}$ is a static uniform electric field normal to the angular momentum. Thus, no singular terms appear in the series expansion. Flügge's calculation shows that the double degeneracy of the zero-field excited states (rotational quantum number $|m|>0$) is unbroken to order $\mathcal{E}^2$. In fact, further application of nondegenerate perturbation theory leads to an unbroken degeneracy to all orders of $\mathcal{E}$. These results differ from those obtained by the method of continued fractions.

A simple symmetry argument would seem to indicate that the analysis of Flügge is not correct. The Hamiltoniam of the field-free two-dimensional rigid rotator is invariant under the elements of the (non-Abelian) rotation-reflection group; the degenerate basis $\psi_{\pm m}(\phi)\sim e^{\pm im\phi}$ spans a two-dimensional irreducible representation of this group.[8] The Hamiltonian including the electric dipole interaction, however, is invariant under a group comprising the identity and reflection across the electric field axis. This group is isomorphic to the (Abelian) symmetric group S_2 and can have only two one-dimensional irreducible representations. Thus, the degenerate basis should split in some order into nondegenerate states belonging to the symmetric and antisymmetric representations of S_2.

In this article we present the exact solution to the Stark effect of the two-dimensional rigid rotator. We show that the degeneracy is indeed broken and that the states possess the requisite symmetries. The results are compared with perturbation theory, and the origin of Flügge's error is explained.

II. STARK EFFECT OF THE TWO-DIMENSIONAL RIGID ROTATOR

The total Hamiltonian of the two-dimensional rigid rotator with moment of inertia I and electric dipole moment $\vec{p}$ in a static uniform electric field $\mathcal{E}\hat{x}$ (normal to the angular momentum) can be written as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_E=L_z^2/2I-\vec{p}\cdot\vec{\mathcal{E}}\ . \tag{1a}$$

In the coordinate representation use of Eq. (1a) leads to the Schrödinger equation

$$(\partial^2/\partial\phi^2+\mu^2+\lambda\cos\phi)\psi(\phi)=0\ , \tag{1b}$$

where we have expressed the energy eigenvalues as

$$E_\mu=\hbar^2\mu^2/2I\ , \tag{2a}$$

and defined the dimensionless interaction parameter

$$\lambda=2Ip\mathcal{E}/\hbar^2\ , \tag{2b}$$

where $p=|\vec{p}|$. By setting

$$\phi=2\theta\ , \tag{3a}$$

$$a=4\mu^2\ , \tag{3b}$$

$$q=-2\lambda\ , \tag{3c}$$

one can reexpress Eq. (1b) in the form

$$\frac{d^2\psi(\theta)}{d\theta^2}+[a-2q\cos(2\theta)]\psi(\theta)=0\ , \tag{4}$$

which is recognizable as the canonical form of Mathieu's equation.[9]

The requirement of continuity and single-valuedness of the wave function

$$\psi(\phi+2\pi)=\psi(\phi)\ , \tag{5a}$$

or, equivalently,

$$\psi(\theta+\pi)=\psi(\theta)\ , \tag{5b}$$

restricts the admissable solutions of Eq. (4) to the Mathieu functions with π periodicity. These Mathieu functions and their characteristic values are traditionally designated as follows (where $m=0,1,2\ldots$).

(1) $ce_{2m}(\theta,q)$—even solutions of period π which reduce to $\cos(2m\theta)$ as $q\to 0$; characteristic values are $a=a_{2m}$.

(2) $se_{2m+2}(\theta,q)$—odd solutions of period π which reduce to $\sin[(2m+2)\theta]$ as $q\to 0$; characteristic values are $a=b_{2m+2}$.

The exact Stark solutions (to within a normalization constant) are therefore

$$\psi_{\mu_{m+}}(\phi,\lambda)=ce_{2m}(\phi/2,-\lambda)\ ,\quad m=0,1,2\ldots \tag{6a}$$

$$E_{\mu_{m+}}(\lambda)=\hbar^2\mu^2_{m+}/2I=\hbar^2a_{2m}(-\lambda)/8I\ , \tag{6b}$$

$$\psi_{\mu_{m-}}(\phi,\lambda)=se_{2m}(\phi/2,-\lambda)\ ,\quad m=1,2,3\ldots \tag{6c}$$

$$E_{\mu_{m-}}(\lambda)=\hbar^2\mu^2_{m-}/2I=\hbar^2b_{2m}(-\lambda)/8I\ . \tag{6d}$$

The states are labeled by the eigenvalues ± of the reflection operator Π_x and by the eigenvalues m of L_z where $\mu^2\to m^2$ as $\lambda\to 0$.

Because the Mathieu equation leads to an irreducible three-term recursion relation, the characteristic values cannot be explicitly expressed in closed form. For small q they can be developed in an infinite series by various methods as, for example, solution of a continued fraction or of Hill's determinant. Using the series given by McLachlan,[10] we summarize in Table I the eigenvalues $\mu^2_{m\pm}$ for the ground state and first six excited states. The eigenvalues for each m are truncated at the lowest order in $\mathcal{E}$ which splits the field-free degeneracy. The unusual broken degeneracy pattern (which extends to all excited levels) is clearly evident: Each degenerate pair of states of fixed $|m|$ is split in order $\mathcal{E}^{2m}$. Thus, the first excited level $|m|=1$ is split by a quadratic Stark effect, contrary to the results of Flügge.

The results of Table I can also be obtained by use of *degenerate* perturbation theory. This requires construction of the unique linear combinations of degenerate states which are analytically continuous with the Stark states at $E=0$. From Eqs. (6a) and (6b) it is seen that these linear combinations are $\cos(m\phi)$ and $\sin(m\phi)$, respectively. It is generally the case that proper application of perturbation theory to degenerate states requires that one start with the appropriate analytically continuous basis as long as the perturbation lifts the degeneracy in some order. That this occurs may often be inferred by a group theoretical analysis. Application of nondegenerate perturbation theory to any other basis is incorrect, even if that basis is uncoupled by the perturbation and the resulting series is free of singularities.

For very large $\mathcal{E}$ the energy eigenvalues are derivable in closed form from the asymptotic properties of the Mathieu functions

$$\mu^2_{m\pm}=-\lambda+(m\pm 1/2)(2\lambda)^{1/2} \tag{7a}$$

or

TABLE I. Series expansion of the Stark eigenvalues μ^2.[a]

$\mu_0^2=-\frac{1}{2}\lambda^2$
$\mu_{1+}^2=2^2+\frac{5}{12}\lambda^2$
$\mu_{1-}^2=2^2-\frac{1}{12}\lambda^2$
$\mu_{2+}^2=4^2+\frac{1}{30}\lambda^2+\frac{433}{216\text{E}03}\lambda^4$
$\mu_{2-}^2=4^2+\frac{1}{30}\lambda^2-\frac{317}{216\text{E}03}\lambda^4$
$\mu_{3+}^2=6^2+\frac{1}{70}\lambda^2+\frac{187}{1096\text{E}03}\lambda^2+\frac{6743617}{58084992\text{E}05}\lambda^6$
$\mu_{3-}^2=6^2+\frac{1}{70}\lambda^2+\frac{187}{1096\text{E}03}\lambda^2-\frac{5861633}{58084992\text{E}05}\lambda^6$

[a] Adapted from Ref. 9 (E0$x\to 10^x$).

$$E_{\mu_{m\pm}} = -p\mathcal{E} + (m \pm 1/2)\hbar(p\mathcal{E}/I)^{1/2} . \qquad (7b)$$

The first term represents the alignment of a classical dipole along the field direction. The second term represents an harmonic oscillator spectrum with equidistant level separations of $\hbar(p\mathcal{E}/I)^{1/2}$. This can be understood by expanding the Hamiltonian in Eq. (1b) about the equilibrium point $\phi = 0$ to obtain an harmonic-oscillator Hamiltonian. The rotator behavior in a strong electric field can be classically interpreted as a small amplitude oscillation of the dipole at frequency $(p\mathcal{E}/I)^{1/2}$ about the field direction.

Finally, it is seen that the solutions of Eqs. (6a) and (6c) span the symmetric and antisymmetric representations of S_2, respectively, where the symmetry and antisymmetry is taken with respect to reflection across the x axis.

A more detailed description of the properties of the eigenvalues and eigenfunctions of the two-dimensional rigid rotator in an electric field will be published elsewhere.[11]

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