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An Asymptotic Expression for the Energy Levels of the Rigid Asymmetric Rotor*

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The energy matrix of the rigid asymmetric rotor, evaluated in terms of symmetric rotor wave functions, has been examined under conditions where J is increased indefinitely. Asymptotically, the energy matrix assumes a form that is very much like the matrix that may be obtained from the characteristic value problem of Mathieu's differential equation. The characteristic values of Mathieu's equation serve as the basis for a good approximation to the energy values of those asymmetric rotor levels which, for a given, large value of J, correspond to a small value of K in the limiting symmetric cases. The differences which exist between the two matrices are accounted for by a perturbation technique which permits an accurate determination of the energy values.

When the characteristic values of Mathieu's equation lead to a successful approximation to the energy values of the asymmetric rotor, an estimate may be made of the asymmetric rotor wave functions.

INTRODUCTION

ALTHOUGH the equations defining the energy levels of the rigid asymmetric rotor have been derived by various authors,[1] the numerical solution of the equations is not available for all values of the rotational quantum numbers. Recently, however, King, Hainer, and Cross[2] have published tables of solutions for $J \leq 10$. There have been three methods for extension of the solutions to higher J values. Numerical solution of the equations becomes increasingly laborious for large J's. The approximations resulting from the usual perturbation theory yield rather slowly convergent series. Finally, there is the application of the correspondence principle.[3]

The result of the correspondence principle arguments is to give an asymptotic expression for the energy levels which fails to reveal one of the most important properties of the asymmetric rotor spectrum; *viz.*, the removal with increasing asymmetry of the twofold degeneracy in K ($K \neq 0$) which exists in the limiting case of the symmetric rotor. It would appear that the applicability of the correspondence principle result is restricted to those asymmetric rotor energy levels which are essentially twofold degenerate, i.e., under conditions of slight asymmetry and large J and K (for the limiting symmetric case).

In order to avoid this restriction, the energy matrix of the rigid asymmetric rotor, evaluated in terms of a basis of symmetric rotor wave functions, has been examined, and the limiting form that it assumes when J is increased indefinitely has been determined. This limiting form differs but slightly from that arising in the characteristic value problem involving Mathieu's differential equation. As a consequence of this asymptotic similarity, the characteristic values of Mathieu's equation have been utilized for a first approximation to the energy levels of the asymmetric rotor. It has been found possible to modify the Mathieu equation by the addition of a suitable perturbation operator that permits a better approximation to the energy values. In principle, a series of suitable perturbation operators may be developed which, together with the matrix equations derived below, will permit the energy values to be determined to as great a degree of accuracy as may be desired.

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[1] E. E. Witmer, Proc. Nat. Acad. Sci. **13**, 60 (1927); S. C. Wang, Phys. Rev. **34**, 243 (1929); H. A. Kramer and G. P. Ittman, Zeits. f. Physik **53**, 533 (1929); **58**, 217 (1929); **60**, 633 (1930); O. Klein, Zeits. f. Physik **58**, 730 (1929); H. B. Casimir, *Rotation of a Rigid Body in Quantum Mechanics* (J. B. Wolter's, The Hague, 1931).

[2] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943). These tables recently have been extended to $J=11$ and 12, R. M. Hainer, Thesis, Brown University, 1947.

[3] G. W. King, Phys. Rev. **70**, 108 (1946); J. Chem. Phys. **15**, 820 (1947); E.E. Witmer, Monthly Progress Reports of the University of Pennsylvania, Thermodynamics Research Laboratory, Contract NObs-2477, Navy Department Bureau of Ships.

ASYMPTOTIC FORM OF THE ENERGY MATRIX[4]

The energy levels of any rigid asymmetric rotor have the form

$$E_\tau^J(a,b,c)=\frac{a+c}{2}J(J+1)+\frac{a-c}{2}E_\tau^J(\kappa), \quad (1)$$

where J is the quantum number associated with the squared total angular momentum of the rotor, $\hbar^2 J(J+1)$; $J=0, 1, 2, \cdots$; τ is a *pseudo* quantum number which indicates the order of the $2J+1$ energy levels having a given value of J; τ takes on integral values between $-J$ for the lowest energy level, and $+J$ for the highest; $a=\hbar^2/2I_a$, $b=\hbar^2/2I_b$, $c=\hbar^2/2I_c$, and $I_a \leq I_b \leq I_c$, the principal moments of inertia; $\kappa=[(2b-a-c)/(a-c)]$, an asymmetry parameter;[5] $E_\tau^J(\kappa)$ is a characteristic value of the energy matrix $\mathbf{E}(\kappa)$ discussed below.

The energy matrix $\mathbf{E}(\kappa)$, when evaluated in terms of symmetric rotor wave functions $\psi(J, K, M)$ as basis functions, does not depend upon M in the absence of an external field. Furthermore, it is diagonal in J, each $J;J$ block being of order $2J+1$. In any $J;J$ block it has the following non-vanishing elements:

$$E_{K;\,K}=FJ(J+1)+(G-F)K^2, \quad (2)$$

and

$$E_{K;\,K+2}=E_{K+2;\,K}=H[f(J,K+1)]^{\frac{1}{2}}. \quad (3)$$

F, G, and H depend upon the manner in which a set of Cartesian axes within the rotor is identified with the principal axes,[6] and upon the asymmetry parameter κ.

$$f(J,n)=f(J,-n)=\tfrac{1}{4}[J(J+1)-n(n+1)]\times[J(J+1)-n(n-1)]. \quad (4)$$

The energy matrix may be written as

$$\mathbf{E}(\kappa)=FJ(J+1)\mathbf{I}+(G-F)\mathbf{E}'(\kappa), \quad (5)$$

where $\mathbf{I}$ is the unit matrix of appropriate order $(2J+1)$, and $\mathbf{E}'(\kappa)$ now has the following non-vanishing elements in each $J;J$ block:

$$E'_{K;\,K}=K^2, \quad (6)$$

and

$$E'_{K;\,K+2}=E'_{K+2;\,K}=\frac{H}{G-F}[f(J,K+1)]^{\frac{1}{2}}, \quad (7)$$

provided $G-F\neq 0$.

Now for finite n, the following asymptotic relationship $(J\to\infty)$ may be obtained:

$$[f(J,n)]^{\frac{1}{2}}\sim\frac{J(J+1)}{2}\left[1+O\left(\frac{n^2}{2J(J+1)}\right)\right]. \quad (8)$$

Thus, if the symmetric rotor wave functions are ordered: $\psi(J,-J,M), \cdots \psi(J,K,M), \cdots \psi(J,J,M)$, the energy matrix $\mathbf{E}'(\kappa)$ assumes the following limiting form.

$$\mathbf{E}'(\kappa)\sim\begin{bmatrix} & \vdots & \vdots & & \vdots & \vdots & \\ \cdots & 2^2 & 0 & \frac{H}{G-F}\frac{J(J+1)}{2} & 0 & 0 & \cdots \\ \cdots & 0 & 1^2 & 0 & \frac{H}{G-F}\frac{J(J+1)}{2} & 0 & \cdots \\ \cdots & \frac{H}{G-F}\frac{J(J+1)}{2} & 0 & 0 & 0 & \frac{H}{G-F}\frac{J(J+1)}{2} & \cdots \\ \cdots & 0 & \frac{H}{G-F}\frac{J(J+1)}{2} & 0 & 1^2 & 0 & \cdots \\ \cdots & 0 & 0 & \frac{H}{G-F}\frac{J(J+1)}{2} & 0 & 2^2 & \cdots \\ & \vdots & \vdots & \vdots & \vdots & \vdots & \end{bmatrix}, \quad (9)$$

[4] The notation used by King, Hainer, and Cross, reference 2, will be adopted here.
[5] The use of κ as an asymmetry parameter is due to B. S. Ray, Zeits. f. Physik **78**, 74 (1932), and results from his choice of diagonalizing the angular momentum about the intermediate axis of inertia.
[6] Reference 2, Table III.

neglecting terms $O([n^2/J(J+1)])$ compared to unity for very large values of J. Equation (9) is similar in structure to the corresponding matrix that arises in the characteristic value problem that involves Mathieu's equation. It differs from the latter in that the former is of order $(2J+1)$, while the latter is of infinite order; also, the latter gives rise to off-diagonal elements which are truly constant, while the off-diagonal elements of the former are only asymptotically and approximately constant for $J \gg K$.

THE MATHIEU EQUATION MATRIX

To obtain the matrix arising from the characteristic value problem of Mathieu's equation, consider the equation itself.[7]

$$\frac{d^2y}{dx^2}+(\alpha-2\theta\cos 2x)y=0, \tag{10}$$

α and θ are parameters which are independent of x.

This equation has both periodic and nonperiodic solutions, depending upon the values of α and θ. However, for those solutions which are periodic in π or 2π it is found that α may assume only special values, which depend upon θ. The characteristic value problem, then, is to determine those values of α, for each value of θ, which permit solutions periodic in π or 2π. This may be accomplished as follows. Let $\theta=0$, obtaining

$$\frac{d^2y_0}{dx^2}+\alpha_0 y_0=0. \tag{11}$$

This equation will have solutions periodic in π or 2π if and only if $\alpha_0=K^2$ so that

$$y_0=\frac{1}{(2\pi)^{\frac{1}{2}}}e^{iKx}, \quad K=0, \pm 1, \pm 2\cdots, \tag{12}$$

which form a complete orthogonal and normalized set of functions in the interval $0\leq x\leq 2\pi$. The quantity $(-2\theta\cos 2x)y$ in Eq. (10) may be regarded as a perturbation term that is added to Eq. (11). This perturbation term, as well as those solutions y which are periodic in π or 2π, may now be expressed in terms of a linear combination of the unperturbed functions y_0. If the unperturbed functions, y_0, are ordered:

$$\cdots\frac{1}{(2\pi)^{\frac{1}{2}}}e^{-iKx},\quad \frac{1}{(2\pi)^{\frac{1}{2}}}e^{-i(K-1)x},\quad \cdots\frac{1}{(2\pi)^{\frac{1}{2}}}\cdots,\quad \frac{1}{(2\pi)^{\frac{1}{2}}}e^{i(K-1)x},\quad \frac{1}{(2\pi)^{\frac{1}{2}}}e^{iKx}\cdots,$$

application of the usual perturbation procedure leads to the matrix

$$\mathbf{M}=\left|\begin{array}{ccccccc} & \cdot & \cdot & \cdot & \cdot & \cdot & \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \\ \cdots & 2^2 & 0 & \theta & 0 & 0 & \cdots \\ \cdots & 0 & 1^2 & 0 & \theta & 0 & \cdots \\ \cdots & \theta & 0 & 0 & 0 & \theta & \cdots \\ \cdots & 0 & \theta & 0 & 1^2 & 0 & \cdots \\ \cdots & 0 & 0 & \theta & 0 & 2^2 & \cdots \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \end{array}\right|, \tag{13}$$

the characteristic values of which determine those values of α for which solutions of Eq. (10) having the required periodicity are obtained. Except for being of infinite order, Eq. (13) is clearly identical with Eq. (9), if

$$\frac{H}{G-F}\frac{J(J+1)}{2}\equiv\theta. \tag{14}$$

With the aid of Eq. (14) and tables of the characteristic values of Mathieu's equation, an estimate may be made of the energy levels of the asymmetric rotor. How this may be done will be considered in greater detail in a later section.

THE ELLIPTIC CYLINDER FUNCTIONS

The elliptic cylinder functions are those solutions of Mathieu's equation which are periodic in π or 2π. Although their properties are well known,[8] a summary will be given of those properties which pertain to the present treatment.

[7] Other forms of Mathieu's equation are frequently used, *viz.*, Eq. (29) below. The particular form here is that used by E. L. Ince, Proc. Roy. Soc. Edin. **52**, 355 (1931). An extensive bibliography relating to Mathieu's equation, with summaries of the contents of the most important papers, is given by W. G. Bickley, Mathematical Tables and Other Aids to Computation **I**, No. 11 (1945); **II**, No. 13 (1946).

[8] See W. G. Bickley, reference 7, for numerous references.

If Mathieu's equation is written as

$$\left(-\frac{d^2}{dx^2}+2\theta\cos 2x\right)y=\alpha y, \tag{15}$$

or

$$\mathcal{L}y=\alpha y,$$

then it is readily verified that the operator $\mathcal{L}$ is left invariant by the transformations

$$\begin{cases} E:\ x\rightarrow 2\pi+x, \\ \mathcal{R}_1:\ x\rightarrow 2\pi-x, \\ \mathcal{R}_2:\ x\rightarrow \pi-x, \\ \mathcal{R}_3:\ x\rightarrow \pi+x. \end{cases} \tag{16}$$

The complete set of orthonormal functions generated by Eq. (15) can, at most, experience a change in sign when subjected to each of the transformations of Eq. (16). Since the set of transformations (16) form a group isomorphic with the point group $\mathbf{D}_2$, the functions generated by Eq. (15) must belong to each of the four irreducible representations of $\mathbf{D}_2$. In this respect the elliptic cylinder functions manifest a close analogy to the asymmetric rotor wave functions, which also belong to the irreducible representations of $\mathbf{D}_2$.

The elliptic cylinder functions have been defined[9] as

$$\begin{cases} ce_{2n}(x,\theta)=\sum_{r=0}^{\infty} A_{2r}^{(2n)}(\theta)\cos 2rx, \\ se_{2n+1}(x,\theta)=\sum_{r=0}^{\infty} B_{2r+1}^{(2n+1)}(\theta)\sin(2r+1)x, \\ ce_{2n+1}(x,\theta)=\sum_{r=0}^{\infty} A_{2r+1}^{(2n+1)}(\theta)\cos(2r+1)x, \\ se_{2n+2}(x,\theta)=\sum_{r=0}^{\infty} B_{2r}^{(2n+2)}(\theta)\sin 2rx, \end{cases} \tag{17}$$

where n takes on all non-negative integral values. The characteristic values corresponding to each of these species of functions are, respectively, $a_{2n}(\theta)$, $b_{2n+1}(\theta)$, $a_{2n+1}(\theta)$, $b_{2n+2}(\theta)$. The limiting values for θ equal to zero are

$$\begin{cases} a_{2n}(0)=(2n)^2, \\ b_{2n+1}(0)=(2n+1)^2, \\ a_{2n+1}(0)=(2n+1)^2, \\ b_{2n+2}(0)=(2n+2)^2. \end{cases} \tag{18}$$

Moreover, from the tabulated values it is found that for any n

$$\cdots\leq a_{2n}(\theta)\leq b_{2n+1}(\theta)\leq a_{2n+1}(\theta) \leq b_{2n+2}(\theta)\leq a_{2(n+1)}(\theta)\cdots, \tag{19}$$

so that a distinct ordering of the characteristic values is possible that is independent of θ.

In view of the isomorphism existing between the elliptic cylinder functions and the asymmetric rotor functions it would seem desirable to find a one-one correspondence between them, based upon symmetry considerations. This would allow the unique identification of each characteristic value approximated by solution of the Mathieu equation with an energy value of the asymmetric rotor. This, unfortunately, is impossible because the transformations in Eq. (16) may not be identified in a unique fashion with the rotations forming the elements of the point group $\mathbf{D}_2$ to which the asymmetric rotor wave functions belong. Depending upon the evenness or oddness of J, a representation may be found which permits of the appropriate identification of elliptic cylinder functions with the wave functions of the rotor.

It is possible, however, to identify the two kinds of functions through their corresponding characteristic values. In the notation of reference 2, an asymmetric rotor energy level is denoted by the two numbers $J_\tau=J_{K_{-1},K_{+1}}$ with $\tau=K_{-1}-K_{+1}$; K_{-1} is the $|K|$ corresponding to the limiting prolate symmetric rotor and K_{+1} is the $|K|$ corresponding to the limiting oblate symmetric rotor.

Observe that either

$$\begin{aligned} K_{-1}+K_{+1}&=J+1 \quad \text{case (a), or} \\ &=J \quad \text{case (b),} \end{aligned} \tag{20}$$

so that

$$\begin{aligned} K_{+1}&=J+1-K_{-1} \quad \text{case (a),} \\ &=J-K_{-1} \quad \text{case (b).} \end{aligned}$$

Hence

$$\begin{aligned} \tau&=2K_{-1}-J-1 \quad \text{case (a),} \\ &=2K_{-1}-J \quad \text{case (b).} \end{aligned}$$

For the same value of K_{-1} (corresponding to the limiting case of K_{-1} degeneracy)

$$2K_{-1}-J>2K_{-1}-J-1.$$

Therefore, levels corresponding to *case* (a) are lower than those corresponding to *case* (b), for the same value of K_{-1}.

[9] Ince, see reference 7.

If J is added to both sides of Eq. (20),

$$J+K_{-1}+K_{+1}=(2J+1) \quad \text{case (a)},$$
$$=2J \quad \text{case (b)},$$

so that

case (a) corresponds to *odd* $(J+K_{-1}+K_{+1})$
case (b) corresponds to *even* $(J+K_{-1}+K_{+1})$.

Equation (19) may now be applied, permitting the following correspondences

$$\begin{cases} b_{K_{-1}} \leftrightarrow J_{K_{-1},K_{+1}} \text{ for } odd\ (J+K_{-1}+K_{+1}), \\ a_{K_{-1}} \leftrightarrow J_{K_{-1},K_{+1}} \text{ for } even\ (J+K_{-1}+K_{+1}). \end{cases} \tag{21}$$

Insofar as the characteristic values of Mathieu's equation approximate the asymmetric rotor energy levels, it should be possible by Eq. (21) to arrive at an estimate of the asymmetric rotor wave functions for J large and $|K|$ small (for the limiting symmetric case).

The asymmetric rotor wave functions are commonly expressed as a linear combination of a basis of the Wang[1] functions, which consist of the sums and differences of those pairs of symmetric rotor wave functions which have the same J and M but have K's of opposite sign. All these basis functions are normalized to unity, and the Wang function for which K is zero is identical with the symmetric rotor wave function for which K is zero.

This combination of the symmetric rotor wave functions corresponds precisely to the combination of the exponential functions generated by Eq. (11) to form either *sines* or *cosines*. It is in terms of these latter functions that the elliptic cylinder functions are commonly expressed. As a consequence, the coefficients employed in expressing the asymmetric rotor wave functions in terms of the Wang functions are simply related to the Fourier coefficients of the corresponding elliptic cylinder function.

In order to employ the tabulated Fourier coefficients of Ince, a slight modification is necessary. This modification arises because of Ince's choice of the basis function for which K is zero. When allowances are made for this, it turns out that all that is needed is to multiply the quantities A_0 by the quantity $\sqrt{2}$. With this modification the transformation coefficients from Wang functions to asymmetric rotor wave functions may be taken directly from the tabulated values, or interpolated when necessary. Some care must be exercised to maintain the proper sign of θ (i.e., as it appears in the energy matrix) if the correct characteristic vectors are to be obtained.

Since the characteristic vectors obtained for the elliptic cylinder functions are of infinite dimensionality, while those for the asymmetric rotor are finite (for finite J), it is necessary to adjust for this disparity. It is suggested that the first m Fourier coefficients of the appropriate elliptic cylinder function be taken as the approximation to the corresponding asymmetric rotor characteristic vector of dimensionality m. Consistency may be attained by normalizing the resulting vector to unity.

MODIFICATION OF MATHIEU'S EQUATION

To obtain a better approximation for the energy levels than that given simply by the characteristic value of Mathieu's equation the higher order terms of Eq. (8) must be considered. The following expansion may be obtained

$$[f(J,n)]^{\frac{1}{2}} \sim \frac{J(J+1)}{2} - \frac{n^2}{2}\left(1+\frac{1}{2J(J+1)}\right)+O\left(\frac{n^2}{J(J+1)}\right)^2. \tag{22}$$

For those cases where $n \ll J \gg 1$, the first two terms give an excellent approximation for the function. With this approximation, then, Eq. (7) becomes

$$E'_{K;\,K+2}=E'_{K+2;\,K}=\left(\frac{H}{G-F}\right)\left[\frac{J(J+1)}{2}-\frac{(K+1)^2}{2}\left(1+\frac{1}{2J(J+1)}\right)\right]$$
$$=\left(\frac{H}{G-F}\right)\left[\frac{J(J+1)}{2}-\frac{1}{2}\left(1+\frac{1}{2J(+1)}\right)\right]$$
$$-\frac{1}{2}\left(\frac{H}{G-F}\right)\left[1+\frac{1}{2J(J+1)}\right](K^2+2K). \tag{23}$$

TABLE I. First-order corrections apart from factor θ'.

θ \ char. value	be_0	bo_1	be_1	bo_2	be_2	bo_3	be_3	bo_4	be_4	bo_5	be_5	bo_6
0	0.00000	−1.00000	1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1	0.09424	−0.32005	1.83468	1.32876	1.25074	1.19579	1.04153	1.07173	1.05792	1.04121	1.04073	1.02826
2	0.41579	0.25006	2.84494	2.63144	2.32442	2.50407	1.91671	2.17244	2.06401	2.08152	2.07401	2.05472
3	0.81976	0.74573	3.97885	3.88779	3.42380	3.88749	2.69191	3.32478	2.97109	3.12456	3.08712	3.07807
4	1.22537	1.18935	5.14014	5.08654	4.66321	5.31776	3.48317	4.38195	3.74826	4.17802	4.06222	4.09782
5	1.61321	1.59454	6.26512	6.22294	6.06460	6.77265	4.37809	5.82805	4.39930	5.25192	4.97741	5.11481
6	1.98021	1.97009	7.33437	7.29965	7.59044	8.23415	5.42184	7.18040	4.97322	6.35700	5.80951	6.13092
7	2.32744	2.32176	8.34847	8.31365	9.17178	9.68775	6.63650	8.59208	5.54855	7.50303	6.53867	7.15008
8	2.65694	2.65367	9.31301	9.29165	10.74443	11.12230	8.02937	10.05370	6.20048	8.69766	7.15560	8.17707
9	2.97075	2.96881	10.23381	10.21786	12.26998	12.52989	9.59010	11.55498	6.98025	9.81414	7.66933	9.21794
10	3.27069	3.26953	11.11594	11.10419	13.73425	13.93145	11.28789	13.08523	7.91630	10.08346	8.11090	10.27919

The first bracketed term is constant for a given J, and may be identified with the θ in Mathieu's equation. It can be verified that the second term in brackets may be obtained from the perturbation operator

$$\mathcal{P}(x) = -2\theta'\left[\cos 2x\frac{d^2}{dx^2} - 2\sin 2x\frac{d}{dx}\right], \tag{24}$$

so that Mathieu's equation, modified by the addition of this perturbation operator, is altered to

$$\frac{d^2y}{dx^2} + (\alpha - 2\theta\cos 2x)y - 2\theta'\left(\cos 2x\frac{d^2y}{dx^2} - 2\sin 2x\frac{dy}{dx}\right) = 0, \tag{25}$$

with

$$\theta = \left(\frac{H}{G-F}\right)\left[\frac{J(J+1)}{2} - \frac{1}{2}\left(1 + \frac{1}{2J(J+1)}\right)\right],$$
$$\theta' = \frac{1}{2}\left(\frac{H}{G-F}\right)\left(1 + \frac{1}{2J(J+1)}\right). \tag{26}$$

Equation (25) will be considered in the next section, where it will be solved by a perturbation procedure. In principle, additional perturbation operators may be found that will permit, with one exception, the construction of a secular equation that is identical with that arising in the asymmetric rotor problem. The exception is the disparity in the magnitudes of the order of the two secular equations. However, this may be handled by a perturbation procedure also.

PERTURBATION TECHNIQUE

To take into account the fact that for any finite J, the energy matrix of the asymmetric rotor is finite, while the matrix generated by Eq. (25) (in terms of the functions of Eq. (11)) is of infinite order, augment the former by rows and columns of zeros, so that $\mathbf{E}'(\kappa)$ remains symmetrical with respect to the main and antidiagonals, i.e., equal numbers of rows and columns added to each side of $\mathbf{E}'(\kappa)$. Then, symbolically, the augmented matrix may be represented as

$$\mathbf{E}''(\kappa) = \mathbf{M} + \mathbf{P} + \mathbf{R}, \tag{27}$$

where $\mathbf{M}$ is the matrix in Eq. (13), $\mathbf{P}$ is the matrix arising from the perturbation operator in Eq. (24), and $\mathbf{R}$ is a remainder added to the sum of $\mathbf{M}$ and $\mathbf{P}$ to complete the equality; all matrix elements are evaluated in terms of the functions generated by Eq. (11).

The remainder matrix $\mathbf{R}$ will have elements that are small in magnitude and vanish asymptotically, connecting those diagonal terms which are of interest ($|K| \ll J$). Hence it will have but slight effect upon the characteristic values as determined from $\mathbf{M}+\mathbf{P}$ alone when J is only moderately large.

Formally, Eq. (27) may be diagonalized as follows. By its construction $\mathbf{M}$ will give characteristic roots of Mathieu's equation. These may be taken as known. $\mathbf{P}$ may be evaluated in terms of the periodic solutions of Mathieu's equation, the elliptic cylinder functions, and the perturbation operator in Eq. (24). Since a perturbation operator corresponding to R has not been obtained it is convenient to first determine R in terms of the basis of functions of Eq. (12). Transformation to a basis of elliptic cylinder functions is then carried out by matrix multi-

TABLE II.

Asymmetric rotor level	$(J+K_{-1}+K_{+1})$	Notation of ref. 7	Notation of ref. 12	Corresponding elliptic cylinder function
$J_{K_{-1},K_{+1}}$	odd	$b_{K\pm1}$	$bo_{K\pm1}$	$se_{K\pm1}(x,\theta)$
$J_{K_{-1},K_{+1}}$	even	$a_{K\pm1}$	$be_{K\pm1}$	$ce_{K\pm1}(x,\theta)$

TABLE III.

Quantity \ Representation	I	III
F	$\frac{\kappa-1}{2}$	$\frac{\kappa+1}{2}$
$G-F$	$\frac{3-\kappa}{2}$	$-\frac{3+\kappa}{2}$
$\left\lvert\frac{H}{G-F}\right\rvert$	$\frac{1+\kappa}{3-\kappa}$	$\frac{1-\kappa}{3+\kappa}$

plication. The required transformation matrices are readily obtained from the Fourier coefficients tabulated by Ince.[10]

In view of their construction both **P** and **R** may be expected to have elements which have absolute values considerably smaller than the differences in the characteristic values of the levels of **M** which they connect. Consequently, a rapid convergence of the usual perturbation series expansion may be expected.

Some comment is required concerning the sign of θ and θ' in Eq. (26). Since the characteristic values of Mathieu's equation are usually tabulated for positive θ, it would be convenient to have θ always positive. However, since the sign of θ (also θ') is determined by $[H/(G-F)]$, it may be either positive or negative,[6] depending upon the representation that is chosen in which to express the symmetric rotor wave functions. It is clearly possible to find an orthogonal transformation that will change the sign of the non-diagonal elements of $\mathbf{E}(\kappa)$, while the sign of the diagonal elements remains unchanged. Since the characteristic values are unaltered by orthogonal transformations, the quantity $[H/(G-F)]$ may be taken positive always. The same does not apply to the quantity $(G-F)$ however.

In evaluating the matrix elements of **P** in in terms of a basis of elliptic cylinder functions, a certain simplification is possible based upon the symmetry properties of these functions. Since the perturbation operator $\mathcal{P}$ has character $+1$ for all operations in Eq. (16), it is clear that **P** factors into four submatrices corresponding to the four species of elliptic cylinder functions. A similar factoring may be applied to **M**, but is unnecessary, since the characteristic values of **M** may be taken as known. This factoring is analogous to the factoring of the secular equation of the asymmetric rotor.

The necessary integrals have been evaluated by the use of Eq. (17). The general matrix element for each of the four species of functions follows:

$ce_{2n}(x,\theta)$:

$$P(2n,2n')=-4\theta\sum_{r=2}^{\infty}(r^2-r)\{A_{2r}{}^{(2n)}A_{2r-2}{}^{(2n')}+A_{2r}{}^{(2n')}A_{2r-2}{}^{(2n)}\};\tag{28a}$$

$se_{2n+1}(x,\theta)$:

$$P(2n+1,2n'+1)=-\theta'\Big[B_1{}^{(2n+1)}B_1{}^{(2n'+1)}+\sum_{r=1}^{\infty}(4r^2-1)\times\{B_{2r+1}{}^{(2n+1)}B_{2r-1}{}^{(2n'+1)}+B_{2r+1}{}^{(2n'+1)}B_{2r-1}{}^{(2n+1)}\}\Big];\tag{28b}$$

$ce_{2n+1}(x,\theta)$:

$$P(2n+1,2n'+1)=-\theta'\Big[-A_1{}^{(2n+1)}A_1{}^{(2n'+1)}+\sum_{r=1}^{\infty}(4r^2-1)\times\{A_{2r+1}{}^{(2n+1)}A_{2r-1}{}^{(2n'+1)}+A_{2r+1}{}^{(2n'+1)}A_{2r-1}{}^{(2n+1)}\}\Big];\tag{28c}$$

$se_{2n+2}(x,\theta)$:

$$P(2n+2,2n'+2)=-4\theta'\sum_{r=2}^{\infty}(r^2-r)\{B_{2r}{}^{(2n+2)}B_{2r-2}{}^{(2n'+2)}+B_{2r}{}^{(2n'+2)}B_{2r-2}{}^{(2n+2)}\}.\tag{28d}$$

[10] Ince, see reference 7; J. A. Stratton, P. M. Morse, L. J. Chu, and R. A. Hunter, *Elliptic Cylinder and Spheroidal Wave Functions* (John Wiley and Sons, Inc., New York, 1941); S. Goldstein, Camb. Phil. Soc. Trans. **23**, 303 (1927).

The diagonal elements of **P**, apart from the factor θ', have been determined from the coefficients given by Ince[11] for a number of the elliptic cylinder functions. These quantities are given in Table I.

COMPUTATIONAL PROCEDURE

The computation of the characteristic values of Mathieu's equation, which form the basis for the approximation considered here, is made particularly simple by the recently published Tables of Characteristic Values of Mathieu's Differential Equation.[12]

Certain differences occur between the notation employed in the latter work and that employed here. These differences will be summarized. Mathieu's differential equation may be written in the form

$$\frac{d^2y}{dx^2}+(b-s\cos^2 x)y=0. \tag{29}$$

Comparison with Eq. (10) reveals that

$$\begin{cases}\alpha=b-\frac{1}{2}s,\\ \theta=\frac{1}{4}s.\end{cases} \tag{30}$$

The tables give the characteristic values b to eight decimal places for various values of s. Interpolation for intermediate values of s is made particularly simple by the simultaneous tabulation of modified second central differences. When Everett's interpolation formula[13] is used with these modified differences the error is less than one half-unit in the last tabulated place.

The notation used for the characteristic values differs from that used above. The following correspondences are obtained.

$$\begin{cases}a_{2n}\leftrightarrow be_{2n}\\ b_{2n+1}\leftrightarrow bo_{2n+1}\\ a_{2n+1}\leftrightarrow be_{2n+1}\\ b_{2n+2}\leftrightarrow bo_{2n+2}.\end{cases} \tag{31}$$

The characteristic value of Mathieu's equation corresponding to a particular asymmetric rotor energy level may be obtained from Table II.

Before carrying out a computation for an energy value approximation it is best to choose a representation that will make $|H/(G-F)|$ small. In general, that representation should be chosen for which the asymmetric rotor energy matrix is most nearly diagonal. Thus for asymmetries in the vicinity of the limiting prolate symmetric case ($\kappa=-1$) a type I representation of reference 2 should be used; in the case of nearly oblate symmetry ($\kappa=+1$) a type III representation should be used. Table III gives the quantities needed in these computations for both representations. It should be remembered that K_{-1} is used with a type I representation, while K_{+1} is used with a type III representation.

The quantities θ and θ' may now be determined with the aid of Eq. (26) and Table III. The appropriate characteristic value to be computed may be determined from Table II. With the aid of Eq. (30) the quantity s may be obtained; the value of the appropriate characteristic value b may then be obtained from the Tables by interpolation, if necessary. The characteristic

TABLE IV. Approximate second-order correction apart from factor $(\theta')^2$.

θ	be_0	bo_1	be_1	bo_2	be_2	bo_3	be_3	bo_4
0	−0.00000	−1.12500	−1.12500	−5.33333	−5.33333	−12.93750	−12.93750	−23.46667
1	−0.39178	−1.20178	−1.37094	−5.41561	−5.00017	−12.88162	−12.71756	−23.40270
2	−0.97928	−1.41298	−2.11591	−5.64637	−4.58435	−12.72354	−12.06048	−23.22154
3	−1.40973	−1.65907	−3.26382	−6.00745	−4.42034	−12.55062	−11.07556	−22.95080
4	−1.72170	−1.90163	−4.48031	−6.44982	−4.42417	−12.39361	−10.10610	−22.62205
5	−1.96944	−2.12919	−5.53756	−6.93442	−4.46974	−12.26193	−9.38104	−22.27251
6	−2.18254	−2.34026	−6.39651	−7.44045	−4.46752	−12.16077	−8.92747	−21.91700
7	−2.37602	−2.53642	−7.09759	−7.94698	−4.40606	−12.09629	−8.67357	−21.57118
8	−2.55769	−2.71991	−7.68968	−8.44328	−4.34503	−12.07602	−8.51668	−21.24234
9	−2.73176	−2.89281	−8.21038	−8.92404	−4.36265	−12.10735	−8.35227	−20.93472
10	−2.77796	−3.05685	−8.67038	−9.38738	−4.51675	−12.19631	−8.11453	−20.65218

[11] Different authors use somewhat different conventions relating to the "normalization" of the functions. Ince "normalizes" the function to π instead of unity. This fact was taken into account in preparing Table I.

[12] A report prepared for the Applied Mathematics Panel, NDRC, by the Mathematical Tables Project, National Bureau of Standards, AMP Report 165.1R.

[13] E. T. Whittaker and G. Robinson, *The Calculus of Observations* (Blackie and Son, Ltd., London, 1932).

TABLE V. Computation of characteristic values of asymmetric rotor.

Level	Tables of ref. 2	Mathieu function approximation	Third-order perturbation formula, ref. 2
		$\kappa=-0.9$	
$10_{0,10}$	−106.11121	−106.11116	−106.40266
$10_{1,10}$	−105.67708	−106.67708	−105.67431
$10_{1,9}$	−100.32958	−100.32955	−100.32513
$10_{2,9}$	−96.96993	−96.96996	−96.97205
$10_{2,8}$	−95.36420	−95.36418	−95.06940
$10_{3,8}$	−86.74965	−86.74966	−86.75226
$10_{3,7}$	−86.59725	−86.59730	−86.60144
$10_{4,7}$	−73.14548	−73.14556	−73.14326
		$\kappa=-0.8$	
$10_{0,10}$	−104.00141	−104.00146	−106.79625
$10_{1,10}$	−103.90124	−103.90131	−103.83947
$10_{1,9}$	−94.02065	−94.02079	−94.04603
$10_{2,9}$	−92.48017	−92.48039	−92.99250
$10_{2,8}$	−87.56942	−87.56856	−84.71850
$10_{3,8}$	−81.32404	−81.32363	−80.28408
$10_{3,7}$	−80.20810	−80.20768	−80.17775
$10_{4,7}$	−67.99406	−67.99363	−67.95775

value α is then determined by Eq. (30). The approximate characteristic value of Eq. (5) is then given by

$$E_{\tau}{}^{J}(\kappa)=FJ(J+1)+(G-F)\alpha. \qquad (32)$$

Corrections to Eq. (32) may be obtained as indicated above. The diagonal elements of **P**, except for the factor θ', are given in Table I, from which the appropriate first-order correction to Eq. (32) may be determined by interpolation. Higher order corrections may be determined by evaluation of the non-diagonal elements of **P**, using Eq. (28a)–(28d), followed by the usual perturbation treatment. However, more non-diagonal elements of **P** are required that can be determined from the few elliptic cylinder functions that have been tabulated. Nevertheless a good *approximate* second-order correction may be obtained from the finite submatrix of **M** and **P** which contains those levels for which coupling elements may be evaluated. The second-order corrections so obtained will be larger than the complete second-order correction. Because of the rapidly increasing difference between successive characteristic values of **M**, the neglect of the influence of higher levels will probably not prove to be serious.

The approximate second-order correction to be applied to α, except for the factor $(\theta')^2$, may be determined from Table IV by interpolation, if necessary.

As an illustration of the procedure outlined above, the eight lowest energy values for $J=10$, with asymmetries of $\kappa=-0.9$, -0.8, have been computed. In Table V they are compared with the accurate values obtained by King, Hainer, and Cross, as well as with the values obtained from the third-order perturbation formulas given by these authors. It is seen that the agreement between the results of the present computation and the accurate values is very good, while the results of the third-order perturbation calculations are quite inadequate for the values of κ considered.

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