THE SYMMETRICAL TOP IN THE UNDULATORY MECHANICS[1]

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Abstract

Schrödinger's method for determining the energy levels of an atomic system is applied to the case of the symmetrical top (moment of inertia about axis of symmetry C, the other one A). The energy values are found to be

$$W_{jn} = \frac{h^2}{8\pi^2}\left[\frac{1}{A}\,j(j+1) + \left(\frac{1}{C} - \frac{1}{A}\right)n^2\right]$$

in agreement with the result obtained by Dennison from the matrix mechanics. The quantum numbers j and n must be integers restricted by $0 \leqq j$, $|n| \leqq j$, while half-integral values are not permissible. The intensities of transitions are also calculated.

Introduction

THROUGH the important work of Schrödinger[2] the problem of finding the energy levels of an atomic system has been reduced to the determination of the characteristic values of a certain second order partial differential equation for a function U of the generalized coordinates, the so-called wave equation. It is the purpose of this paper to apply his procedure to the case of the symmetrical top, a mechanical system useful in the interpretation of molecular spectra. Dennison[3] has obtained the energy values and intensities of this system in terms of three quantum numbers, j, n, m on the basis of the matrix mechanics. He has, however, only shown that his solution satisfies certain conditions following directly from the fundamental equations of the matrix mechanics without proving that all these equations are obeyed themselves, although a comparison with the amplitudes of the top in the classical theory made it probable that his results are entirely satisfactory. Moreover the question remained unsettled whether j and n had to be given integral or half integral values. For these reasons a treatment of the same problem by Schrödinger's method does not appear superfluous.

[1] See the preliminary note, Nature **118**, 805 (1926). In a paper which came to our attention after this article was sent in for publication F. Reiche, (Zeit. f. Phys. **39**, 444, 1926), also investigates the energy values of the symmetrical top by the same method and arrives at results identical with ours. He does not, however, treat the intensities, and therefore it was thought worth while to publish our results.

[2] E. Schrödinger—Ann. d. Phys. **79**, 361, 489, 734, (1926).

[3] D. Dennison—Phys. Rev. **28**, 318, (1926).

The Wave Equation and its Separation

Schrödinger's wave equation states that

$$\Delta U+\frac{8\pi^2}{h^2}(W-V)U=0, \tag{1}$$

where Δ denotes the gradient of the divergence in the non-Euclidean configurational space and $V(q^i)$ the potential energy of the system under consideration. The question to be answered is: For what values of the constant W do solutions U exist which are finite throughout the configurational space (and zero at infinity if the space extends to infinity)? These values W shall represent the energies of the stationary states.

To describe the motion of the symmetrical top we shall use Euler's angles θ, ϕ, ψ; θ denoting the angle between the z-axis in space and the axis of symmetry z' of the top, ϕ and ψ the angles between the line of nodes (line of intersection between the x'- and x-axes respectively). The kinetic energy in terms of the generalized momenta is given by

$$2T=\frac{1}{A}p_\theta^2+\left(\frac{\cos^2\theta}{A\sin^2\theta}+\frac{1}{C}\right)p_\phi^2+\frac{1}{A\sin^2\theta}p_\psi^2-\frac{2\cos\theta}{A\sin^2\theta}p_\phi p_\psi,$$

A and C being the moments of inertia of the top about the x'- and z'-axes respectively. For our system the partial differential equation (1) for U becomes

$$\begin{aligned}\frac{\partial^2 U}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial U}{\partial\theta}+\left(\frac{A}{C}+\frac{\cos^2\theta}{\sin^2\theta}\right)\frac{\partial^2 U}{\partial\phi^2}+\frac{1}{\sin^2\theta}\frac{\partial^2 U}{\partial\psi^2}\\ -\frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2 U}{\partial\phi\partial\psi}+\frac{8\pi^2 AW}{h^2}U=0.\end{aligned} \tag{2}$$

This equation will be separated by the substitution

$$U=\Theta(\theta)\begin{cases}\sin(n\phi+m\psi)\\ \cos(n\phi+m\psi)\end{cases} \tag{3}$$

where $\Theta(\theta)$ is a function of θ alone. It is necessary that U returns to the same value if ϕ and ψ are increased by integral multiples of 2π, since then the mechanical system takes up the same position. This can only be accomplished by having the constants n and m equal to integers. Substituting (3) in Eq. (2) gives an ordinary second order differential equation for Θ

$$\frac{d^2\Theta}{d\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta}-\frac{(m-n\cos\theta)^2}{\sin^2\theta}\Theta+\sigma\Theta=0, \tag{4}$$

$$\sigma=\frac{8\pi^2AW}{h^2}-\frac{A}{C}n^2. \tag{5}$$

Determination of the Characteristic Values[4]

Eq. (4) can be transformed into the hypergeometric equation by a suitable change of variables. We shall introduce the following notation:

$$\begin{matrix} \lambda_1 \\ \mu_1 \end{matrix}\left\{\begin{matrix} \frac{1}{2}(m+n) \\ -\frac{1}{2}(m+n) \end{matrix}\right. \qquad \begin{matrix} \lambda_2 \\ \mu_2 \end{matrix}\left\{\begin{matrix} \frac{1}{2}(m-n) \\ -\frac{1}{2}(m-n) \end{matrix}\right. \qquad \begin{matrix} \lambda_3=\frac{1}{2}+\left(\frac{1}{4}+\sigma+n^2\right)^{1/2} \\ \mu_3=\frac{1}{2}-\left(\frac{1}{4}+\sigma+n^2\right)^{1/2} \end{matrix} \tag{6}$$

The brackets in the first two expressions mean that λ_1 and λ_2 shall be so chosen from the two quantities behind the bracket that $\lambda_1 \geqq 0$, $\lambda_2 \geqq 0$; e. g. if $(m+n)\geqq 0$, $(m-n)\leqq 0$, then $\lambda_1=\frac{1}{2}(m+n)$, $\mu_1=-\frac{1}{2}(m+n)$, $\lambda_2=-\frac{1}{2}(m-n)$, $\mu_2=\frac{1}{2}(m-n)$. Furthermore we introduce in Eq. (4) the new independent variable

$$x=\frac{1}{2}(\cos\theta+1) \tag{7}$$

and the new dependent variable

$$X=x^{-\lambda_1}(x-1)^{-\lambda_2}\Theta. \tag{8}$$

Eq. (4) then takes the form of the hypergeometric equation

$$x(1-x)\frac{d^2X}{dx^2}+[\gamma-(\alpha+\beta+1)x]\frac{dX}{dx}-\alpha\beta X=0, \tag{9}$$

where

$$\alpha=\lambda_1+\lambda_2+\lambda_3, \qquad \beta=\lambda_1+\lambda_2+\mu_3, \qquad \gamma=2\lambda_1-1. \tag{10}$$

From these and our choice of λ_1 and λ_2 it follows always that

$$\gamma-1=2\lambda_1\geqq 0, \qquad \alpha+\beta-\gamma=2\lambda_2\geqq 0.$$

Moreover $\gamma-1=p$, where p is an integer $\geqq 0$.

[4] See L. Schlesinger—Differentialgleichungen, (Sammlung Schubert No. 13, Göschen 1900, Chapter 4.)

To the interval of our old variable θ from 0 to π there corresponds the interval from 0 to 1 of the new variable x. From Eq. (8) it follows that if Θ is to be finite in this interval including the limits, then (since λ_1 and $\lambda_2 \geqq 0$) X must be regular inside this interval and at the limits must not become infinite of higher order than $x^{-\lambda_1}$ and $(x-1)^{-\lambda_2}$.

The solution of Eq. (9) is expressible in terms of hypergeometric series. We know that $\gamma - 1 = p$, where p is zero or a positive integer. We distinguish the following cases:

(a). If $p > 0$ and neither α nor β is equal to one of the numbers $1 \cdots p$; or if $p = 0$ and neither α nor β is equal to zero, then two independent particular solutions in the neighborhood of $x = 0$ are given by

$$X_1 = F(\alpha,\beta,\gamma,x),$$
$$X_2 = G(\alpha,\beta,\gamma,x) + F(\alpha,\beta,\gamma,x) \log x,$$

where

$$F(\alpha,\beta,\gamma,x) = 1 + \frac{\alpha \cdot \beta}{1 \cdot \gamma} x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1 \cdot 2\gamma(\gamma+1)} x^2 + \cdots$$

is the hypergeometric series, and G is a series

$$G(\alpha,\beta,\gamma,x) = x^{1-\gamma} \sum c_k x^k, \qquad c_0 \neq 0.$$

(b). If $p > 0$ and at least one of the quantities α or β is equal to one of the quantities $1 \cdots p$, then

$$X_1 = F(\alpha,\beta,\gamma,x),$$
$$X_2 = x^{1-\gamma} F(\alpha + 1 - \gamma, \beta + 1 - \gamma, 2 - \gamma, x).$$

In the second series the zero factors in the numerators and denominators of the coefficients are to be omitted.

(c). If $p = 0$ and at least one of the quantities α and β is zero, then

$$X = \text{Const.}$$

will be a solution.

We see that there are no solutions Θ fulfilling the requirements of finiteness inside the interval unless at least one of the quantities α and β is zero or a negative integer. For if that is the case, the solution X_1 will have only a finite number of terms and hence be finite throughout the interval. However, if neither α not β is a negative integer or zero, X_1 will become infinite for $x = 1$, since $F(\alpha, \beta, \gamma, x)$ diverges for $x = 1$ if, as in our case, the real part of $\gamma - \alpha - \beta \leqq 0$, becoming infinite as $(1-x)^{\gamma-\alpha-\beta} = (1-x)^{-2\lambda_2}$ (or as $\log(1-x)$ if $\gamma - \alpha - \beta = 0$). The solution X_2 on the other hand becomes infinite as $x^{1-\gamma}=x^{-2\lambda_1}$ (or as $\log x$ if $1-\gamma=0$).

From Eq. (6) and Eq. (10) it follows that if α and β are real, $\alpha \geqq \beta$ so that for convergence β must be zero or a negative integer. That will only be the case if

$$\sigma=j(j+1)-n^2, \qquad j=(\lambda_1+\lambda_2),(\lambda_1+\lambda_2+1)\cdots, \tag{11}$$

as is easily seen from (6) and (10). Hence j must be a positive integer or zero since $\lambda_1+\lambda_2$ is always a positive integer or zero. As a direct consequence of the condition expressed in Eq. (11),

$$j \geqq \lambda_1+\lambda_2,$$

we have

$$j \geqq |n|, \qquad j \geqq |m|, \tag{12}$$

since, according to the definition (6) of λ_1 and λ_2, $(\lambda_1+\lambda_2)$ is always the larger of the two quantities $|n|$ and $|m|$.

Introducing our value σ into Eq. (5) we get for the energy levels

$$W_{jn}=\frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1)+\left(\frac{1}{C}-\frac{1}{A}\right)n^2\right]$$

in harmony with Dennison's[3] results, but with the additional information that j and n must be integers. The requirements (12) shows that for a given j and n there exist $2j+1$ values of m. This $(2j+1)$-fold occurrence of the value W_{jn} among the characteristic value of the wave equation corresponds to the fact that the state (j, n) will divide into $(2j+1)$ levels under the action of an external field. The quantum number j determines the total moment of momentum, n the moment of momentum about the axis of symmetry.

Calculation of Intensities

As shown by Schrödinger[2] and Eckart[5] the matrix elements of the coordinate q^i in the Born-Heisenberg mechanics are given by

$$q^i(k,l)=C_kC_l\int dvq^iU_kU_l, \tag{13}$$

where U_k and U_l are the characteristic functions belonging to the states k and l respectively, while dv is the element of volume of the

[5] C. Eckart—Phys. Rev. **28**, 711, (1926).

configurational space. The integration extends over the whole domain of the variables. C_k is defined by

$$C^2_k \int dv U^2_k = 1. \tag{14}$$

If in our problem we consider a radiating charge attached to the top such that its coordinates in the system of axes x', y', z' rigidly connected to the top are a, 0, c, then its coordinates in space are given by

$$\begin{aligned} x &= c \sin\theta \sin\psi + a \cos\phi \cos\psi - a \cos\theta \sin\phi \sin\psi, \\ y &= -c \sin\theta \cos\psi + a \cos\phi \sin\psi + a \cos\theta \sin\phi \cos\psi, \\ z &= c \cos\theta + a \sin\theta \sin\phi. \end{aligned}$$

We have but to substitute these and our characteristic functions in Eqs. (13) and (14) and to evaluate the definite integrals.

As an example we shall take the coordinate z. For the matrix element corresponding to the transition j, n, $m-j'$, n', m' we find with the aid of Eq. (13)

$$\begin{aligned} z(j,n,m\,;j',n',m') = C_{jnm}C_{j'n'm'} \int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} A(C)^{1/2} \sin\theta d\theta d\phi d\psi \\ \cdot (c\cos\theta + a \sin\theta \sin\phi)\Theta(j,n,m,\theta)\Theta(j',n',m',\theta) \\ \cdot \begin{cases} \sin(n\phi + m\psi) \\ \cos(n\phi + m\psi) \end{cases} \begin{cases} \sin(n'\phi + m'\psi) \\ \cos(n'\phi + m'\psi) \end{cases} \end{aligned}$$

the volume element dv in the non-Euclidean space being given by

$$dv = (g)^{1/2} d\theta d\phi d\psi = A(C)^{1/2} \sin\theta d\theta d\phi d\psi.$$

It is immediately evident that due to the integration over ϕ and ψ $z(j, n, m; j', n', m')$ will be different from zero only when $n'=n$, $n'=n\pm 1$ and $m'=m$. These conditions correspond to the well-known selection rules for the radiation emitted by the top. It will be sufficient for the purpose of illustration to restrict ourselves now to the case $n'=n$. We then have

$$\begin{aligned} z(j,n,m\,;j',n,m) = 4\pi^2 c C_{jnm} C_{j'nm} A(C)^{1/2} \\ \cdot \int_0^{\pi} d\theta \sin\theta \Theta(j,n,m,\theta)\Theta(j',n,m,\theta). \end{aligned} \tag{15}$$

For C_{jnm} we integrate over ϕ and ψ in Eq. (14) and obtain

$$4\pi^2 A(C)^{1/2} C_{jnm}^2 \int_0^\pi d\theta \sin\theta \Theta^2(j,n,m,\theta) = 1 \tag{16}$$

and similarly for $C_{j'nm}$.

We now proceed with the evaluation of the integrals. Expressing Θ in terms of the hypergeometric series according to Eqs. (7) and (8) and writing

$$\beta = -\nu, \qquad \alpha = \epsilon + \nu, \tag{17}$$

where ν is a positive integer or zero, we get for the first integral

$$I_1 = \int_0^\pi d\theta \sin\theta \cos\theta \Theta(j,n,m,\theta)\Theta(j',n,m,\theta)$$
$$= (-1)^{\epsilon-\gamma} \int_0^1 dx(1-2x)F(\epsilon+\nu, -\nu,\gamma,x)F(\epsilon+\nu', -\nu',\gamma,x)x^{\gamma-1}(1-x)^{\epsilon-\gamma}.$$

Both ϵ and γ are the same in the two functions F, since they are given by

$$\epsilon = 2(\lambda_1+\lambda_2)+\lambda_3+\mu_3, \quad \gamma = 2\lambda_1 - 1$$

according to Eqs. (10) and (17), and are hence independent of j according to Eq. (6).

All integrals occurring in this and the remaining calculations can be reduced to the general form

$$\int_0^1 dx F(\epsilon+\nu, -\nu,\gamma,x)F(\epsilon'+\nu', -\nu',\gamma',x)x^{\gamma-1}(1-x)^{\epsilon-\gamma} \tag{18}$$

by means of the relation valid for any hypergeometric series

$$xF(\epsilon+\nu, -\nu,\gamma,x) = \frac{(\gamma-1)(\gamma-2)}{(\epsilon+\nu-1)(\nu+1)}[F(\epsilon+\nu-1, -\nu-1,\gamma-1,x) - F(\epsilon+\nu-1, -\nu-1,\gamma-2,x)]$$

Multiplying the differential equation (9) for $F(\epsilon+\nu,-\nu,\gamma,x)$, which in our new notation is

$$x(1-x)F'' + [\gamma-(\epsilon+1)x]F' = -\nu(\nu+\epsilon)F, \tag{19}$$

by $x^{\gamma-1}(1-x)^{\epsilon-\gamma}$, it is seen that

$$-(\epsilon+\nu)\nu F x^{\gamma-1}(1-x)^{\epsilon-\gamma} = \frac{d}{dx}[F' x^\gamma (1-x)^{\epsilon-\gamma+1}]. \tag{20}$$

Substituting $F(\epsilon+\nu,-\nu,\gamma,x)$ from this relation in (18) and integrating by parts we get

$$\frac{1}{\nu(\epsilon+\nu)}\int_0^1 dxF'(\epsilon+\nu,\ -\nu,\gamma,x)F'(\epsilon'+\nu',\ -\nu',\gamma',x)x^{\gamma}(1-x)^{\epsilon-\gamma+1}.$$

This procedure can be continued by differentiating Eq. (19) and getting a relation similar to Eq. (20) with F' and F'' instead of F and F'. Since the F's are polynomials in x it is thus possible to reduce the integral (18) after a finite number of steps to the form

$$\text{const.}\int_0^1 dx\cdot x^p(1-x)^q=\frac{\text{const.}\,p!q!}{(p+q+1)!}\,.$$

In our example I_1 vanishes except when $\nu'=\nu\pm1$, $\nu'=\nu$ or $j'=j\pm1$, $j'=j$. This result represents the selection rule for j. If $\nu'=\nu$ i. e. $j'=j$, then

$$I_1=\frac{2(-1)^{\epsilon-\gamma}\nu![(\gamma-1)!]^2(\epsilon+\nu-\gamma)!(\epsilon-1)(\epsilon-2\gamma+1)}{(\gamma+\nu-1)!(\epsilon+\nu-1)!(\epsilon+2\nu)(\epsilon+2\nu-1)(\epsilon+2\nu+1)}\,.$$

The integral in Eq. (16) is evaluated in the same fashion and gives

$$C_{j\,nm}^2=-\frac{(-1)^{\epsilon-\gamma}(\gamma+\nu-1)!(\epsilon+\nu-1)!(\epsilon+2\nu)}{8\pi^2A(C)^{1/2}\nu![(\gamma-1)!]^2(\epsilon+\nu-\gamma)!}\,.$$

Then from Eq. (18)

$$z(j,n,m\,;j,n,m)=-c\frac{(\epsilon-1)(\epsilon-2\gamma+1)}{(\epsilon+2\nu-1)(\epsilon+2\nu+1)}=c\frac{n\,m}{j(j+1)}\,.$$

This agrees with Dennison's[3] expression, our notation j, n, m corresponding to his m, n, σ. In the same way the other intensities are computed. They too are found to agree with Dennison's values except that the quantities called by him $B^{m\,n\quad\sigma}_{m\,n-1\,\sigma\mp1}$ and $B^{m\quad n\quad\sigma}_{m-1\,n-1\,\sigma\mp1}$ must be

$$\left(B^{mn\quad\sigma}_{mn-1\sigma\mp1}\right)^2=\frac{(m\pm\sigma)(m\mp\sigma+1)(m+n)(m-n+1)}{16m^2(m+1)^2}\,,$$

$$\left(B^{m\quad n\quad\sigma}_{m-1n-1\sigma\mp1}\right)^2=\frac{(m\pm\sigma)(m\pm\sigma-1)(m+n)(m+n-1)}{64m^2(m^2-\frac{1}{4})}\,,$$

a difference probably due to a misprint arising from the inversion of a $\pm$ sign.

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November 4, 1926.