TABLE IV.

	Ne	A	Kr	Xe
Li^+	228	85	385	237
Na^+	82	67	314	306
K^+	109			
Rb^+	81			
Cs^+	58			

Correlation similar to that found in other cases does not appear here.

K^+ in Ne	109	Rb^+ in Ne	81	Cs^+ in Ne	58
Na^+ in A	67	Na^+ in Kr	314	Na^+ in Xe	306
Difference	42		−233		−248

The potentials do not even drop off uniformly in one direction as might be anticipated. The difficulties of avoiding secondary electrons becomes increasingly great with ions of higher speeds, and this interference of secondaries may possibly explain the results of Beeck and Mouzon. It is to be noted that the ionization potentials they observed are in most cases up in the range of 300 to 400 volts. Oliphant[11] and others have shown that the emission of secondary electrons when positive ions strike metal surfaces increases strongly with increasing energy. Nordmeyer[10] has also discussed in detail the strong likelihood of certain disagreements between his results and Beeck's being due to secondary electrons.

Finally, it may be pointed out that the investigation was carried out on the ionization at energies from 5 volts up. Although the behavior of the ion detector is difficult to analyze when such slow ions are used in the beam, it was concluded that no ionization occurred at energies below those given in the table of results.

The writer is particularly indebted to Professor L. B. Loeb and Professor E. O. Lawrence who suggested the application of the space-charge method to this problem, and to the helpful direction of Professor Loeb. Doctor C. H. Kunsman, Chief of the Fertilizer Investigations of the U. S. Bureau of Chemistry and Soils, very kindly furnished the catalysts used as ion sources. The writer is also indebted to Doctor O. Beeck for numerous discussions of the problem.

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[11] Oliphant, Proc. Roy. Soc. **A127**, 373 (1930).

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The Rotational Energy of Polyatomic Molecules

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It is shown that the quantized energy of a polyatomic molecule is approximately separable into the internal electronic and vibrational energy plus the rotational energy with the latter determined by solving the conventional problem of the rigid asymmetrical top. Because of the large oscillating terms in the Hamiltonian function due to interaction between vibration and rotation, this conclusion is not as obvious as it sounds, and seemed, if anything, to be contradicted by Eckart's recent investigation on the choice of a reference frame. The discrepancy, however, disappears when a second order perturbation calculation is made with Eckart's coordinates.

It has commonly been supposed in the literature that the rotational energy of a polyatomic molecule is very approximately the same as that of a rigid body with three unequal moments of inertia I_1, I_2, I_3. In other words, it is assumed that the total energy can be obtained by computing first the internal electronic and the vibrational energy, and then adding an eigenvalue of the "asymmetrical top" problem, whose Hamiltonian function is

$$H_{\mathrm{rot}}=\sum_{i=1,\,2,\,3}(P_i-\zeta_i)^2/2I_i, \tag{1}$$

where P_1, P_2, P_3 are the components of total angular momentum relative to the three principal axes. In order to cover the most general case, we have here assumed that the mean angular momentum connected with the nuclear vibrations does not necessarily vanish, but instead may have components ζ_1, ζ_2, ζ_3 relative to the principal axes. In this event one must subtract the vibrational from the total angular momentum to obtain the purely rotational angular momentum, whose squares enter in (1). The ζ_i terms arise only if there is degeneracy, i.e., if several normal vibrations coincide in frequency. The possibility of such terms was first suggested by Kramers and Pauli,[1] and they have recently been employed by Teller and Tisza[2] and by Dennison and Johnston[3] in analyzing the spectra of symmetrical molecules. The case $\zeta_i \neq 0$ corresponds not to the ordinary or true asymmetrical top, but rather to a gyroscopic one with flywheels mounted thereon. We wish to stress that our primary interest is in the coefficients of P_1^2, P_2^2, P_3^2 in (1), not in the ζ terms, and we hope that the reader will not be unduly distracted by their inclusion.

The legitimacy of using (1) has recently been questioned by Eckart.[4] Although the first reaction of one's physical intuition is in favor of (1), closer examination (see below) shows that the interaction of rotation and vibration yields oscillatory terms in the Hamiltonian function which are of a larger order of magnitude than those due to rotation alone, so that conceivably the rotation-vibration coupling might make the energy structure different from that given by (1). In fact by devising a very ingenious coordinate scheme, Eckart derives a Hamiltonian function which suggests that the coefficient of P_i^2 is more nearly equal to $I_i/2(I_{i+1}-I_{i+2})^2$ than to the conventional value $1/2I_i$. The same anomalous coefficients of P_1^2, P_2^2, P_3^2 also appear in a rotational wave equation given by Hirschfelder and Wigner.[5] As the main result of the present paper, we shall prove that the anomalies are illusory,[6] and disappear when the perturbation calculations with either the Eckart or H–W Hamiltonian function are pushed through to the proper approximation. Thus the final outcome is to restore the conventional form (1).

A simple two-dimensional example. Before we proceed to the general proof for the actual, three-dimensional case, the nature and solution of the paradox will be clearer if we first treat by way of illustration a hypothetical two-dimensional system, consisting of a set of n particles subject to forces exerted by each other and by a fixed attracting center. These forces are to be of such character that all particles can have equilibrium positions.[7] The general motion can be approximately described as harmonic vibrations about equilibrium superposed on a rigid rotation of the equilibrium configuration about the center of attraction. If r_k, φ_k be the polar coordinates of a typical particle, the Lagrangian function is

$$L=\tfrac{1}{2}\sum_{k=1}^{n} m_k(\dot{r}_k^{\,2}+r_k^{\,2}\dot{\varphi}_k^{\,2})-V(r_1,\cdots r_n,\ \varphi_2-\varphi_1,\ \cdots\varphi_n-\varphi_1),$$

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[1] Kramers and Pauli, Zeits. f. Physik **13**, 343 (1923).

[2] Teller and Tisza, Zeits. f. Physik **73**, 791 (1932); also especially the article by Teller in *Hand- und Jahrbuch der Chemischen Physik*, band 9, p. 151 ff.

[3] D. M. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935).

[4] C. Eckart, Phys. Rev. **46**, 383 (1934).

[5] J. O. Hirschfelder and E. Wigner, Proc. Nat. Acad. Sci., Feb. 1935. I am indebted to these writers for sending me the manuscript in advance of publication.

[6] I must by all means mention that in his dissertation, Groningen 1931, p. 103 ff., H. B. G. Casimir derives Eq. (1) for a model consisting of a single heavy particle oscillating about an equilibrium position on a rotating rigid frame whose mass is not negligible. This model is doubtless a sufficiently close approximation to the behavior of a real molecule to make it reasonably clear that (1) is the correct result. Further, in a letter to Professor Eckart, of which the writer learned after the present calculation was made, Casimir sketches a method whereby (1) can be derived with Eckart's coordinates and without the restriction to the "special model." Casimir's procedure differs from mine in using a contact transformation rather than second order perturbation theory. For instance, an alteration in the definition of the canonical momenta corresponding to the transformation

$$\psi\rightarrow\psi\exp\left[(-2\pi i/h)\Sigma_i\chi_i P_i E_i/2D_i\right]$$

in the wave function eliminates the troublesome linear terms from Eckart's Hamiltonian function in the case $\zeta_i=0$. The meaning of the notation is explained after our Eq. (17).

The difference between Casimir's method and mine is mainly superficial. The utilization of the contact transformation is the more elegant procedure, while perturbation theory is more explicit in showing how orders of magnitude enter in removal of the Eckart paradox, and seems to be easier to apply to unsymmetrical coordinate systems, as in our two-dimensional example.

[7] In the interest of simplicity we assume that the mean electronic angular momentum is zero, or, more generally, we do not include the interaction between rotation and the instantaneous electronic motion. Standard methods are available for handling this interaction (cf., for instance, Kronig, *Band Spectra and Molecular Structure*, Chaps. I, II) and so it need not be considered here.

with the understanding that the potential energy V has a sharp minimum at the equilibrium configuration

$$r_k=r_k^0, \quad \varphi_k-\varphi_1=\varphi_k^0-\varphi_1^0. \tag{2}$$

At the same time that we pass to the Hamiltonian form, it will be convenient to introduce in place of $\varphi_2, \cdots, \varphi_n$ a set of relative angular coordinates $\gamma_k=\varphi_k-\varphi_1$ $(k=2, \cdots f)$ whose apse line is the radius vector to the first particle. One readily finds that

$$H=\frac{1}{2m_1}p_{r_1}{}^2+\sum\frac{1}{2m_k}\left(p_{r_k}{}^2+\frac{p_k{}^2}{r_k{}^2}\right)+\frac{1}{2m_1r_1{}^2}(P-\sum p_k)^2+V, \tag{3}$$

where

$$p_{r_1}=m_1\dot r_1, \quad p_{r_k}=m_k\dot r_k, \quad p_k=m_kr_k{}^2(\dot\gamma_k+\dot\varphi_1), \tag{4}$$

$$P=m_1r_1{}^2\dot\varphi_1+\sum m_kr_k{}^2(\dot\gamma_k+\dot\varphi_1). \tag{5}$$

Here and elsewhere, to simplify printing, we write p_k for p_{γ_k}, and it is to be understood that all sums over k whose limits are unspecified are to extend from $k=2$ to $k=n$, with exclusion of $k=1$. The total angular momentum of the system is P, and is a constant of the motion since P is canonically conjugate to a cyclic coordinate φ_1. Our calculation can be regarded equally well as a classical or quantum-mechanical one. In the quantum version, expressions such as p_k, γ_k, P, φ_1, etc., are, of course, to be regarded as matrices, and the average values denoted by bars are the diagonal matrix elements.

Let us imagine that we have found a solution of the dynamical problem (3) such that all the coordinates, including φ_1, are periodic functions of the time (i.e., in quantum mechanics are matrices of the simple Heisenberg type, with time factors $e^{2\pi i\nu(n;n')t}$). Such a solution represents a motion devoid of mass rotation, since by hypothesis φ_1 contains no linear term in t. Let ζ be the value of the expression (5) for this solution. The quantity ζ can be termed the vibrational angular momentum, since it exists because instantaneously $r_k\neq r_k^0$. If we could replace $r_k{}^2$ by $r_k{}^{02}$, the expression (5) would vanish for the type of solution under consideration, since it has $\bar{\dot\gamma}_k=\bar{\dot\varphi}_1=0$. Such a replacement is not in general allowable, because $m_k\overline{r_k{}^2\dot\gamma_k}$ is not necessarily the same as $m_k\bar r_k{}^2\bar{\dot\gamma}_k$.

We now use perturbation theory to treat the general rotational case where $\bar{\dot\varphi}_1\neq 0$ and so $P\neq\zeta$. This is done by replacing P by $\zeta+\lambda$ and making the perturbation calculation as a series development in the parameter λ. Actually, P can only have the quantized values $mh/2\pi$ in wave mechanics, and so is not an arbitrary number, but this difficulty may be circumvented by solving a hypothetical perturbation problem in which λ is arbitrary, and then substituting the proper quantized value of λ at the end.[8] This procedure is allowable since it is only when the last degree of freedom is introduced that P has any physical significance, and P plays only a parametric role for the reduced problem of $n-1$ degrees of freedom obtained by ignoring φ_1.

The unperturbed Hamiltonian function is thus obtained by taking $P=\zeta$ in (3) and represents irrotational motion. The perturbing potential is

$$[\lambda(\zeta-\sum p_k)+\tfrac{1}{2}\lambda^2]/m_1r_1{}^2, \tag{6}$$

as this is the difference between the values of (3) with $P=\zeta+\lambda$ and of (3) with $P=\zeta$. The effect of the first term of (6) vanishes in the lowest approximation, since by (4) and (5) with[9] $P=\zeta$

$$(\zeta-\sum p_k)/m_1r_1{}^2=\dot\varphi_1, \tag{7}$$

and since by hypothesis the mean value of $\dot\varphi_1$ taken over the unperturbed motion is zero. The coefficient of λ^2 in (6), or what is the same, of P^2 in (3), does not have the value $1/2I$ which is characteristic of the rigid rotator. This is the Eckart paradox when specialized to our two-dimensional system. There is, however, the difference that in our two-dimensional example, the anomalous coefficient $1/2m_1r_1{}^2$ cannot possibly, on symmetry grounds, be the right coefficient of λ^2 in the final expression for the energy, since the first particle surely cannot be preferred above all others. On the other hand, the anomalous coefficient yielded by Eckart's three-dimensional coordinate system is symmetrical in

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[8] In particular, the unperturbed motion $\lambda=0$ need not be a quantized one as far as P is concerned, since ζ need not be an eigenvalue of P, although of course it is in the commonest case $\zeta=0$.

[9] In using (5) one can take $P=\zeta$ since the unperturbed motion has $\lambda=0$.

all particles, and so presents a much more recondite problem.

The answer to the paradox is that even though the linear term of (6) in λ does vanish on the average, its root mean square is of a larger order of magnitude than the part of (6) which is quadratic in λ. Hence, as mentioned to the writer by Professor Eckart, it is necessary to make a perturbation calculation which includes the second rather than just the first order effect of the linear term. For brevity, call the two parts of (6) $\alpha\lambda$ and $\beta\lambda^2$, respectively. One way of seeing that the root mean square of $\alpha\lambda$ is larger than $\beta\lambda^2$ is by actual performance of the perturbation calculation, as it will turn out that the second order effect of $\alpha\lambda$ is comparable in magnitude with the first order effect of $\beta\lambda^2$. Another way is by explicit dimensional examination, which shows that the orders of the unperturbed vibrational energy, of the r.m.s. of $\alpha\lambda$ and of $\beta\lambda^2$ are, respectively, $h\nu$, $h\nu x$, and $h\nu x^2$, where ν is a typical vibrational frequency, and x is of the order of magnitude $[\overline{(\gamma_k-\gamma_k^0)^2}/4\pi^2]^{\frac{1}{2}}$. As long as we are dealing with small vibrations, x is clearly a small quantity. For an actual molecular system it can be shown of the order of the fourth root of the ratio of electronic to nuclear mass.[10]

One must be careful to distinguish between two things, *viz.*, the coefficient of $\lambda^2=(P-\zeta)^2$ in the original perturbing potential (6), and the coefficient of λ^2 in the finally computed energy constant W. The two are, of course, not necessarily the same, and their difference is the cause of the Eckart paradox.

We now proceed to the requisite perturbation calculation, which we shall make in quantum-mechanical form. By standard formulas, the perturbed energy is

$$W=W_0+(\lambda^2/m_1^2r_1^{0 4})F(\zeta-\sum p_k;\,\zeta-\sum p_k)+(\lambda^2/2m_1r_1^{0 2}). \qquad (8)$$

Here, in accord with previous remarks, we have included the second and first order effects of $\alpha\lambda$ and $\beta\lambda^2$, respectively. We find it convenient to use in many places the abbreviation,

$$F(u;w)=\sum\nolimits_{n'(n'\neq n)}\frac{u(n;n')w(n';n)}{h\nu(n;n')}, \qquad (9)$$

wherein $u(n;n')$ designates a typical matrix element of a quantity u, with n and n' symbolizing the totality of vibrational quantum numbers for the initial and final states, respectively. In virtue of (7) and (5), with $P=\zeta$,[9] we have

$$\zeta-\sum p_k=m_1r_1^{0 2}(\zeta-\sum m_kr_k^{0 2}\dot{\gamma}_k)/I, \qquad (10)$$

where

$$I=m_1r_1^{0 2}+\sum m_kr_k^{0 2}. \qquad (11)$$

In writing (8), (10) and (11) we have replaced r_k by r_k^0, which, unlike r_k itself, is a c-number independent of vibrational structure. This approximation is a great simplification, and is allowable because we have already reached the second order stage, making the corresponding error third order. A corresponding approximation was not permissible in earlier stages of the calculation; in fact we saw that it was the difference between r_k and r_k^0 which made $\zeta\neq 0$. By using (10) we find

$$F(\zeta-\sum p_k;\,\zeta-\sum p_k)=m_1r_1^{0 2}I^{-1}F(-\sum p_k;\,-\sum m_kr_k^{0 2}\dot{\gamma}_k), \qquad (12)$$

inasmuch as r_k^0 is a constant which can be taken outside the summation in (9). It has been allowable to omit ζ as an argument of F since ζ is also a constant or c-number, and so does not contribute to a sum such as (9) in which diagonal members $n'=n$ are excluded. The advantage of manipulating results into the form (12) is that now the sum in (9) can readily be evaluated with the aid of the quantum conditions

$$p_k\gamma_l-\gamma_lp_k=(h/2\pi i)\delta_k{}^l, \qquad (13)$$

which are valid since $\gamma_2, \cdots\gamma_n$, $p_2, \cdots p_n$ can be regarded as a set of multiply periodic canonical coordinates for the unperturbed problem obtained by taking $P=\zeta$ in (3). Furthermore, because the matrix elements all relate to the Heisenberg system of representation, the time factor is $e^{2\pi i\nu(n;n')t}$ and consequently

$$\dot{\gamma}(n;n')=2\pi i\nu(n;n')\gamma(n;n'). \qquad (14)$$

Eqs. (14) and (9) show that the diagonal elements of (13) can be written as

$$-F(p_k;\dot{\gamma}_l)-F(\dot{\gamma}_l;p_k)=\delta_k{}^l, \qquad (15)$$

inasmuch as $\nu(n';n)=-\nu(n;n')$. (There is no

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

trouble from the fact that the matrix multiplication involved in (13) has a sum inclusive of the term $n'=n$, whereas $n'=n$ is excluded in (9): Namely, the two left-hand members of (13) cancel insofar as this term is concerned, since obviously $p_k(n;\, n)\gamma_l(n;\, n)=\gamma_l(n;\, n)p_k(n;\, n)$ meaning that effectively $n'=n$ can be excluded from (13).) Since our problem involves no vector potentials or magnetic forces, we can without loss of generality suppose the coordinate matrices for the unperturbed problem all to be real, and the momentum matrices, which are linear functions of the first time derivatives of these coordinates (cf. Eqs. 4–5), to all be pure imaginaries. Then $F(p_k;\, \dot{\gamma}_l)=F(\dot{\gamma}_l;\, p_k)$, and combination of this relation with (15) yields

$$-2F(p_k;\, \dot{\gamma}_l)=\delta_k{}^l. \qquad (16)$$

Eqs. (16) show that the expression (12) has the value $-\frac{1}{2}m_1r_1{}^{02}\sum m_kr_k{}^{02}/I$ and so after putting $\lambda=P-\zeta$ (8) reduces by (11) to $W=W_0+\frac{1}{2}(P-\zeta)^2/I$, the two-dimensional equivalent of (1).

In this demonstration we have used ostensibly a quantum-mechanical calculation, but classical theory could have been employed equally well instead. It is well known that there is a general agreement of classical and quantum results for harmonically oscillating systems. With the classical treatment, the quantum conditions (13) would be replaced by corresponding expressions involving Poisson brackets. One would then use Fourier series containing action and angle variables instead of Heisenberg matrices, and in place of (8) one would employ the classical second order perturbation formula,[11] which involves derivatives with respect to the action variables. The quantum proof is fully as easy as the classical, since the difference quotients in the former are quite as readily handled as the derivatives in the latter.

Calculation with Eckart's coordinates. The procedure for the three-dimensional case is very similar to that for the preceding example. In terms of Eckart's coordinates,[12] the formula for the second order perturbation energy analogous to (8) with $\lambda=P-\zeta$ is

$$H'=W_0+\sum_{i,\,j}E_iE_jF(N_i,\, N_j)(P_i-\zeta_i)(P_j-\zeta_j)$$
$$+\sum_i D_i(P_i-\zeta_i)^2, \qquad (17)$$

where F still has the significance (9), and where the D's and E's have the values

$$\begin{aligned} D_i&=(R^2{}_{i+1}+R^2{}_{i+2})/2M(R^2{}_{i+1}-R^2{}_{i+2})^2,\\ E_i&=2R_{i+1}R_{i+2}/M(R^2{}_{i+1}-R^2{}_{i+2})^2,\ (i=1,\,2,\,3) \end{aligned} \qquad (18)$$

in terms of the principal radii of gyration R_1, R_2, R_3 of the molecule. The corresponding principal moments of inertia are

$$I_i=M(R^2{}_{i+1}+R^2{}_{i+2}). \qquad (19)$$

Here and elsewhere, the total mass of the system is denoted by M, and $i+3$ is the same as i. Since (17) is a second-order expression, no harm will be done if the R's are calculated for the equilibrium position, so that the C's, E's, I's and R's can all now be regarded as constants independent of the vibrational structure. To facilitate printing, we do not, however, any longer attach zero superscripts to show explicitly that they relate to the equilibrium position. As in the previous example, it is nevertheless the difference between R_i and $R_i{}^0$, important in the earlier stages of the calculation, which makes $\zeta_i\neq 0$. If we forgot the second order effect of the terms which were linear in $(P_i-\zeta_i)$ in the original Hamiltonian function (Eq. (26) of Eckart), the F terms in (17) would be wanting, and the coefficient of $(P_i-\zeta_i)^2$ would have the anomalous value D_i rather than $1/2I_i$ as demanded by (1). This discrepancy is what we have called the Eckart paradox.

The expressions N_i appearing in (17) are momenta conjugate to certain oscillatory coordinates χ_i,[13] and from the quantum and reality

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[11] Cf., for instance, M. Born, *Vorlesungen über Atommechanik*, p. 291, Eq. (24).

[12] The complete Hamiltonian function corresponding to (3) is given in Eq. (26) of Eckart's paper, and so is not reproduced here. Our expressions P_i, N_i, $\dot{\chi}_i$, D_i, E_i are respectively the same as M_i, $N_{i+1\ i+2}$, $\omega_{i+1\ i+2}$, $1/2B_i$, $1/C_i$ in Eckart's notation, and we do not choose the scale constants so as to make the mass of each particle unity. The signs of the coefficients of N_{ij} are in error in his Eqs. (25) and (26) as is seen by reference to his Eqs. (21.2) and (22), which are the same as our (22) and (21), respectively.

[13] Eckart's Eq. (13) gives an explicit expression for $\dot{\chi}_i$ rather than χ_i. To find χ_i itself, one can integrate his Eq. (13) with his $\omega_{\beta\gamma,\,\kappa}$ regarded as constant coefficients, which is allowable for our second order perturbation calculation. As a matter of fact, one can see that the χ_i are purely oscillatory coordinates even without making this approximation, since the second of Eckart's relations (12) integrates rigorously into $\frac{1}{2}\Sigma c_{\beta\alpha}c_{\gamma\alpha}$.

conditions it follows in the same way as did (16), that

$$-2F(N_j,\ \dot{\chi}_i)=\delta_j^{\,i}. \tag{20}$$

We shall need the following relations given by Eckart which are the analogs for his problem of our previous formulas (4–5)

$$P_i=I_i\omega_i-2MR_{i+1}R_{i+2}\dot{\chi}_i, \tag{21}$$

$$N_i=I_i\dot{\chi}_i-2MR_{i+1}R_{i+2}\omega_i. \tag{22}$$

Here ω_1, ω_2, ω_3 are linear functions of the time derivatives of the Eulerian angles specifying rigid rotation of the molecule. The unperturbed problem is to be so chosen as to make the motion devoid of mass rotation, so that the mean values of ω_1, ω_2, ω_3 are all zero. Let ζ_1, ζ_2, ζ_3 be the corresponding mean values of P_1, P_2, P_3 which, as previously noted, need not be zero. Strictly speaking, there are vibrational oscillations in the expression (21), as (21) gives the components of angular momentum projected upon the instantaneous principal axes of inertia of the molecule,[14] instead of upon axes fixed in space, and the vibrations will cause small nutations in the positions of these instantaneous axes. The resulting oscillations in (21) are, however, unimportant, *viz.*, of the order $h(\gamma_k-\gamma_k^{\,0})/2\pi \sim h(m/M)^{\frac{1}{4}}$ whereas the oscillations in (22) are of the order h itself. The mean value of (21) likewise is of the order h if it does not vanish, i.e., if there really is vibrational angular momentum. For our purposes it is thus legitimate to regard (21) as constant over the vibration, and equal to the angular momentum relative to the equilibrium position. We cannot emphasize too strongly that one cannot correspondingly neglect the vibrational oscillations in (22) which are much greater and which will prove responsible for the removal of the Eckart paradox. One finds that in the perturbation calculation, the first order effect of the linear terms in the $P_i-\zeta_i$ equals[15] $\sum\bar{\omega}_i(P_i-\zeta_i)$ and so vanishes, since by hypothesis, the unperturbed motion has $\bar{\omega}_i=0$ (cf. Eq. (7) in two-dimensional example). In fact, the whole point of using $P_i-\zeta_i$ rather than P_i as an argument is to eliminate this first order effect. Hence in writing (17), we have included only the second order effect of the linear terms.

When we use (21) with $P_i=\zeta_i$ and (22), and remember that ζ_i is a constant which does not contribute to the sum in (9), we obtain

$$2D_iF(N_i,\ N_j)=F(N_i,\ \dot{\chi}_j), \tag{23}$$

with D_i as in (18). From (18) and (19) we have $D_i-(E_i^2/4D_i)=1/2I_i$. Hence (23) and (20) reduce (17) to the desired form (1), and the proof is thereby completed.

In the two-dimensional illustrative example, the angular momentum P could be treated as a c-number. In the actual, three-dimensional case, P_1, P_2, P_3 must be regarded instead as matrices, since they obey the usual commutation (or rather, non-commutation) rules for angular momentum. We have seen, however, that the vibrational oscillations in (21) could be neglected, and so their non-diagonal elements are in the rotational rather than vibrational quantum number, and they commute with all of the N's to our degree of approximation. (The kinematical interpretation is that in the perturbed motion, P_1, P_2, P_3 vary slowly with time due to rigid rotation of the molecule.) Hence the matrices P_1, P_2, P_3 could be regarded as parameters as far as our preceding vibrational perturbation calculation embodied in Eqs. (17–23) was concerned. However, even when the result (1) is obtained, the secular problem connected with (1), namely that of the asymmetrical top, must be solved. Hence we have used the notation H' rather than W for the left side of (17). It is convenient to use a system of representation in which say P_3 is diagonal: the matrix elements of P_1, P_2, P_3 can then be deduced from the commutation rules, and the secular problem connected with (1) formulated, giving the Wang-Kramers-Ittmann[16, 17] determinant for the asymmetrical top. We omit

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[14] This projection is the same as the angular momentum relative to fixed axes which instantaneously coincide with the principal axes of inertia, and the choice of which hence varies continuously with time (cf. Eckart's Eq. (24)). Do not confuse with the angular momentum in an *accelerated* coordinate system which travels with the principal axes; the latter angular momentum presumably involves oscillations of the same order of magnitude as those in (22).

[15] This result is derived from Eqs. (21.2), (22), (26) of Eckart's paper, with sign correction mentioned at end of our footnote 12.

[16] S. C. Wang, Phys. Rev. **34**, 243 (1929).

[17] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **53**, 533; **58**, 217; **60**, 663 (1929–30).

details, as they are found in Klein's[18] paper or Casimir's thesis. The only point we need emphasize is that the rotational secular problem is to be solved after the vibrational matrix structure has been diagonalized. This is allowable in virtue of the general result of perturbation theory[19] that when degeneracy difficulties do not appear in the first approximation (i.e., for us, retention of the first order effect of the linear terms in $P_i-\zeta_i$) due to the vanishing of average values, it is not necessary to lift the degeneracy until after one has pushed a perturbation calculation for the non-degenerate or high frequency part of the problem sufficiently far to introduce trouble from the degeneracy.

Calculation with Hirschfelder and Wigner's coordinates. Instead of using the Eckart scheme, one may alternatively start the perturbation calculation from the wave equation for polyatomic molecules given by Hirschfelder and Wigner. Their system of reference resembles Eckart's in that it presents the same anomalous initial coefficients D_i of $(P_i-\zeta_i)^2$ defined in (18), but differs in the choice of internal coordinates. Also it exhibits explicitly the matrix elements of P_1, P_2, P_3, giving us the Wang determinant as the immediate result of the perturbation calculation, whereas in Eckart's paper it was not necessary to choose a scheme of representation for P_1, P_2, P_3.

We shall here outline briefly how the Wang determinant is extracted from the H–W wave equation, and shall for simplicity consider only molecules in which the vibrations do not involve angular momentum, so that the irrotational case has $P_i=\zeta_i=0$, and corresponds to zero values for the H–W quantum numbers l and γ. The first step is to establish the relation

$$\begin{aligned}\dot{y}_{n_1}=(p_{n_1}/m_n)+y_{n_2}Q_3-y_{n_3}Q_2\\ -(\Sigma p_{n_1}/M)-(MR_1^2-MR_2^2)^{-1}y_{n_2}M_3\\ -(MR_3^2-MR_1^2)^{-1}y_{n_3}M_2-2D_3y_{n_2}M_3+2D_2y_{n_3}M_2,\end{aligned}\qquad(24)$$

which is the content of the Hamiltonian equation $\dot{y}_{n_1}=\partial H/\partial p_{n_1}$ for a molecule devoid of mass rotation. The expression D_i is defined as in (18), and

$$\begin{aligned}Q_3&=(MR_1^2-MR_2^2)^{-1}\Sigma_n(y_{n_1}p_{n_2}+y_{n_2}p_{n_1}),\\ M_3&=\Sigma(y_{n_1}p_{n_2}-p_{n_1}y_{n_2}),\end{aligned}$$

where y_{n_1}, y_{n_2}, y_{n_3} are the Cartesian coordinates of particle n relative to the principal axes of inertia with origin at the center of gravity. The H–W paper gives the explicit form of the wave equation rather than Hamiltonian function, but the latter is obtained in the usual way by replacing $h\partial\cdots/2\pi i\partial y_{n_1}$ by p_{n_1}. With the aid of the formulas

$$\Sigma_n m_n y_{n_i} y_{n_j}=MR_i^2\delta_j^{\,i}\qquad(25)$$

one finds from (24), and equations symmetrical therewith, that

$$-I_3^{-1}\Sigma m_n(y_{n_1}\dot{y}_{n_2}-y_{n_2}\dot{y}_{n_1})=Q_3-2D_3M_3.$$

The sums encountered in the perturbation calculation are, except for a constant factor, all of the form $F(Q_i-2D_iM_i;\ Q_j-2D_jM_j)$. When one uses relations $-2F(p_{n_i};\ \dot{y}_{n_j})=\delta_j^{\,i}$ analogous to (16) or (20), and notices that the y's, R's, and D's may be considered as constant coefficients in the second order perturbation calculation, one deduces that

$$F(Q_i-2D_iM_i;\ Q_j-2D_jM_j)=[\tfrac{1}{2}I_i^{-1}-D_i]\delta_j^{\,i}.\qquad(26)$$

The zero value when $i\neq j$ is a consequence of the vanishing of the products of inertia in (25). The role of the second term in the right side of (26) is clearly to cancel the anomalous coefficient D_i found if F terms are omitted, while the first term substitutes the normal value. As a typical case, we shall indicate how one derives the matrix element $H'(\gamma;\ \gamma+2)$ of the Wang determinant. This element must be the same as the matrix element of the transformed Hamiltonian for which the non-diagonal elements in the vibrational quantum number have been eliminated by making a second order perturbation calculation. Hence

$$\begin{aligned}&H'(\gamma;\ \gamma+2)=H^{(2)}(n\gamma;\ n\gamma+2)\\ &+\Sigma_{n'}H^{(1)}(n\gamma;\ n'\gamma+1)H^{(1)}(n'\gamma+1;\ n\gamma+2)/h\nu(n;\ n'),\end{aligned}\qquad(27)$$

where $H^{(2)}(n\gamma;\ n\gamma+2)$, $H^{(1)}(n\gamma;\ n'\gamma+1)$ are, except for a constant factor $h^2/8\pi^2$, the same as $H_1^{(2)}$ and $H_1^{(1)}+H_2^{(1)}$ in the H–W notation, which is not well adapted to our perturbation calculation, since their subscripts have no meaning regarding orders of magnitude. When explicit values of the right-hand members of (27) are substituted from the H–W paper, and the sum evaluated by means of (26), it is found that (27) acquires the proper Wang value

$$\begin{aligned}(h^2/32\pi^2)[l^2+l-\gamma^2-\gamma]^{\frac{1}{2}}[l^2+l-(\gamma+1)^2\\ -(\gamma+1)]^{\frac{1}{2}}[I_2^{-1}-I_1^{-1}].\end{aligned}$$

Case of two or more equal moments of inertia. This case requires special consideration, for, although the conventional formula (1) involves no singularity, the anomalous coefficients D_i found by Eckart and by Hirschfelder and Wigner are seen by (18) to become infinite here. Hence a perturbation calculation cannot be made with their coordinate system as a starting point. One way of partially sidestepping the difficulty is to let the moments of inertia approach equality after rather than before the perturbation calculation is made. The formula (1) then holds as one approaches the limiting case of equal moments of inertia, and so presumably holds in the limit. Another, and more solid procedure is to choose the three Eulerian angles so as to specify not a rotating coordinate frame coincident with the principal axes of inertia, but rather a different rotating frame in which the first axis coincides with the radius vector of one particle, the second axis is in the plane determined by this vector and the radius vector of another particle, and the third axis is of course normal to this plane. Such a set of axes has been used by Wigner in

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[18] O. Klein, Zeits. f. Physik **58**, 730 (1929). An anomaly in sign is found in the commutation relations, because the angular momentum is projected on moving rather than fixed axes.

[19] Born and Jordan, *Elementare Quantenmechanik*, pp. 209 ff; J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

connection with formal applications of group theory to atomic spectra.[20] With this new choice of Eulerian angles, there is no catastrophe when the moments of inertia become equal. The difficulty is rather that the anomalous coefficients, now different from (18), show an undue preference for one particle. In fact, the situation is analogous to that upon which we commented after Eq. (7) in the two-dimensional example, where we chose the coordinate φ_1 to specify the radius vector of one particle. The second order perturbation calculation, of course, removes the dissymmetry, and restores the conventional result (1). This calculation might not be easy to make explicitly, due to the clumsy, unsymmetrical nature of the coordinates, but can only lead to (1), at least when the moments of inertia are unequal, since we have proved by means of Eckart's coordinates that (1) then is inevitable. With the unsymmetrical coordinates, there is nothing to single out the case of equal moments of inertia, so that (1) must remain valid in the limit of equality. This argument furnishes the safest way to see that the terms of the third degree in P_1, P_2, P_3 neglected in our perturbation calculation extending to the second order, are not unduly important when the moments of inertia nearly coincide. This result is not obvious when the symmetrical coordinate system is used.

We may remark incidentally, that it is only when two or more moments of inertia coincide that the expressions ζ_i involved in (1) can have non-vanishing values, for otherwise the molecule will not have sufficient symmetry to permit the vibrational degeneracy requisite for $\zeta_i \neq 0$.

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[20] E. Wigner, Zeits. f. Physik **43**, 624 (1927).

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On the Plasticity of Crystals

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In the following, a theory is given with the purpose of establishing a mathematical relation between the stress and the strain in a crystal when plastically deformed. The existence of a "secondary structure" in crystals is adopted as a basic hypothesis. This structure was pointed out by Professor F. Zwicky to be a consequence of what he calls "cooperative phenomena." The assumption that gliding in crystals takes place between the blocks of the secondary structure is the starting point of the following theory. The additional hypothesis of assuming a statistical distribution of the different forces which produce gliding between the blocks, gives us the means for going further in the calculations. The final result which is the stress strain curve of a crystal, is an exponential law containing three constants, i.e., the torsional modulus G, the elastic limit, (γ_s, τ_s) and the maximum applicable stress τ_m. The form of the hysteresis cycles is deduced from the same considerations and moreover a formula is obtained for the areas of the cycles. Experimental verifications were made on a single crystal of copper, and also on ordinary microcrystalline copper.

Part I

It is well known that when the yield point is reached in a crystal, gliding takes place between some of the crystallographic planes. If we plastically deform a crystal through application of a sufficiently high stress in a given direction, and then reverse the stress, the gliding is reversed also, but we never obtain the initial state. Plastic deformation of a crystal at low temperatures in general leads to "cold hardening." The conception of the ideal crystal, defined by a geometrical arrangement of particles in a lattice, cannot explain the phenomenon of cold hardening. Zwicky[1–6] has studied other physical properties of crystals which are incompatible with the idea of an ideal lattice. He comes to the conclusion that these properties may be understood in terms of a "secondary structure" in crystals. In this discussion we admit the existence of this secondary structure, and, following Zwicky, we denote as π-planes the crystallographic planes characterizing the secondary lattice. Gliding

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[1] F. Zwicky, Proc. Nat. Acad. Sci. **15**, 253 (1929).
[2] F. Zwicky, Phys. Rev. **40**, 63 (1932).
[3] F. Zwicky, Phys. Rev. **43**, 270 (1933).
[4] F. Zwicky, Helv. Phys. Acta **16**, 210 (1933).
[5] F. Zwicky, Mech. Eng. **28**, 427 (1933).
[6] F. Zwicky, Rev. Mod. Phys. **6**, 193 (1934).