

## The Vibration-Rotation Energy Levels of Polyatomic Molecules I. Mathematical Theory of Semirigid Asymmetrical Top Molecules

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# The Vibration-Rotation Energy Levels of Polyatomic Molecules

## I. Mathematical Theory of Semirigid Asymmetrical Top Molecules

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The exact classical kinetic energy for a system of point masses is obtained. From this the correct form for the quantum-mechanical Hamiltonian operator is derived. If the assumption of small vibrations is applied to this operator, the familiar approximation of a rigid top plus normal coordinate vibrator is obtained. In order to secure better approximations, in which larger amplitudes of vibration are admitted, a perturbation method is introduced which permits the change of moment of inertia with vibration, the coupling of rotation and vibration, and the centrifugal stretching effects to be taken into account. If the stretching terms alone are neglected, it is possible to reduce the secular equation for the rotational energy levels to the Wang form, except that "effective moments of inertia"

must be used whose magnitude depends on the vibrational quantum state. The relation of these quantities to the equilibrium moments of inertia or to the instantaneous moments of inertia averaged over the vibrational motion is not simple, although the numerical deviation from them may not be great. In addition, for molecules with less than orthorhombic symmetry there is the further possibility that the orientation of the principal axes of inertia will vary with the vibrational quantum number. It is also pointed out that the Wang equation should not fit the data when a nearby vibrational state perturbs the state under examination or when the centrifugal effects are large. A method is indicated whereby the latter terms may in principle be calculated.

THE usual method of treating the rotational energy levels of polyatomic molecules has been to regard the molecule as a rigid top.<sup>1</sup> Recently, however, it has been realized that the rotational fine-structure is influenced by the non-rigidity of the molecule, especially through the coupling of the angular momenta of vibration and rotation.<sup>2</sup> Furthermore, it is well known that different empirical moments of inertia are required<sup>3</sup> in applying the Wang<sup>1</sup> secular equation for the asymmetric top to each vibration-rotation band, presumably due to the changing of the effective moments of inertia by the vibrational motion. Finally, the rigid top model does not allow centrifugal stretching effects, whereas such effects occur experimentally.

It is the purpose of this paper to give a rigorous treatment of the rotational energy levels of a

system of point masses, representing the atoms, connected by forces such that the resulting system is semirigid; i.e., each mass vibrates about an equilibrium position which is fixed relative to the equilibrium positions of the other masses. In this treatment all the effects discussed above will enter and may be taken into account in principle to any desired degree of approximation.

### CLASSICAL KINETIC ENERGY

In order to obtain the correct Schrödinger equation for the system of point masses, we shall first have to derive the classical kinetic energy. This we shall do using the angular velocity of a rotating system of axes fixed in the molecule and internal coordinates relative to these axes. The problem is conveniently set up vectorially. Let the position of the  $i$ th particle be given by the vector  $\mathbf{r}_i$  from a point  $O$ , which is the origin of a moving (translating and rotating) system of coordinates. Let  $x_i$ ,  $y_i$ ,  $z_i$  be the components of  $\mathbf{r}_i$  in the moving system of axes. The point  $O$  is in turn described by a vector  $\mathbf{R}$  from a space-fixed origin. The equilibrium position of the  $i$ th particle is given by  $\mathbf{a}_i$ , which is a vector fixed to the rotating-axis system. We define the displacement vector  $\mathbf{q}_i$  by the equation  $\mathbf{q}_i = \mathbf{r}_i - \mathbf{a}_i$ .

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<sup>1</sup> D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931). H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics*. Dissertation (Leyden, 1931). The original treatments of the asymmetric top are, S. C. Wang, *Phys. Rev.* **34**, 243 (1929); H. A. Kramers and G. P. Ittmann, *Zeits. f. Physik* **53**, 553 (1929), etc.; O. Klein, *Zeits. f. Physik* **58**, 730 (1929).

<sup>2</sup> E. Teller and L. Tisza, *Zeits. f. Physik* **73**, 791 (1932); E. Teller, *Hand- und Jahrbuch d. chem. Physik*, Vol. 9 (1934), p. 125; J. H. Van Vleck, *Phys. Rev.* **47**, 487 (1935); C. Eckart, *Phys. Rev.* **47**, 552 (1935); H. A. Jahn, *Ann. d. Physik* **23**, 529 (1935); M. Johnston and D. M. Dennison, *Phys. Rev.* **48**, 868 (1935).

<sup>3</sup> R. Mecke, *Zeits. f. Physik* **81**, 313 (1933), etc.

If the rotating system of axes has an angular velocity  $\omega$  and if the vector  $\mathbf{v}_i$  is defined as the vector with components  $\dot{x}_i, \dot{y}_i, \dot{z}_i$  in the moving system, then the velocity of the  $i$ th particle in space is<sup>4</sup>

$$\dot{\mathbf{R}} + \omega \times \mathbf{r}_i + \mathbf{v}_i. \quad (1)$$

Consequently the kinetic energy  $T$  of the whole system is given by

$$2T = \dot{\mathbf{R}}^2 \sum m_i + \sum m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) + \sum m_i v_i^2 + 2\dot{\mathbf{R}} \cdot \sum m_i \mathbf{v}_i + 2\dot{\mathbf{R}} \times \omega \cdot \sum m_i \mathbf{r}_i + 2\omega \cdot \sum m_i \mathbf{r}_i \times \mathbf{v}_i. \quad (2)$$

We have not yet defined the rotating system. Following Eckart,<sup>5</sup> we do so by introducing the conditions

$$\sum m_i \mathbf{v}_i = 0 \quad \text{and} \quad \sum m_i \mathbf{a}_i \times \mathbf{v}_i = 0. \quad (3)$$

The first of these implies also that  $\sum m_i \mathbf{r}_i = 0$ , or that the origin of the moving system is at the center of gravity of the molecule. The second condition states that there is no angular momentum, to the first approximation (i.e.,  $\mathbf{a}_i$  replacing  $\mathbf{r}_i$ ), relative to the moving system.

Replacing  $\mathbf{r}_i$  by  $\mathbf{a}_i + \mathbf{q}_i$  in the last term of Eq. (2) and using the conditions (3), we obtain

$$2T = \dot{\mathbf{R}}^2 \sum m_i + \sum m_i (\omega \times \mathbf{r}_i) \cdot (\omega \times \mathbf{r}_i) + \sum m_i v_i^2 + 2\omega \cdot \sum m_i \mathbf{q}_i \times \mathbf{v}_i. \quad (4)$$

The first term is the translational energy of the system and will be omitted hereafter because it can always be separated from the other terms. The second term is the rotational energy, the third the vibrational energy, and the last the coupling between rotation and vibration. By standard methods,<sup>4</sup> the kinetic energy expression above can be reduced to the form

$$2T = A\omega_x^2 + B\omega_y^2 + C\omega_z^2 - 2D\omega_x\omega_y - 2E\omega_y\omega_z - 2F\omega_z\omega_x + \sum m_i v_i^2 + 2\omega_x \sum m_i (\mathbf{q}_i \times \mathbf{v}_i)_x + 2\omega_y \sum m_i (\mathbf{q}_i \times \mathbf{v}_i)_y + 2\omega_z \sum m_i (\mathbf{q}_i \times \mathbf{v}_i)_z, \quad (5)$$

in which  $A, B, C$  are the instantaneous moments

<sup>4</sup> For a closely similar treatment of rigid bodies which gives more of the intermediate steps see L. Page, *Introduction to Theoretical Physics*, Chapter II.

<sup>5</sup> C. Eckart, *Phys. Rev.* **47**, 552 (1935).

of inertia with respect to the moving  $x, y, z$  axes, respectively;  $D, E$ , and  $F$  are the products of inertia with respect to the  $x$  and  $y, y$  and  $z, z$  and  $x$  axes, respectively;  $\omega_x, \omega_y, \omega_z$  are the components of the angular velocity  $\omega$  of the rotating system of axes. It is to be emphasized that  $A, B, C$ , etc., are not constants, but are functions of the positions of the particles which change as the molecule vibrates.

### Introduction of normal coordinates

It is now convenient to introduce a set of  $3N-6$  internal coordinates, which are best chosen to be the normal coordinates  $Q_k$  of the vibration problem. These are defined in terms of the components  $\xi_i/(m_i)^{1/2}$ ,  $\eta_i/(m_i)^{1/2}$ , and  $\zeta_i/(m_i)^{1/2}$  of the displacement vector  $\mathbf{q}_i$  by the equations

$$\xi_i = \sum_k l_{ik} Q_k, \quad \eta_i = \sum_k m_{ik} Q_k, \quad \zeta_i = \sum_k n_{ik} Q_k, \quad (6)$$

in which  $\xi_i, \eta_i, \zeta_i$  measure the displacement from the equilibrium position in terms of a mass-adjusted scale, and  $l_{ik}, m_{ik}, n_{ik}$  are constant coefficients.

Consequently, since the normal coordinates are normalized and orthogonal,

$$\sum m_i \dot{v}_i^2 = \sum (\dot{\xi}_i^2 + \dot{\eta}_i^2 + \dot{\zeta}_i^2) = \sum_k \dot{Q}_k^2, \quad (7)$$

and

$$\begin{aligned} \sum m_i (\mathbf{q}_i \times \mathbf{v}_i)_x &= \sum (\eta_i \dot{\zeta}_i - \zeta_i \dot{\eta}_i) = \sum_k \mathfrak{X}_k \dot{Q}_k, \\ \sum m_i (\mathbf{q}_i \times \mathbf{v}_i)_y &= \sum \mathfrak{Y}_k \dot{Q}_k, \\ \sum m_i (\mathbf{q}_i \times \mathbf{v}_i)_z &= \sum \mathfrak{Z}_k \dot{Q}_k, \end{aligned} \quad (8)$$

in which

$$\begin{aligned} \mathfrak{X}_k &= \sum_{i,l} (n_{ik} m_{il} - m_{ik} n_{il}) Q_l, \\ \mathfrak{Y}_k &= \sum_{i,l} (l_{ik} n_{il} - n_{ik} l_{il}) Q_l, \\ \mathfrak{Z}_k &= \sum_{i,l} (m_{ik} l_{il} - l_{ik} m_{il}) Q_l. \end{aligned} \quad (9)$$

The kinetic energy is therefore

$$2T = A\omega_x^2 + B\omega_y^2 + C\omega_z^2 - 2D\omega_x\omega_y - 2E\omega_y\omega_z - 2F\omega_z\omega_x + 2\omega_x \sum_k \mathfrak{X}_k \dot{Q}_k + 2\omega_y \sum_k \mathfrak{Y}_k \dot{Q}_k + 2\omega_z \sum_k \mathfrak{Z}_k \dot{Q}_k + \sum_k \dot{Q}_k^2. \quad (10)$$

### Hamiltonian form

It is now necessary to express the kinetic energy in terms of the angular momenta instead of the angular velocities. The components of the total angular momentum are given by<sup>6</sup>

$$\begin{aligned} P_x &= \partial T / \partial \omega_x = A \omega_x - D \omega_y - F \omega_z + \sum \mathfrak{X}_k \dot{Q}_k, \\ P_y &= \partial T / \partial \omega_y = -D \omega_x + B \omega_y - E \omega_z + \sum \mathfrak{Y}_k \dot{Q}_k, \\ P_z &= \partial T / \partial \omega_z = -F \omega_x - E \omega_y + C \omega_z + \sum \mathfrak{Z}_k \dot{Q}_k. \end{aligned} \quad (11)$$

The momentum  $p_k$ , conjugate to  $Q_k$ , is

$$p_k = \partial T / \partial \dot{Q}_k = \dot{Q}_k + \mathfrak{X}_k \omega_x + \mathfrak{Y}_k \omega_y + \mathfrak{Z}_k \omega_z. \quad (12)$$

These equations may be solved for  $\omega_x$ ,  $\omega_y$ ,  $\omega_z$  and the  $\dot{Q}_k$ 's in terms of  $P_x$ ,  $P_y$ ,  $P_z$  and the  $p_k$ 's and the results when substituted in Eq. (10) lead to the Hamiltonian form of the kinetic energy. It is thus found (see fine print below) that the complete Hamiltonian form may be written

$$\begin{aligned} 2T &= \mu_{xx}(P_x - p_x)^2 + \mu_{yy}(P_y - p_y)^2 \\ &+ \mu_{zz}(P_z - p_z)^2 + 2\mu_{xy}(P_x - p_x)(P_y - p_y) \\ &+ 2\mu_{yz}(P_y - p_y)(P_z - p_z) \\ &+ 2\mu_{zx}(P_z - p_z)(P_x - p_x) + \sum p_k^2. \end{aligned} \quad (13)$$

Here  $p_x$ ,  $p_y$ ,  $p_z$  are the components of angular momentum arising from vibration alone and are given by the expressions

$$p_x = \sum \mathfrak{X}_k p_k, \quad p_y = \sum \mathfrak{Y}_k p_k, \quad p_z = \sum \mathfrak{Z}_k p_k, \quad (14)$$

with  $\mathfrak{X}_k$ ,  $\mathfrak{Y}_k$ ,  $\mathfrak{Z}_k$  defined by Eq. (9) above. The coefficients  $\mu_{\alpha\beta}$  are functions only of the normal coordinates.

The following method was used to obtain the coefficients  $\mu_{\alpha\beta}$  in Eq. (13). From Eqs. (10), (11) and (12) we have

$$2T = P_x \omega_x + P_y \omega_y + P_z \omega_z + \sum p_k \dot{Q}_k. \quad (15)$$

If we substitute in Eq. (15) the expression for  $\dot{Q}_k$  obtained from the solution of Eq. (12), the kinetic energy becomes

$$2T = (P_x - p_x) \omega_x + (P_y - p_y) \omega_y + (P_z - p_z) \omega_z + \sum p_k^2. \quad (16)$$

Substituting in Eq. (11) the same expression for  $\dot{Q}_k$  and rearranging, we have

<sup>6</sup> The angular momentum is defined by  $\mathbf{P} = \sum m_i \mathbf{r}_i \times \dot{\mathbf{r}}_i = \sum m_i [\mathbf{r}_i \times (\boldsymbol{\omega} \times \mathbf{r}_i)] + \sum m_i \mathbf{r}_i \times \mathbf{v}_i$ . From this it can be seen that Eq. (11) is correct.

$$\begin{aligned} P_x - p_x &= A' \omega_x - D' \omega_y - F' \omega_z, \\ P_y - p_y &= -D' \omega_x + B' \omega_y - E' \omega_z, \\ P_z - p_z &= -F' \omega_x - E' \omega_y + C' \omega_z, \end{aligned} \quad (17)$$

in which

$$A' = A - \sum \mathfrak{X}_k^2; \quad B' = B - \sum \mathfrak{Y}_k^2; \quad C' = C - \sum \mathfrak{Z}_k^2; \quad (18)$$

$$D' = D + \sum \mathfrak{X}_k \mathfrak{Y}_k; \quad E' = E + \sum \mathfrak{Y}_k \mathfrak{Z}_k; \quad F' = F + \sum \mathfrak{Z}_k \mathfrak{X}_k.$$

If the inverse of transformation (17) is written

$$\begin{aligned} \omega_x &= \mu_{xx}(P_x - p_x) + \mu_{xy}(P_y - p_y) + \mu_{xz}(P_z - p_z), \\ \omega_y &= \mu_{yx}(P_x - p_x) + \mu_{yy}(P_y - p_y) + \mu_{yz}(P_z - p_z), \\ \omega_z &= \mu_{zx}(P_x - p_x) + \mu_{zy}(P_y - p_y) + \mu_{zz}(P_z - p_z), \end{aligned} \quad (19)$$

and if these expressions are substituted in Eq. (16), we obtain the form (13) of the kinetic energy.

### QUANTUM-MECHANICAL HAMILTONIAN

In this section we shall obtain the Schrödinger wave equation (in operator form) corresponding to the classical Hamiltonian given above. The difficulty is that the Hamiltonian is expressed in terms of momenta which are not conjugate to any coordinates so that the customary procedure for transforming the Hamiltonian from the classical to the quantum-mechanical form requires a slight extension. It is well known that when the classical kinetic energy is given by

$$2T = \sum_{i,j} g_{ij} \dot{q}_i \dot{q}_j \quad (20)$$

in terms of the generalized coordinates  $q_i$ , and consequently by

$$2T = \sum_{i,j} g^{ij} p_i p_j \quad (21)$$

in terms of the momenta  $p_i$  conjugate to the  $q_i$  ( $g^{ij}$  are the elements of the matrix inverse to the matrix  $(g_{ij})$ ), then the wave-mechanical Hamiltonian operator is<sup>7</sup>

$$\mathbf{H} = \frac{1}{2} g^{\frac{1}{2}} \sum_{i,j} \mathbf{p}_i g^{ij} g^{-\frac{1}{2}} \mathbf{p}_j + V. \quad (22)$$

Here  $\mathbf{p}_i = (\hbar/2\pi i) \partial / \partial q_i$ ,  $g$  is the determinant of the coefficients  $g^{ij}$ , and  $V$  is the potential energy.

If we now transform to a new set of momenta  $P_m$  which are not conjugate to any set of coordinates but which are defined by the transformation

$$p_i = \sum_m s_{im} P_m, \quad (23)$$

<sup>7</sup> See, for example, B. Podolsky, Phys. Rev. **32**, 812 (1928).

$$\text{then} \quad 2T = \sum_{m, n} G^{mn} P_m P_n, \quad (24)$$

$$\text{with} \quad G^{mn} = \sum_{i, j} s_{im} g^{ij} s_{jn}. \quad (25)$$

We inquire concerning the condition under which it is possible to express the wave-mechanical Hamiltonian in a form analogous to Eq. (22), namely, as

$$\mathbf{H} = \frac{1}{2} G^{\frac{1}{2}} \sum_{m, n} \mathbf{P}_m G^{mn} G^{-\frac{1}{2}} \mathbf{P}_n + V, \quad (26)$$

in which  $G$  is the determinant of the matrix  $(G^{mn})$ . To obtain this condition we substitute in Eq. (26) the expression

$$\mathbf{P}_m = \sum_i s^{mi} \mathbf{p}_i, \quad (27)$$

which is the inverse of the transformation in Eq. (23). Noting that  $G = s^2 g$ , where  $s$  is the determinant of the matrix  $(s_{im})$ , and using Eq. (25), we find

$$\mathbf{H} = \frac{1}{2} g^{\frac{1}{2}} \sum_{i, j, k, m} s s^{mi} \mathbf{p}_i s_{km} s^{-1} g^{kj} g^{-\frac{1}{2}} \mathbf{p}_j. \quad (28)$$

In order that Eq. (28) reduce to Eq. (22) the following condition must obviously be fulfilled:

$$\sum_{im} s^{mi} \mathbf{p}_i s_{km} = (1/s) \mathbf{p}_k s. \quad (29)$$

If the kinetic energy of our system were expressed in terms of the Eulerian angles  $\varphi$ ,  $\theta$ ,  $\chi$  and the normal coordinates  $Q_k$ , together with the conjugate momenta  $p_\varphi$ ,  $p_\theta$ ,  $p_\chi$  and  $p_k$ , the Hamiltonian operator would assume the form (22). We wish to apply condition (29) to the transformation from the momenta  $p_\varphi$ ,  $p_\theta$ ,  $p_\chi$ ,  $p_k$  to the set of momenta defined by Eqs. (11) and (12). The coefficients  $s^{mi}$  of Eq. (27) are readily obtained. For example, we can write for the  $x$  component of the total angular momentum

$$P_x = \frac{\partial T}{\partial \omega_x} = \frac{\partial T}{\partial \dot{\varphi}} \frac{\partial \dot{\varphi}}{\partial \omega_x} + \frac{\partial T}{\partial \dot{\theta}} \frac{\partial \dot{\theta}}{\partial \omega_x} + \frac{\partial T}{\partial \dot{\chi}} \frac{\partial \dot{\chi}}{\partial \omega_x} \\ = \frac{\partial \dot{\varphi}}{\partial \omega_x} p_\varphi + \frac{\partial \dot{\theta}}{\partial \omega_x} p_\theta + \frac{\partial \dot{\chi}}{\partial \omega_x} p_\chi$$

and similar expressions for  $P_y$  and  $P_z$ . The complete transformation corresponding to Eq.

(27) is thus found to be\*

$$P_x = \sin \chi p_\theta - \cos \chi \csc \theta p_\varphi + \cos \chi \cot \theta p_\chi, \\ P_y = \cos \chi p_\theta + \sin \chi \csc \theta p_\varphi - \sin \chi \cot \theta p_\chi, \quad (30) \\ P_z = p_\chi, \quad p_k = p_k.$$

The further transformation to the components of momenta defined by Eq. (17) and (14) is obviously

$$(P_x - p_x) = P_x - \sum \mathfrak{X}_k p_k, \\ (P_y - p_y) = P_y - \sum \mathfrak{Y}_k p_k, \quad (31) \\ (P_z - p_z) = P_z - \sum \mathfrak{Z}_k p_k, \\ p_k = p_k.$$

It is easily verified that the condition (29) is satisfied by both of these transformations. Consequently we may write the Hamiltonian operator corresponding to the classical kinetic energy (13) as<sup>8</sup>

$$\mathbf{H} = \frac{1}{2} \mu^{\frac{1}{2}} \sum_{\alpha, \beta} (\mathbf{P}_\alpha - \mathbf{p}_\alpha) \mu_{\alpha\beta} \mu^{-\frac{1}{2}} (\mathbf{P}_\beta - \mathbf{p}_\beta) \\ + \frac{1}{2} \mu^{\frac{1}{2}} \sum_k \mathbf{p}_k \mu^{-\frac{1}{2}} \mathbf{p}_k + V, \quad (32)$$

in which  $\alpha, \beta$  denote  $x, y$  or  $z$  and  $\mu$  is the determinant of  $(\mu_{\alpha\beta})$ . When we expand this expression, noting that  $\mathbf{P}_\alpha$  commutes with  $\mathbf{p}_k$  and that the coefficients  $\mu_{\alpha\beta}$  are functions only of the normal coordinates, we finally obtain as the desired form of the quantum-mechanical Hamiltonian operator

$$\mathbf{H} = \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta} \mathbf{P}_\alpha \mathbf{P}_\beta - \sum_\alpha h_\alpha \mathbf{P}_\alpha + \frac{1}{2} \sum_{\alpha, \beta} \mu^{\frac{1}{2}} \mathbf{p}_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} \mathbf{p}_\beta \\ + \frac{1}{2} \sum_k \mu^{\frac{1}{2}} \mathbf{p}_k \mu^{-\frac{1}{2}} \mathbf{p}_k + V. \quad (33)$$

Here

$$h_\alpha = \frac{1}{2} \sum_\beta \{ 2\mu_{\alpha\beta} \mathbf{p}_\beta + (\mathbf{p}_\beta \mu_{\alpha\beta}) + \mu_{\alpha\beta} \mu^{\frac{1}{2}} (\mathbf{p}_\beta \mu^{-\frac{1}{2}}) \}, \quad (34)$$

in which  $\mathbf{p}_\beta$  operates only on what is included in the parentheses.

\* These equations may be determined from the vectorial relations between the components of  $\boldsymbol{\omega}$  and  $\dot{\varphi}$ ,  $\dot{\theta}$ ,  $\dot{\chi}$ .

<sup>8</sup> When the dependence of  $\mu_{\alpha\beta}$  on the normal coordinates is neglected this expression reduces to

$$\mathbf{H} = \frac{1}{2} \sum_\alpha (\mathbf{P}_\alpha - \mathbf{p}_\alpha)^2 / I_\alpha + \frac{1}{2} \sum_k \mathbf{p}_k^2 + V,$$

where  $I_\alpha$  is a principal moment of inertia. This expression has also been justified by Van Vleck by another method, reference 2.

## THE RIGID ROTATOR APPROXIMATION

If the potential energy  $V$  has a deep and sharp minimum at the equilibrium configuration, the classical motion of the atoms will be limited to small regions near their equilibrium positions (for small values of the vibrational energy) and, quantum-mechanically, the vibrational wave functions will be appreciable only near this configuration. As a first approximation, we may therefore neglect all powers of  $Q_k$  but the zeroth power in the kinetic energy (retaining  $V(Q_1 \cdots)$ , however), obtaining as the expression for the Hamiltonian operator

$$\frac{1}{2}(\mathbf{P}_x^2/A_0 + \mathbf{P}_y^2/B_0 + \mathbf{P}_z^2/C_0) + \frac{1}{2}\sum \mathbf{p}_k^2 + V, \quad (35)$$

since  $\mu_{xx} \rightarrow 1/A_0$ , etc., when terms in  $Q_k$  are dropped.  $A_0$ ,  $B_0$ , and  $C_0$  are the equilibrium moments of inertia.

It is seen that the problem of finding the approximate energy levels is separable into two problems: the determination of the rotational energy levels from

$$\mathbf{H}_R^0 = \frac{1}{2}(\mathbf{P}_x^2/A_0 + \mathbf{P}_y^2/B_0 + \mathbf{P}_z^2/C_0) \quad (36)$$

and the determination of the vibrational energies from the other terms. The vibrational problem is usually solved by the use of normal coordinates, while the rotational problem is that of the rigid asymmetrical top (if  $A_0 \neq B_0 \neq C_0$ ) which has been solved<sup>1</sup> by Wang with Schrödinger mechanics and by Klein directly with operator calculus. By replacing  $p_\theta$  by  $(\hbar/2\pi i)\partial/\partial\theta$ , etc., in Eq. (30), the explicit expressions for the operators  $\mathbf{P}_x$ ,  $\mathbf{P}_y$  and  $\mathbf{P}_z$  may be obtained. From these we can verify the commutation rules<sup>9</sup>

$$\begin{aligned} \mathbf{P}_x\mathbf{P}_y - \mathbf{P}_y\mathbf{P}_x &= (\hbar/2\pi i)\mathbf{P}_z; \\ \mathbf{P}_y\mathbf{P}_z - \mathbf{P}_z\mathbf{P}_y &= (\hbar/2\pi i)\mathbf{P}_x; \\ \mathbf{P}_z\mathbf{P}_x - \mathbf{P}_x\mathbf{P}_z &= (\hbar/2\pi i)\mathbf{P}_y. \end{aligned} \quad (37)$$

Klein<sup>1</sup> used these relations and the fact that the operator for the total angular momentum,  $\mathbf{P}_x^2 + \mathbf{P}_y^2 + \mathbf{P}_z^2$ , has the eigenvalues  $J(J+1)\hbar^2/4\pi^2$

<sup>9</sup> It is to be noted that the sign is different in these relations, which refer to moving axes, from that for fixed axes. See Klein and Casimir, reference 1. The expressions for the operators  $\mathbf{P}_x$ ,  $\mathbf{P}_y$ ,  $\mathbf{P}_z$  in Eq. (30) are the same whether the molecule is rigid or not, even though in the latter case the total angular momentum includes vibrational momentum.

to obtain Wang's secular equation for the rotational energy levels. These levels are given by

$$W_{J,\sigma} = (\hbar^2/8\pi^2) \{ J(J+1)\frac{1}{2}(1/A_0 + 1/B_0) + [1/C_0 - \frac{1}{2}(1/A_0 + 1/B_0)]\epsilon \}, \quad (38)$$

in which  $\epsilon$  is a root of the secular equation of degree  $2J+1$  in  $\epsilon$  whose elements are

$$(K|K) = K^2 - \epsilon, \quad (K \pm 2|K) = bf(J, K \pm 1), \\ \text{others zero}, \quad (39)$$

with  $K = -J, -J+1, \dots, +J$  and

$$b = \frac{1}{2}(1/A_0 - 1/B_0) \times [1/C_0 - \frac{1}{2}(1/A_0 + 1/B_0)]^{-1}, \quad (40)$$

$$f(J, K) = -\frac{1}{2} \{ [J^2 - K^2][(J+1)^2 - K^2] \}^{\frac{1}{2}}.$$

## HIGHER APPROXIMATIONS FOR ASYMMETRICAL TOP MOLECULES

## Perturbation theory

In order to get better approximations, in which finite amplitudes of vibration are considered, the full expression (33) for  $\mathbf{H}$  must be used. We may, however, divide this into two parts,  $\mathbf{H}^0$  and  $\lambda\mathbf{H}'$ , and apply perturbation theory. The unperturbed part  $\mathbf{H}^0$  is given by

$$\mathbf{H}^0 = \mathbf{H}_R^0 + \mathfrak{B} \quad (41)$$

in which  $\mathbf{H}_R^0$  has been given in Eq. (36) while  $\mathfrak{B}$  is the vibration operator, comprising the last three terms of Eq. (33). The perturbation  $\lambda\mathbf{H}'$  consists of those terms of  $\mathbf{H}$  not included in  $\mathbf{H}^0$  and is to be considered as of smaller magnitude than  $\mathbf{H}^0$ . Let us set up the matrices for  $\mathbf{H}^0$  and  $\lambda\mathbf{H}'$  in terms of basis functions  $\psi_R\psi_V$ , where  $\psi_R$  is a function of the rotational coordinates only and has quantum numbers denoted by  $R$ , while  $\psi_V$  is a function of the internal coordinates (normal coordinates) only and has the quantum number  $V$ . Furthermore, let the  $\psi_V$  be normalized and orthogonal solutions of the vibrational wave equation. Then  $\mathbf{H}^0$  will be diagonal in  $V$  but not necessarily diagonal in  $R$ , because  $\psi_R$  is not necessarily a solution of the rotational problem.  $\lambda\mathbf{H}'$  will not be diagonal in either  $R$  or  $V$  but its elements will be small.

Under these circumstances, it has been shown, for example by Jordahl,<sup>10</sup> that it is possible to

<sup>10</sup> O. M. Jordahl, Phys. Rev. **45**, 87 (1934).

find a transformation which transforms the matrix  $\mathbf{H} = \mathbf{H}^0 + \lambda \mathbf{H}'$  into a matrix in which the only terms nondiagonal in  $V$  are of order  $\lambda^2$  or higher. These nondiagonal terms may be neglected in obtaining the energy correct to  $\lambda^2$ . With their neglect the transformed matrix factors into smaller matrices  $\mathfrak{H}$ , one for each vibrational state, whose elements  $\mathfrak{H}_{R, R'}$  are labeled by the  $R$  quantum numbers only, it being understood that these elements are diagonal in  $V$ .  $\mathfrak{H}$  is given by

$$\mathfrak{H} = \mathfrak{H}_0 + \lambda \mathfrak{H}_1 + \lambda^2 \mathfrak{H}_2 + \cdots, \quad (42)$$

in which the elements of  $\mathfrak{H}_0 + \lambda \mathfrak{H}_1$  are given by  $H_{RV, R'V}^0 + \lambda H_{RV, R'V}'$  or  $H_{RV, R'V}$ , while the elements of  $\lambda^2 \mathfrak{H}_2$  are

$$\lambda^2 (\mathfrak{H}_2)_{R, R'} = \sum'_{R'', V''} \frac{H_{RV, R''V''} H_{R''V'', R'V}}{h\nu_{V, V''}}, \quad (43)$$

in which it has been assumed that the spacing of the rotational levels is small compared with that of the vibrational levels so that  $W_{RV}^0 - W_{R''V''}^0$  can be replaced by  $W_V^0 - W_{V''}^0 = h\nu_{V, V''}$ , the difference of the vibrational energies. Terms in which  $V'' = V$  are omitted in the summation.

Fig. 1 shows the nature of the matrix  $\mathbf{H}$  before and after transformation ( $\mathbf{H}$  is really an infinite matrix). Before transformation  $\mathbf{H}$  can be factored and therefore separated into a problem of rotation and one of vibration only by neglecting terms of order  $\lambda$  (as was done in the rigid rotator approximation). After transformation the factoring is possible when terms nondiagonal in  $V$  of order  $\lambda^2$  are neglected. However, this approximation, in addition to giving the energy levels correct in terms of the order  $\lambda^2$ , also differs from the first approximation in that the small rotational matrices  $\mathfrak{H}$  are not the same for each vibrational state because the elements of  $\lambda \mathfrak{H}_1$  and  $\lambda^2 \mathfrak{H}_2$  are functions of  $V$ .

#### Nature of the rotational energy matrix $\mathfrak{H}$

By the use of the transformation just discussed, the infinite energy matrix has been factored into smaller *rotational* matrices (shaded squares in Fig. 1b). The eigenvalues of one of these small matrices are the rotational energy levels for that particular vibrational state and are accurate in terms of order  $\lambda^2$ . Let us now consider the general nature of one of these small matrices.

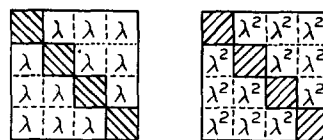


FIG. 1. The energy matrix  $\mathbf{H}$  before and after transformation. The blocks have different sets of vibrational quantum numbers  $VV'$ ; each block should be subdivided into elements with different rotational sets  $RR'$ . The shaded areas are of zeroth order in  $\lambda$ ; the unshaded areas of first or second order as indicated.

The elements of zeroth and first order in  $\lambda$  are given by

$$(\mathfrak{H}_0)_{R, R'} + \lambda (\mathfrak{H}_1)_{R, R'} = H_{RV, R'V} = \int \psi_V^* \psi_R^* \mathbf{H} \psi_V \psi_{R'} d\tau,$$

where  $\mathbf{H}$  is the complete Hamiltonian given in Eq. (33). Each of the terms of  $\mathbf{H}$ , except the purely vibrational terms, is a product of a rotational factor and a vibrational factor. A typical example is  $\mu_{xy} \mathbf{P}_x \mathbf{P}_y$ . Inserting in the integral, we get

$$\begin{aligned} & \int \psi_V^* \psi_R^* \mu_{xy} \mathbf{P}_x \mathbf{P}_y \psi_V \psi_{R'} d\tau \\ &= \int \psi_V^* \mu_{xy} \psi_V d\tau_V \int \psi_R^* \mathbf{P}_x \mathbf{P}_y \psi_{R'} d\tau_R \quad (44) \\ &= \overline{\mu_{xy}} (P_x P_y)_{R, R'}, \end{aligned}$$

where the bar denotes the quantum-mechanical average.  $\overline{\mu_{xy}}$  is independent of the quantum number  $R$ . Therefore if we denote by  $\mathbf{P}_x \mathbf{P}_y$  not only the operator but also the matrix with elements  $(P_x P_y)_{R, R'}$ , then we can write a matrix equation

$$\mathfrak{H}_0 + \lambda \mathfrak{H}_1 = \mathbf{W}_V + \frac{1}{2} \sum_{\alpha, \beta} \overline{\mu_{\alpha\beta}} \mathbf{P}_\alpha \mathbf{P}_\beta - \sum_{\alpha} \overline{h_\alpha} \mathbf{P}_\alpha, \quad (45)$$

in which  $\mathbf{W}_V$  is a diagonal matrix in  $R$  whose diagonal elements are all equal to  $W_V^0$ , the vibrational energy. This term comes from the purely vibrational terms of  $\mathbf{H}$ .

The terms of order  $\lambda^2$  can now be considered. They are given by Eq. (43). The element  $(\mathfrak{H}_2)_{R, R'}$  is a sum of terms because  $H_{RV, R''V''}$  is a sum. A typical term is

$$-\frac{1}{2} \sum'_{R'', V''} (\mu_{xx} P_x^2)_{RV, R''V''} \times (h_y P_y)_{R''V'', R'V} / h\nu_{V, V''}, \quad (46)$$

We have just seen, however, that elements such

as  $(\mu_{xx}P_x^2)_{RV, R'V'}$  factor, becoming  $(\mu_{xx})_{V, V'} \cdot (P_x^2)_{R, R'}$ . Therefore we get

$$-\frac{1}{2} \sum_{R''} (P_x^2)_{RR''} (P_y)_{R'', R'} \\ \times \sum_{V''}' (\mu_{xx})_{V, V''} (h_y)_{V'', V} / h\nu_{V, V''} \quad (47) \\ = -\frac{1}{2} (P_x^2 P_y)_{R, R'} \sum_{V''}' (\mu_{xx})_{V, V''} (h_y)_{V'', V} / h\nu_{V, V''}.$$

Here again each term reduces to a constant independent of  $R$  times a matrix element of a monomial in  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$ .

It is thus evident that the matrix  $\mathfrak{H}$  can be written as a polynomial in the matrices  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$  with constant coefficients which are formed from integrals involving the vibrational wave functions. Further examination shows that the linear terms in  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$  vanish identically and the cubic terms vanish or reduce to quadratic terms. The coefficients of  $\mathbf{P}_x, \mathbf{P}_y$ , and  $\mathbf{P}_z$  in  $\mathfrak{H}$  are  $-\bar{h}_x, -\bar{h}_y$ , and  $-\bar{h}_z$ , respectively.  $\mathfrak{H}$  and  $\mathbf{P}_\alpha$  are Hermitian matrices; consequently the matrix formed from the elements  $(h_\alpha)_{V, V'}$  is Hermitian. But  $h_\alpha$  is a pure imaginary operator, since every term contains  $(h/2\pi i)$  and all the other quantities are real. Furthermore, for asymmetric top molecules (excluding cases of accidental degeneracy)  $\psi_V$  is real. Consequently,<sup>11</sup> the diagonal term

$$(h_\alpha)^*_{V, V} = -(h_\alpha)_{V, V} = (h_\alpha)_{V, V} = 0.$$

The cubic terms in  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$  can likewise be eliminated. The coefficients of  $\mathbf{P}_x^3, \mathbf{P}_y^3$ , and  $\mathbf{P}_z^3$  vanish; for example

$$\frac{1}{2} \mathbf{P}_x^3 \sum_{V''}' \{ (\mu_{xx})_{V, V''} (h_x)_{V'', V} \\ + (h_x)_{V, V''} (\mu_{xx})_{V'', V} \} / h\nu_{V, V''} = 0$$

because  $(h_x)_{V, V''} = -(h_x)_{V'', V}$  and  $(\mu_{xx})_{V, V''} = (\mu_{xx})_{V'', V}$ , since  $h_x$  is a pure imaginary operator while  $\mu_{xx}$  is a real one. The other cubic terms all occur in pairs of the type  $\mathbf{P}_x^2 \mathbf{P}_y - \mathbf{P}_y \mathbf{P}_x^2$  with some coefficient. But

$$\mathbf{P}_x^2 \mathbf{P}_y - \mathbf{P}_y \mathbf{P}_x^2 = \mathbf{P}_x (\mathbf{P}_x \mathbf{P}_y - \mathbf{P}_y \mathbf{P}_x) \\ + (\mathbf{P}_x \mathbf{P}_y - \mathbf{P}_y \mathbf{P}_x) \mathbf{P}_x = (h/2\pi i) (\mathbf{P}_x \mathbf{P}_z + \mathbf{P}_z \mathbf{P}_x) \quad (48)$$

from the commutation relations, Eq. (37), so that these reduce to quadratic terms.

The conclusion is that, as a consequence of the perturbation treatment, we may write the small rotational matrix  $\mathfrak{H} = \mathfrak{H}_0 + \lambda \mathfrak{H}_1 + \lambda^2 \mathfrak{H}_2$ , which corresponds to a single vibrational quantum state, as a polynomial of the following sort in the matrices  $\mathbf{P}_x, \mathbf{P}_y$ , and  $\mathbf{P}_z$ :

$$\mathfrak{H} = \mathbf{W}_V + \frac{1}{2} \sum_{\alpha, \beta} \sigma_{\alpha\beta} \mathbf{P}_\alpha \mathbf{P}_\beta \\ + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} \mathbf{P}_\alpha \mathbf{P}_\beta \mathbf{P}_\gamma \mathbf{P}_\delta, \quad (49)$$

in which the coefficients  $\sigma_{\alpha\beta}$  and  $\tau_{\alpha\beta\gamma\delta}$  depend upon the vibrational quantum state to which  $\mathfrak{H}$  corresponds. If the vibrational wave functions are known with sufficient accuracy, the coefficients can be computed. The matrices for  $\mathbf{P}_x, \mathbf{P}_y$  and  $\mathbf{P}_z$  are known,<sup>12</sup> so that in principle the secular equation for the rotational problem can be set up, including quartic terms in  $\mathbf{P}_x, \mathbf{P}_y$  and  $\mathbf{P}_z$ . The solution of this problem would permit the change of moment of inertia with vibration, the coupling of rotation and vibration, and the centrifugal stretching effects to be taken into account.

Unfortunately, the error introduced by using the harmonic oscillator approximation to  $\psi_V$  may be as large as the perturbation effects we have been considering (the anharmonicity will be important in  $\mu_{xx}$ , for example) so that one cannot, at the present time, evaluate the coefficients theoretically. However, we can by making certain approximations reduce the secular equation to the Wang form [Eq. (39)], in which  $A_0, B_0$ , and  $C_0$  are replaced by three empirical parameters to be determined from experimental data. This is the procedure which has generally been used, without justification; we shall show that it is often, but not always, justified.

### Transformation to Wang form

In order to obtain the Wang form of the secular equation, the quartic terms in  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$  in Eq. (49) must be neglected. These terms, by analogy with diatomic molecules, correspond at least in part to centrifugal stretching effects. Experimentally it is observed that such effects are detectable for higher rotational states; they are not therefore entirely negligible. For low

<sup>11</sup> This can also be proved by partial integration.

<sup>12</sup> O. Klein, Zeits. f. Physik 58, 730 (1929).



rotational states, however, they are small. A rough method of classification of terms in  $\mathfrak{H}$  according to magnitude is by powers of the vibrational frequency  $\nu$ . On this basis the coefficients of the quadratic terms are of order  $\nu^0$ , plus corrections of order  $\nu^{-1}$  and  $\nu^{-1}$ , etc., while the coefficients of the quartic terms are of order  $\nu^{-2}$ . For this reason we omit the quartic terms for the present.

In case no other vibrational state perturbs the state under investigation, we can therefore, with the omission of the quartic terms, write the Hamiltonian  $\mathfrak{H}$  in the form

$$\mathfrak{H} = W_V + \frac{1}{2} \{ \sigma_{xx} \mathbf{P}_x^2 + \sigma_{yy} \mathbf{P}_y^2 + \sigma_{zz} \mathbf{P}_z^2 + \sigma_{xy} (\mathbf{P}_x \mathbf{P}_y + \mathbf{P}_y \mathbf{P}_x) + \sigma_{yz} (\mathbf{P}_y \mathbf{P}_z + \mathbf{P}_z \mathbf{P}_y) + \sigma_{zx} (\mathbf{P}_z \mathbf{P}_x + \mathbf{P}_x \mathbf{P}_z) \}. \quad (50)$$

This quadratic form may be reduced to principal axes by means of an orthogonal transformation on the matrices (or operators)  $\mathbf{P}_x$ ,  $\mathbf{P}_y$ ,  $\mathbf{P}_z$ , the transformation coefficients being ordinary numbers.<sup>13</sup> For molecules with orthorhombic symmetry, it can be shown from symmetry arguments that the cross terms in Eq. (50) vanish, so that no transformation is required. For molecules of lower symmetry, since the coefficients  $\sigma_{\alpha\beta}$  depend upon the vibrational quantum state, the transformation, and consequently the orientation of the principal axes of inertia, will also vary somewhat with the vibrational state.

When the reduction to principal axes has been made, there results

$$\mathfrak{H}' = W_V + \frac{1}{2} \{ \mathfrak{P}_x^2/A_e + \mathfrak{P}_y^2/B_e + \mathfrak{P}_z^2/C_e \} \quad (51)$$

with

$$\mathfrak{P}_x^2 + \mathfrak{P}_y^2 + \mathfrak{P}_z^2 = \mathbf{P}_x^2 + \mathbf{P}_y^2 + \mathbf{P}_z^2. \quad (52)$$

Furthermore the commutation rules for  $\mathfrak{P}_x$ ,  $\mathfrak{P}_y$  and  $\mathfrak{P}_z$  are the same as those given in Eq. (37) for  $\mathbf{P}_x$ ,  $\mathbf{P}_y$  and  $\mathbf{P}_z$ .<sup>14</sup> Consequently, the problem is now formally identical with the rigid asymmetric top previously discussed, except that  $A_0$ ,

$B_0$  and  $C_0$  must be replaced by  $A_e$ ,  $B_e$  and  $C_e$ . The energy levels are given by the Wang equation [Eqs. (39) and (40)] with these new "effective moments of inertia." For orthorhombic molecules,  $\sigma_{\alpha\alpha}$  is given by

$$\begin{aligned} \sigma_{\alpha\alpha} = & \frac{1}{2} \overline{\mu_{\alpha\alpha}} + \sum_{V'}' (h_{\alpha})_{VV'} (h_{\alpha})_{V'V} / h\nu_{VV'} \\ & - (h/2\pi i) \sum_{V'}' \{ (\mu_{\alpha\beta})_{VV'} (h_{\gamma})_{V'V} \\ & - (\mu_{\alpha\gamma})_{VV'} (h_{\beta})_{V'V} \} / h\nu_{VV'}. \quad (53) \end{aligned}$$

It is seen that even in this simplest case, in which  $\sigma_{xx} = 1/A_e$ , etc.,  $A_e$ ,  $B_e$  and  $C_e$  are not simply related to either the equilibrium moments of inertia  $A_0$ ,  $B_0$  and  $C_0$  or the instantaneous moments of inertia  $A$ ,  $B$ , and  $C$ . Therefore, the geometrical interpretation which has been given these quantities for excited vibrational states of observed molecules, for example water, may be misleading, if  $A_e$ ,  $B_e$  and  $C_e$  differ appreciably from  $A_0$ ,  $B_0$  and  $C_0$ .

### Centrifugal expansion terms

For energy levels with high  $J$  values, the quartic terms in  $\mathbf{P}_x$ ,  $\mathbf{P}_y$  and  $\mathbf{P}_z$  in Eq. (49) will be of importance, since they correspond to centrifugal expansion of the molecule. In the general case there are a great many of these terms. The coefficient of the term  $\mathbf{P}_\alpha \mathbf{P}_\beta \mathbf{P}_\gamma \mathbf{P}_\delta$ , where  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are selected from  $x$ ,  $y$ , and  $z$ , is

$$\frac{1}{4} \sum_{V'}' (\mu_{\alpha\beta})_{V, V'} (\mu_{\gamma\delta})_{V', V} / h\nu_{V, V'}. \quad (54)$$

In specific examples, many of these coefficients may vanish. Since the matrices for  $\mathbf{P}_x$ ,  $\mathbf{P}_y$  and  $\mathbf{P}_z$  have been given, the contributions of these quartic terms to the secular equation can be computed. It is planned to discuss these in a later paper.

### Accidental degeneracy

In case another vibrational state  $V''$  has an energy close to the state  $V$  under consideration, the treatment given in this paper may break down. If the matrix element  $H'_{RV, R''V''}$  is not very small, the term  $H_{RV, R''V''} H'_{R''V'', R'V} / h\nu_{V, V''}$  in Eq. (43) will be very large for such an accidental degeneracy and the perturbation technique used will not hold. Such cases are quite likely to occur in practice. The modifications of

<sup>13</sup> We are indebted to Professor J. H. Van Vleck for suggesting this method of reduction, as well as for calling our attention to the possibility of using the perturbation technique described earlier.

<sup>14</sup> The properties of the components of angular momentum should be independent of the choice of rotating axes. A more explicit proof can easily be given, however.

the theory necessary for treating such cases will be given in a subsequent paper.

### CONCLUSION

It has been shown that the rotational energy levels of a semirigid asymmetric polyatomic molecule are given by the Wang equation for the

rigid rotator with three "effective moments of inertia" if no accidental degeneracy occurs, and if centrifugal stretching terms are small enough to neglect. If these conditions are not fulfilled, the Wang equation may not apply.

In conclusion, we should like to thank Professor J. H. Van Vleck for several important suggestions.

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## The Relative Atomic Weight of Oxygen in Water and in Air

### A Discussion of the Atmospheric Distribution of the Oxygen Isotopes and of the Chemical Standard of Atomic Weights

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A difference in the density of water made from atmospheric oxygen plus tank hydrogen and aqueous oxygen plus tank hydrogen is interpreted as indicating that the atomic weight of oxygen in the air is 0.000108 atomic weight units heavier than the oxygen of Lake Michigan water. This observation finds experimental confirmation in the work of several other investigators and can be applied in certain cases to the reinterpretation of already existing data, clarifying several anomalous and inexplicable effects. The difference in atomic weights can be accounted for quantitatively by assuming that an isotopic exchange

equilibrium of the type discussed by Urey and Greiff occurs at a temperature of  $-50^{\circ}\text{C}$  in the lower regions of the stratosphere. The distribution of oxygen isotopes in the atmosphere is calculated by means of the usual hypsometric equation, but the separation due to gravity is not sufficient to explain quantitatively the excess atomic weight of atmospheric oxygen. The chemical and physical standards of atomic weights are discussed and the proposal is made that a single standard based on the mass of a pure isotope such as protium be adopted.

THE original discovery of isotopes gave rise to a considerable number of researches designed to test the constancy of chemical atomic weights of elements from a variety of natural sources, but no variation in the weights was observed, leading Aston,<sup>1</sup> for example, to conclude "that the evolution of the elements must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and, since we know of no natural process of separation, has remained constant ever since." However, shortly after the discovery of deuterium, slight differences in the density of water from many sources were observed;<sup>2</sup> these differences were smaller than the

experimental errors involved in previous atomic weight determinations, which explains why they had not been noted hitherto, but to the present time, however, no one has determined whether these differences in density are caused by variations in the isotopic composition of hydrogen or oxygen, the differences being usually attributed to variations in the abundance of deuterium.

Since the atomic weight of oxygen is the basis for the chemical atomic weight scale, it is especially interesting and important to know whether the isotopic ratios of oxygen in different compounds are the same. Manian, Urey and Bleakney<sup>3</sup> in a careful research investigated the relative abundance of the oxygen isotopes in

<sup>1</sup> F. W. Aston, *Mass-Spectra and Isotopes* (Edward Arnold and Company, London, 1933), p. 188.

<sup>2</sup> For a review see H. C. Urey and G. K. Teal, *Rev. Mod. Phys.* **7**, 34 (1935).

<sup>3</sup> S. H. Manian, H. C. Urey and W. Bleakney, *J. Am. Chem. Soc.* **56**, 2601 (1934). This paper contains references to earlier work. See also W. Bleakney and J. A. Hipple Jr., *Phys. Rev.* **47**, 800 (1935).