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ON THE ASYMMETRICAL TOP IN QUANTUM MECHANICS[1]

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ABSTRACT

An elaboration and a more complete analysis of Witmer's work on the asymmetrical top treated as a perturbation of the symmetrical one show that one can deduce the rigorous solution of the problem from those of the algebraic equations of degree $2j+1$ or less. Without actually solving such equations, we find the terms divisible into even and odd groups just as in the case of the sigma-type doubling in diatomic molecules treated by Kronig, Van Vleck and others. For the case where the asymmetry is slight, an explicit expression for the separation of such similar doublets is obtained. The selection rules, which are rigorous for any degree of asymmetry, consist of the following: (a) Kronig's rule; (b) $\Delta j=0, \pm 1; \Delta m=0, \pm 1$; and (c) rule for the quantum number sigma, $\Delta\sigma=$even for electric moment in z direction and $\Delta\sigma=$odd for moment in $x-y$ plane. The effect of the electronic motions on the rotation of a polyatomic molecule as a whole is also briefly discussed.

THE problem of the asymmetrical top has been treated in the old quantum theory by many authors[2] and in the new quantum theory by Witmer[3] and very recently also by Kramers and Ittmann.[4] Witmer regarded the problem as a perturbation of that of the symmetrical top, the solution of which is well known.[5] He thus obtained the energy values as power series in what we may call the parameter of dissymmetry. In the present paper, using a method which is an elaboration of Witmer's, we shall show that the exact solution of this problem is reducible to the solving of an infinite set of algebraic equations of finite degree and the characteristic functions are thus expressible as linear combinations of a finite number of those for the symmetrical top.

Before the work presented below was undertaken, Professor Kramers suggested[6] to the author the possibility of attacking the problem by a method of separation of variables analogous to that used by Reiche[2] in the old quantum theory. In a short note[7] presented to the American Physical Society,

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[1] A preliminary report of this paper was presented to the New York Meeting of the American Physical Society, Dec. 31, 1928; see Phys. Rev. **33**, 289 (1929).

[2] Epstein, Phys. Zeits. **20**, 289 (1919); Verh. d. D. Phys. Ges. **17**, 398 (1916); Reiche, Phys. Zeits. **19**, 394 (1918); Kramers, Zeits. f. Physik **13**, 343 (1923); Witmer, Proc. Nat. Acad. **12**, 602 (1926); Luetgemeier, Zeits. f. Physik **38**, 251 (1926).

[3] Witmer, Proc. Nat. Acad. **13**, 60 (1927).

[4] Kramers and Ittmann, Zeits. f. Physik **53**, 553 (1929).

[5] Reiche and Rademacher, Zeits. f. Physik **39**, 444 (1926); **41**, 453 (1927); Kronig and Rabi, Phys. Rev. **29**, 262 (1927); also Dennison, Phys. Rev. **28**, 318 (1926).

[6] I take this opportunity to thank Prof. Kramers for this kindness.

[7] Wang, Phys. Rev. **33**, 123 (1929). Unfortunately the writer made an algebraic mistake in the abstract as printed in the Bulletin of the American Phys. Soc., Vol. **3**, No. 5. This was

the present author reported that the Schroedinger's equation for the asymmetrical top is separable in the same set of elliptical coordinates and under under the same conditions as Reiche[2] found in the old quantum theory. The resulting differential equations are exactly of the form of Lamé's equation. Due to an oversight in interpreting the boundary conditions, the writer did not pursue further the solution of the problem by integrating Lamé's equation.

Instead of using Lamé's equation, we shall use an elaboration of Witmer's method[3] which is more closely akin to the standard perturbation technique. At first thought, it might be presumed that the use of the ordinary differential equation might be preferable to a perturbation theory. But, on closer examination, it can be seen that the solution of Lamé's equation involves the use of identically the same algebraic equations met here. Perhaps, the use here of the term perturbation theory is somewhat misleading. One might construe this as some approximate method of obtaining numerical results. Actually our method is an accurate one; all we mean is the use of an orthogonal transformation whereby the matrix representation of the Hamiltonian, generally non-diagonal, in one scheme is transformed into a diagonal one in some other scheme.

The first part of our work consists largely of transferring Witmer's work into orthodox matrix symbolism and removing his restriction $m=j$. Witmer's results on the energy values are correct in the main except for neglecting the sigma-doubling.[8] We now proceed to obtain the matrix elements of the Hamiltonian of the asymmetrical top, referred to the scheme of the set of characteristic functions for the symmetrical top.

The Matrix hamiltonian for the asymmetrical top. By applying Shroedinger's rule to the classical Hamiltonian of a free asymmetrical top, we readily obtain, using the notation of Witmer, the following wave equation:

$$H\Phi \equiv -(A+b\cos 2\phi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right)-\frac{A-b\cos 2\phi}{\sin^2\theta}\left[\frac{\partial^2\Phi}{\partial\psi^2}-2\cos\theta\frac{\partial^2\Phi}{\partial\phi\delta\psi}+\frac{\partial^2\Phi}{\partial\phi^2}\right]-(1+b\cos 2\phi)\frac{\partial^2\Phi}{\partial\phi^2}-\frac{2b\sin 2\phi}{\sin\theta}\left[\frac{\partial^2\Phi}{\partial\theta\partial\psi}-\cos\theta\frac{\partial^2\Phi}{\partial\theta\partial\phi}\right] \qquad (1)$$

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corrected when the abstract was reprinted in the Phys. Rev., except for a purely typographical error (the correct equation is of the exact Lamé form and should be $f(\lambda)^{1/2}d/d\lambda\,[f(\lambda)^{1/2}dU/d\lambda]+(a+b\lambda)U=0$). Kramers and Ittmann saw only the abstract in its first form when they wrote their paper.

[8] Witmer's formulas (16) and (17) are valid for $\sigma>4$ (Witmer calls them n). For $\sigma<4$, the corrected formulas, inclusive of the terms of the order b^3, are as follows:

$\sigma=0$) $W-W_0=-F(2)b^2$;
$\sigma=1$) $W-W_0=\pm F(1)b+8F(3)b^2/F(1)\mp F(3)b^3$;
$\sigma=2$) $W-W_0=[F^2(1)+3F(1)-9\pm 6F(2)]b^2/6$;
$\sigma=3$) $W-W_0=[F^2(1)+8F(1)-54]b^2/16\pm F(3)b^3$;
$\sigma=4$) $W-W_0=[F^2(1)+15F(1)-180]b^2/30$;

where W_0 is the energy for the symmetrical top and $F(k)$ is abbreviation for $(j+k)!/2^{\sigma^2}(j-k)!$. The plus and minus signs correspond to the sigma doublets. For $\sigma=4$, the formula is, $W-W_0=\lambda_2b^2+b^4[\lambda_4\pm 16F(4)/9]$, where λ_2 and λ_4 are those quantities given by Witmer.

$$+2b\cos 2\phi\cot\theta\frac{\partial\Phi}{\partial\theta}-b\sin 2\phi(1+2\cot^2\theta)\frac{\partial\Phi}{\partial\phi}+2b\sin 2\phi\cot\theta\csc\theta\frac{\partial\Phi}{\partial\psi}$$

$$=\frac{8\pi^2}{h^2c}E\Phi$$

where θ, ϕ, ψ are the Eulerian angles of the system of principal axes of the top, E is the energy and A_x, A_y, A_z are the three principal moments of inertia. Also we have used the following abbreviations:

$$c=\frac{1}{A_z}-\frac{1}{2}\left(\frac{1}{A_x}+\frac{1}{A_y}\right),\quad A=\frac{1}{2c}\left(\frac{1}{A_x}+\frac{1}{A_y}\right),\quad b=\frac{1}{2c}\left(\frac{1}{A_x}-\frac{1}{A_y}\right).\qquad(2)$$

We also assume that A_y lies between the other two in magnitude so that $-1\leqq b\leqq 0$.

The characteristic functions for the symmetrical top have been obtained by several authors already mentioned. We shall adopt here the following expression given by Reiche and Rademacher[5] (multiplied by a proper normalization factor):

$$\begin{aligned}u_{j\sigma m}(\theta,\phi,\psi)&\equiv u_{dsp}(t,\phi,\psi)\\&=\left[\frac{(d+s+p)!(1+d+s+\rho+p)!(d+p)!t^d(1-t)^s}{d!^2\,p!(s+p)!\,4\pi^2}\right]^{\frac{1}{2}}\\&\qquad F(-p;1+d+s+p;1+d;t)\,e^{i\sigma\phi+im\psi}\end{aligned}\qquad(3)$$

where $t=\frac{1}{2}(1-\cos\theta)$, $s=|m+\sigma|$, $d=|m-\sigma|$, $j=p+\frac{1}{2}(d+s)$ and we have, following the nomenclature of Van Vleck,[9] used the quantum numbers σ and m in place of the τ and τ' used by Reiche. For the sake of convenience, we also introduce a function defined by the equation:

$$2\pi u_{dsp}(t,\phi,\psi)=U_{dsp}(t)e^{i\sigma\phi+im\psi}.$$

As usual, we now apply the operator H, as given by Eq. (1), to the function $u_{j\sigma m}$.[10] After some simplification, particularly by using the fact that $U_{j\sigma m}(\cos\theta)$ satisfies the differential equation

$$d^2U/d\theta^2+\cos\theta dU/d\theta-[((m-\sigma\cos\theta)\csc\theta)^2-j(j+1)+\sigma^2]U=0,$$

we get

$$\begin{aligned}Hu_{j\sigma m}=[Aj(j+1)+\sigma^2]u_{j\sigma m}-be^{\pm 2i\phi}\{\tfrac{1}{2}[\pm\sigma(1\pm\sigma)-j(j+1)]u_{j\sigma m}\\+\csc\theta(\pm m-(1\pm\sigma)\cos\theta)[(du_{j\sigma m}/d\theta)+\csc\theta(\pm m\mp\sigma\cos\theta)u_{j\sigma m}]\}\end{aligned}\qquad(5)$$

The matrix elements $H(j',\sigma',m';j,\sigma,m)$ are then just the coefficients in the expansion of the right hand member of (5) in the form

$$\textstyle\sum_{j'\sigma'm'}H(j',\sigma',m';j,\sigma,m)\,u_{j'\sigma'm'}.$$

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[9] Van Vleck, Phys. Rev. **33**, 467 (1929).

[10] From the definitions of d, s, and p given in Eqs. (4), corresponding to any given set of values for j, σ, m, there is one and only one set of d, s, p although the converse is not unique.

The first term of (5) is already in the form of constant$\times u$. We shall next consider the second term with the upper sign. It now becomes necessary to distinguish between the four separate cases governed by the following explicit relations between σ, m, and d, s: (a) $\sigma-m=d$, $\sigma+m=s$; (b) $\sigma-m=d$, $\sigma+m=-s$; (c) $\sigma-m=-d$, $\sigma+m=s$; (d) $\sigma-m=-d$, $\sigma+m=-s$. For all the four cases, this second term of (5) is of the form $g(t)dU/dt+h(t)U$ and we find that the following recursion formulas reduce that expression to a single term for the respective cases:[11]

$$
\begin{aligned}
&(a)\quad \left[(-d+1+(s+d+2)t)\frac{d}{dt}+\frac{1}{2}\left(\frac{s}{1-t}-\frac{d}{t}\right)-p(p+d+s+1)\right]U_{dsp}\\
&\qquad\qquad =[p(p-1)(p+d+s+1)(p+d+s+2)]^{1/2}U_{d+2,s+2,p-2}\;;\\
&(b)\quad \left[(-d-1+(d-s+2)t)\frac{d}{dt}+\frac{1}{2}\left(-\frac{s}{1-t}-\frac{d}{t}\right)-(p+s)(p+d+1)\right]U_{dsp}\\
&\qquad\qquad =[(p+s)(p+s-1)(p+d+1)(p+d+2)]^{1/2}U_{d+2,s-2,p}\;;\\
&(c)\quad \left[(d-1+(s-d+2)t)\frac{d}{dt}+\frac{1}{2}\left(\frac{d}{t}+\frac{s}{1-t}\right)-(p+d)(p+s+1)\right]U_{dsp}\\
&\qquad\qquad =[(p+d)(p+d-1)(p+s+1)(p+s+2)]^{1/2}U_{d-2,s+2,p}\;;\\
&(d)\quad \left[(d-1+(-s-d+2)t)\frac{d}{dt}+\frac{1}{2}\left(\frac{d}{t}-\frac{s}{1-t}\right)-(p+1)(p+s+d)\right]U_{dsp}\\
&\qquad\qquad =[(p+d+s)(p+d+s-1)(p+1)(p+2)]^{1/2}U_{d-2,s-2,p+2}.
\end{aligned}
\tag{6}
$$

It must be mentioned, however, that there are, in addition, five exceptional cases for which special recursion formulas different from those above must be used; these five cases are: (i) case (*b*) when $s=1$, (ii) case (*d*) when $s=1$, (iii) case (*c*) when $d=1$, (iv) case (*d*) when $d=1$, and (v) when $d=1$, $s=1$, We shall not reproduce the formulas here, which are quite similar to those in (6). But, collecting the results, we find that the second term of (5) with the upper sign reduces in all cases to the following single term:

$$-\tfrac{1}{2}b[(j-\sigma-1)(j-\sigma)(j+\sigma+1)(j+\sigma+2)]^{1/2}u_{j,\sigma+2,m} \tag{7}$$

except that the sign should be plus instead of minus whenever $m-\sigma=1$. This irregularity of sign is removed if we redefine the characteristic functions u' as done by Van Vleck;[12] namely, by putting $u'=(-1)^{\sigma}u$ for $m\geqq\sigma$ and $u'=(-1)^{m}u$ for $\sigma\geqq m$, where u is defined as in (3).

The second term of (5) with the *lower* sign can be reduced to the one with the *upper* sign by the substitution $\sigma=-\bar{\sigma}$, $m=-\bar{m}$, and evaluated accordingly. But since the latter contributes exclusively to matrix elements

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[11] To derive these recursion formulas, we find it most convenient to make use of the relations between contiguous hypergeometric functions given explicitly by Gauss (Ges. Werke, III. 123 ff., 207 ff.).

[12] Van Vleck, reference 9, especially footnote 25.

of the type $H(j', \sigma+2, m'; j, \sigma, m)$ while the former to those of the type $H(j', \sigma-2, m'; j, \sigma, m)$, we see that we can readily deduce the one from the other by using the Hermitian property of the H-matrix.

As a result, the entire expression (5) simplifies to

$$Hu_{j\sigma m} = [Aj(j+1)+\sigma^2]u_{j\sigma m} + bf(j,\sigma+1)u_{j,\sigma+2,m} + bf(j,\sigma-1)u_{j,\sigma-2,m} \qquad (8)$$

where

$$f(j,\sigma) \equiv -\tfrac{1}{2}[(j-\sigma)(j-\sigma+1)(j+\sigma)(j+\sigma+1)]^{1/2}$$

Eq. (8) shows that the H-matrix is diagonal both in j and in m; it is in fact independent of m. The diagonality with respect to j could have been suspected from the constancy of the square of the angular momentum vector of a free body while the complete independence of (8) of the magnetic quantum number m is, of course, due to the arbitrariness of orientation in space.

The infinite secular determinant constructed in accordance with (8) consequently factors into finite determinants, each having the two fixed indices j and m and the running index sigma. Since sigma extends from $+j$ to $-j$, these factored determinants have the order $2j+1$ in every case. Explicitly the corresponding secular equations are of the form:

$$\begin{vmatrix} j^2-W & & & & & & \\ & \cdot & & & & & \\ & \cdot & & & & & \\ & \cdot & 0 & bf(j,\sigma+1) & & & \\ & \cdot & (\sigma+1)^2-W & 0 & bf(j,\sigma) & & \\ & \cdot & 0 & \sigma^2-W & 0 & \cdot & \\ & & bf(j,\sigma) & 0 & (\sigma-1)^2-W & \cdot & \\ & & & bf(j,\sigma-1) & 0 & \cdot & \\ & & & & & \cdot & \\ & & & & & & j^2-W \end{vmatrix} = 0, \qquad (9)$$

where we have included the constant term $-Aj(j+1)$ in the quantity W, which is the energy measured in units of $h^2c/8\pi^2$;[13] the actual energy E would be

$$E = (h^2c/8\pi^2)[Aj(j+1)+W] \qquad (10)$$

It is at once evident that the determinant in (9) can be at least factored into two, one connected with the even sigmas and the other the odd ones. In addition, the determinant is symmetrical not only about its main diagonal (Hermitian) but also about the other diagonal owing to the fact $f(j,\sigma) = f(j,-\sigma)$; this enables one to factor the determinant once more and this is closely connected with the possibility of dividing the terms according to the type of Kronig symmetry first pointed out by him in two papers.[14] We shall discuss this division of terms a little more in detail in a later section.

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[13] The constant c, not to be confused with the velocity of light, has been defined in Eq. (2).

[14] Kronig, Zeits. f. Physik **46**, 814; **50**, 347 (1928). See also Wigner and Witmer, Zeits. f. Physik **51**, 859 (1928).

Because of the above simplification, Eq. (9) reduces, for the cases $j=1,2,3$. to quadratic equations at most; the resulting energy values we thus obtained agree with those given in the paper of Kramers and Ittmann and will not be repeated here. In this connection, it may be mentioned, however, that in their work using elliptical coordinates and obtaining Lamé's equation, these four factored algebraic equations are those belonging to four separate types of Lamé's functions; but here we find that these separate equations, when combined, could be embodied in the single symmetrical form (9).

We may also point out the relation between the characteristic functions given in the two papers. Our result in Eq. (9) shows that in general the characteristic function for the asymmetrical top can be written:

$$\Phi_{j\sigma m} = e^{im\psi}\Sigma_{\sigma'} S_{\sigma\sigma'} U_{j\sigma' m}(\cos\theta) e^{i\sigma'\phi} \tag{11}$$

where the $S_{\sigma\sigma'}$'s are the orthogonal sets of solutions of the system of homogeneous equations whose eleminant is (9). Kramers and Ittmann treat the case $m=0$ and obtain as characteristic functions the products of Lamé's functions of the two elliptical coordinates; these products can be also expressed, as they have pointed out, as linear combinations of ordinary tesseral harmonics (in which θ and ϕ are regarded, however, as two of the Eulerian angles used here). Now Eq. (11) reduces just to this latter form when we put $m=0$ because the U's reduce to the associated Legendre functions when $m=0$. From the arbitrariness of the spatial orientation, one can get all the energy values by considering some special cases, like $m=0$ (Kramers and Ittmann) or $m=j$ (Witmer). Also the intensities could be obtained because of the resulting independence of the coefficients $S_{\sigma\sigma}'$ in (11) of m. It seems, however, to be a satisfying check to have shown explicitly this independence of m.

Sigma-type doubling phenomena. In the problem of the symmetrical top there is the degeneracy with respect to m and also with respect to the pairs of states $(j,+\sigma),(j,-\sigma)$. In the case of an asymmetrical top this latter degeneracy is removed i.e., for given j and m there are $2j+1$ distinct states. For cases where the departure from the symmetrical case is small, the terms will appear as doublets (except the term sigma $=0$, which always remains single), each grouped around the $\pm\sigma$ term of the symmetrical top. Borrowing the terminology of Mulliken[15] for a similar splitting up of sigma terms in diatomic molecules, we shall call this the sigma-type doubling in the asymmetrical top.

We shall now seek an explicit formula for this doublet separation on the assumption that the dissymmetry factor $|b| \ll 1$. Perhaps the most straightforward way of calculating this is to follow the procedure of Van Vleck[9] in an analogous calculation for the sigma doublet in diatomic molecules. In that paper, he extended Born, Heisenberg and Jordan's perturbation technique to systems where the degeneracy is removed only after one reaches a

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[15] Mulliken, Phys. Rev. **28**, 1202 (1926). The theory of sigma-type doubling in diatomic molecules has been worked out by Kronig,[14] Hill and Van Vleck, Phys. Rev. **32**, 250 (1928) and Van Vleck.[9]

higher order of approximation than the first. Using Van Vleck's formula (41), we find the doublet separation in our case is

$$h\Delta\nu = b^\sigma [h^2 c(j+\sigma)!]/[2^{3\sigma}\pi^2 (j-\sigma)!(\sigma-1)!^2] \tag{12}$$

which appears first in the sigma-*th* order of approximation. Since the quantity b measures the departure from the case of the symmetrical top, the experimental detection of this separation would furnish a useful method of estimating the magnitude of molecular dissymmetry. We note here that the separation should be large for low sigmas and should disappear as sigma increases.

From the secular Eq. (39) in Van Vleck's paper, we also find that the proper linear combination of the functions $u_{j,\sigma,m}$ and $u_{j,-\sigma,m}$ to be used as the zero order characteristic functions for the asymmetrical case are:[16]

$$v_+(j,\sigma,m) = (u_{j,\sigma,m} + u_{j,-\sigma,m})/2^{1/2} \tag{13}$$

and

$$v_-(j,\sigma,m) = (u_{j,\sigma,m} - u_{j,-\sigma,m})/2^{1/2} \tag{14}$$

From here on we shall call states of the type (13) the plus sigma states and (14) the minus sigma states. We then find that the $2j+1$ states of same j and m, arranged in the order of increasing or decreasing energy (according as $A_z < A_x$, or vice versa), run as follows: $\sigma = 0+, 1-, 1+, 2-, 2+$, and so on.

Rules of combination. Theoretically, once the Eq. (9) is solved, the matrix elements $S_{\sigma\sigma'}$ can be computed and the characteristic functions are given by (11). The intensity for any transition $(j', \sigma', m'; j'\ \sigma, m)$ can then be calculated from the already known results for the symmetrical top and the total intensity for the actual transition $(j', \sigma'; j, \sigma)$ can be calculated by summing over all possible Zeeman components. We shall not attempt to make any calculation in this direction. Instead, we shall draw from Eq. (9) some conclusions about the selection rules that are quite general in nature and do not depend on any particular solution of (9).

In the series of papers on band spectra in diatomic molecules, Kronig[14] pointed out that since the wave equation is invariant to a reflection of all particles about the x-z plane, which he represents by his transformation (15) in his second paper, the characteristic functions should also be transformed into their own multiples by such a reflection; or, if all functions are normalized, they should merely be multiplied by $+1$ or -1. Kronig calls such functions "even" or "odd" respectively. In the present case of an asymmetrical top, we have the same invariance of the wave equation, hence we expect each of the states is also either even or odd in the Kronig sense. To verify this, we first note that all the $v_+(\sigma)$'s for given j and m have the same Kronig symmetry and also the $v_-(\sigma)$'s.[17] If now we use in our representation of the Hamiltonian as a matrix these v functions as our fundamental set instead

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[16] The state $\sigma = 0$ is an exception; it will have $v_+(0) = u_{j0m}$ and there will be no states $v_-(0)$.

[17] Functions having the same sigma (with regard to sign also) but different j's have the same or opposite Kronig symmetry according as the difference in j is even or odd. See Fig. 1.

of the u's we find that the secular equation corresponding to (9) factors into two, with the one factor involving only the positive sigmas (including zero) and the other the negative ones. This means that the new characteristic functions will be linear combinations of the v's having the same Kronig symmetry and hence will themselves also have the property of being either even or odd in the Kronig sense.

Since the electric moment operator is odd with respect to Kronig transformation, the Kronig rule of combination holds in our case; namely, transition can occur only between states of different Kronig symmetry.

In the case of symmetrical top we have the additional selection rules $\Delta j=0, \pm 1$; $\Delta m=0, \pm 1$; $\Delta\sigma=0, \pm 1$. Clearly the first rwo rules remain

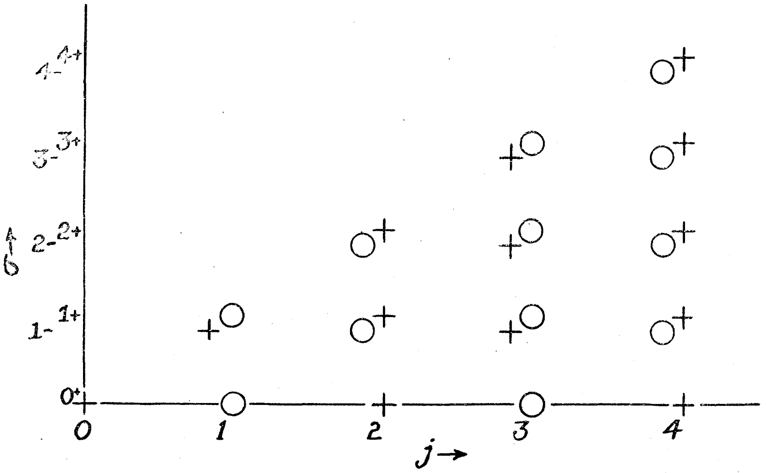

Fig. 1. Kronig rule: ○ states combine only with + states. Rule for j: Only states in same column or adjacent columns combine. Rule for σ: Corresponding to a $\substack{z\\x-y}$ component of the electric moment, the only transitions are those with an $\substack{\text{even}\\\text{odd}}$ number of jumps in the rows $(\Delta\sigma=\substack{\text{even}\\\text{odd}})$.

unchanged in passing to the present problem. As for the last one, from the fact mentioned before that the determinant (9) factors into two, separating the even and the odd sigmas,[18] we readily find the following rule concerning the sigmas:

(a) Corresponding to an electric moment in the z direction in the top, transition can occur only between states both with even sigmas or both with odd ones, and

(b) Corresponding to an electric moment in the x-y plane, transition can occur only from a state with even sigma to one with an odd sigma or vice versa.

The accompanying diagram gives a summary of all the essentials about the rules discussed above.

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[18] These are even and odd in the ordinary sense of the words and are not to be confused with the "even" and "odd" in the Kronig sense.

Polyatomic molecules. In an important paper on moleculer spectra, Born and Oppenheimer[19] showed that in the wave equation of a polyatomic molecule, the predominant rotational term is the operator for an asymmetrical top. In addition, due to the coupling of the electronic and the nuclear vibrational motions to the rotation of the molecule, correction terms enter which are in general complicated if explicit expressions are desired (except in the case of diatomec molecules, for which see the papers of Konig[14] and Van Vleck[9]). However, if we consider the ideal case where the nuclear vibrational effects are vanishingly small ("frozen nuclei"), a calculation similar to that of the last two authors can be made for the general polyatomic molecule. It is found that the following elements should then be added to the H-matrix given in (9)[20]

$$H_1(n',j,\sigma,m\,;n,j,\sigma,m)=\frac{1}{2}\left(\frac{M_x^2}{A_x}+\frac{M_y^2}{A_y}+\frac{M_z^2}{A_z}\right)(n'\,;n)-(h/2\pi)\frac{\sigma M_z(n'\,;n)}{A_z} \tag{15}$$

$$H_1(n',j,\sigma\pm 1,m\,;n,j,\sigma,m)=(h/4\pi)(M_y\pm iM_x)(n'\,;n)\left[(j\mp\sigma)(j\pm\sigma+1)\right]^{1/2} \tag{16}$$

where M_x, M_y etc. are the ordinary angular momentum matrices or their squares for the stationary molecule and where n or n' designates the totality of the electronic quantum numbers.

The most important parts of (15) and (16) are obtained, however, by taking an average over the electronic frequencies i.e. taking $n'=n$. Then the first term of (15) merely shifts the energy scale by a constant amount and it corresponds to the results obtained by Kramers and Pauli[21] in the old quantum theory. The second term[22] of (15) will change the spacing of the different sigma terms belonging to the same j. As for the elements (16), they will vanish when the molecule has a regularity around an axis of symmetry (symmetrical top). That this is so can be seen as follows: These matrix elements are $I=\int V^*_n(M_y\pm iM_x)V_n dv$, where V_n is the characteristic function of the stationary molecule. The operators $(M_y\pm iM_x)$, when transformed in terms of those in cylindrical coordinates about the axis of symmetry, will involve the angle ϕ only through the factors $e^{\pm i\phi}$; and, if the nuclear distribution in the molecule has a periodicity in ϕ of modulus $w=2\pi/k$ (k an integer), the product $V^*_n V_n$[23] will be simply periodic in ϕ with period w. Now since we can evaluate the integral I equally well after making the tranformation in ϕ given by $\phi'=\phi+a$, we shall evaluate it k times with $a=w$, $2w$, $3w \cdots kw$, and add them up. We get

$$kI=I\Sigma_{l=1,2,k}\,e^{2\pi il/k}\ ;\ \therefore I=0.$$

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[19] Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927).

[20] We must mention that the H's in (15) and (16) are measured in absolute units, while in (9) it is in units of $h^2c/8\pi^2$.

[21] Kramers and Pauli, Zeits. f. Physik **13**, 351 (1923).

[22] The average of M_z will vanish if the characteristic function is invariant with respect to a reflection about some plane passing through the axis of symmetry.

[23] Although the product $V_n^* V_n$ is invariant after the rotation, the separate functions V_n and V_n^* may be multiplied by some kth root of unity after such a rotation.

To take all the averaged terms in (15) and (16) into account in the more general case of polyatomic molecules, one can proceed in two ways; if the new perturbation elements are small compared to those in (9), one can first solve the asymmetrical top problem and consider (15) and (16) as perturbations of the latter; on the other hand, if both are of the same order of magnitude, one has to solve the combined problem obtained by adding the H and H_1 matrices. In the latter case, the presence of the elements of the type (16) in particular will invalidate most of our previous statements concerning the division of the secular determinant according to even and odd sigmas and the selection rule for sigma.

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