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Aaron Sayvetz

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The Kinetic Energy of Polyatomic Molecules

AARON SAYVETZ
Ryerson Physical Laboratory, The University of Chicago, Chicago, Illinois
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The theory of rotating axes and polyatomic molecules is extended in a form applicable to linear and anomalous molecules. It is applied to a linear tetratomic molecule and to an anomalous ammonia-like molecule, to obtain, in each case, a Hamiltonian kinetic energy lacking first-order terms. A second-order perturbation calculation yields the energy of interaction between rotation and vibration for the linear molecule. The relationship to Howard's theory of ethane is also given.

INTRODUCTION

The systematic theory of the motion of polyatomic molecules referred to moving axes has been developed by Eckart for the case of nonlinear normal molecules. In this theory, the unique definition of the axes is provided by certain conditions on the coupling terms in the kinetic energy, which were suggested by Casimir's study of rigid bodies in quantum mechanics. It is possible, however, to treat the interaction of rotation and vibration from a more general viewpoint, such as that considered by Welker, which is applicable to linear molecules, and to various types of anomalous molecules as well. For the purposes of application, this general theory may be specialized so that it assumes a form similar to the method of rotating axes, and for nonlinear normal molecules, is, in fact, identical with it. In illustration, the method is applied to a linear tetratomic molecule and to an anomalous molecule like ammonia.

4 H. Welker, Zeits. f. Physik 101, 95 (1936).

THE GENERAL METHOD

Many polyatomic molecules are known to behave like approximately rigid bodies while still others possess only one or two degrees of internal freedom. Thus, it might be said that a general $N$ atomic molecule consists of approximately rigid parts which may move relative to each other while the whole structure translates and rotates freely through space. Let it be assumed, for the time being, that the parts are perfectly rigid and that their relative motion is unconstrained. The system is thus in neutral equilibrium since it follows that the potential energy is identically zero. To specify the position in space of the equilibrium configuration defined in this way, fewer than $3N$ coordinates are needed, and these may be taken to be of two types: (a) six (or five) coordinates $\alpha'$, whose variation describes the over-all translation and rotation of the molecule, and (b) one or more coordinates $\alpha''$ which describe the gross internal motions.

The equations of transformation from Cartesian coordinates,

$$x_k = F_k(\alpha_p),$$

extracted from the image.
$k = 1, 2, \cdots, 3N; p = 1, 2, \cdots, M < 3N,$ are simply the equations of rigid constraint under which the motion takes place, and this will be termed the “rigidly constrained” motion. It is convenient to let the $x_k$ represent the coordinates of an atomic particle multiplied by the square root of its mass, and to use (in this section only) the summation convention. The properties of the system, in both classical and quantum mechanics, depend upon the Hamiltonian, which is readily obtained:

\[
\dot{x}_k = (\partial F_k / \partial \alpha_p) \dot{\alpha}_p \\
2T = \sum_\epsilon (\partial F_k / \partial \alpha_p) (\partial F_k / \partial \alpha_r) \dot{\alpha}_p \dot{\alpha}_r,
\]

which may be written:

\[
2T = A_p^{(0)} \dot{\alpha}_p \dot{\alpha}_r.
\]

The Hamiltonian is then

\[
2H = A_p P_p P_r,
\]

where the matrix $A_p^{(0)}$ is the reciprocal of $A_p^{(0)}$, and $P_p$ is conjugate to $\alpha_p$. Since the solution of the characteristic value problem for this Hamiltonian is known in most cases, the rigidly constrained motion can be considered as part of the zeroth-order approximation to the true motion.

To secure a more accurate molecular model, the atoms hitherto supposed to constitute one of the rigid parts must be allowed to vibrate about their equilibrium positions but, as a first approximation, with very small amplitudes, so that the configuration departs only slightly from the rigid structure. If the $3N-M$ additional degrees of freedom, $q_\lambda$, are introduced in the form:

\[
x_k = F_k(\alpha_p) + f_{k\lambda}(\alpha_p) q_\lambda,
\]

$\lambda = 1, 2, \cdots, 3N-M,$ so that they describe the deviation from equilibrium, and the zeroth-order potential energy is written as a (positive definite) quadratic form in the $q_\lambda$:

\[
2U_0 = b_{\lambda\mu}(\alpha^\mu) q_\lambda q_\mu,
\]

the motion will have the desired characteristics. Thus, Eq. (1) represents a loosening of the rigid constraints, and the motion might now be described as the “elastically constrained” motion. The solution of the “elastic constraint” problem enables the prediction of the major features of the molecule’s infra-red spectrum.

As usual, the Hamiltonian must be computed. The velocities are:

\[
\dot{x}_k = [\partial F_k / \partial \alpha_p] + (\partial f_{k\lambda} / \partial \alpha_p) q_\lambda \dot{\alpha}_p + f_{k\lambda} \dot{q}_\lambda,
\]

and the Lagrangian kinetic energy has the form:

\[
2T = A_p^{(0)} \dot{\alpha}_p \dot{\alpha}_r + 2B p \dot{\alpha}_p q_\lambda + C_{\lambda\mu} q_\lambda q_\mu,
\]

in which the coefficients $A_p^{(0)}$ have the form:

\[
A_p^{(0)} + A_{p\lambda} q_\lambda + A_{p\mu} \dot{q}_\mu.
\]

The first group of terms in (3) constitutes the energy of the system under the constraints $q_\lambda = \text{constant},$ and includes the energy of translation and rotation; the third sum is the kinetic energy of vibration, while the second represents the energy of interaction between rotation and vibration.

It is desired, first, that the interaction terms be small enough to be considered as a perturbation of second order or higher, and second, that the $q_\lambda$ be the normal coordinates. To see how the first requirement, which is a generalization of what has been called Casimir’s condition,\(^1\)\(^3\) can be effected, consider the explicit form of the $B_{\lambda\mu}$, which is

\[
B_{\lambda\mu} = (\partial F_k / \partial \alpha_p) f_{k\lambda} + (\partial f_{k\lambda} / \partial \alpha_p) f_{k\mu} q_\lambda,
\]

or, for short,

\[
B_{\lambda\mu} = B_{\lambda\mu}^{(0)} + B_{\lambda\mu} q_\lambda.
\]

If, as usual, one sets

\[
B_{\lambda\mu}^{(0)} = 0,
\]

the $B_{\lambda\mu}$ will be small for small vibrations. These may be considered as equations partially determining the $3N(3N-M)$ functions $f_{k\lambda}$. Since there are $M$ equations for each value of $\lambda$, $3N-M$ of the $f_{k\lambda}$ remain arbitrary. These are determined by the solution of the normal vibration problem in the $3N-M$ coordinates $q_\lambda$ as follows. The potential energy,

\[
U(x_k) = U(F_k + f_{k\lambda} q_\lambda),
\]

may be expanded in a Taylor’s series about the equilibrium values of the coordinates:

\[
U = \frac{1}{2} (\partial^2 U / \partial x_k \partial x_l) x_k f_{l\lambda} f_{k\lambda} q_\lambda + \cdots
\]

\[
= \frac{1}{2} \beta_{kl} f_{k\lambda} f_{l\lambda} q_\lambda + \cdots,
\]

this being a definition of $\beta_{kl}$. The $b_{\lambda\mu}$ (Eq. (2)), are therefore,

\[
b_{\lambda\mu} = \beta_{kl} f_{k\lambda} f_{l\mu},
\]
while the $C_{\mu}$, (Eq. (3)), are readily verified to be

$$C_{\mu} = f_{\lambda} f_{\mu}.$$  

The remaining $f_{\lambda}$ are then uniquely determined by the conditions:

$$b_{\lambda \mu} = 0 \quad (\lambda \neq \mu),$$  

$$C_{\lambda} = A_{\lambda} (a_{\mu}) \delta_{\lambda \mu},$$  

where the $A_{\lambda}$ are any preassigned functions.

The explicit definition of the $a_{\mu}$ depends on the particular type of molecule to which the method is to be applied, and for this purpose, normal and anomalous molecules may be distinguished, and discussed separately.

**Normal Molecules**

A molecule which, in the vibrationless state (neglecting zero-point energy), behaves like a completely rigid body may be called normal. If it is nonlinear, the $a_{\mu}$ are six in number ($M = 6$), and are most conveniently chosen to specify the position in space of a set of axes moving with the molecule, namely; the three components, $X$, $Y$, $Z$, of the vector $\mathbf{R}$ to the origin, and the three Eulerian angles, $\theta$, $\phi$, $\psi$, of the axes. Let the unit vectors along the moving axes be $e_i$ remembering that these are functions of the Eulerian angles. Also, let the index $k$ of Eq. (1) be an abbreviation for two indices, $i$, $a$, ($i = x, y, z$; $a = 1, 2, \ldots, N$), so that $x_{ia}$ are the coordinates of the $a$th atom in fixed axes. If $e_i$ are the fixed unit vectors, the rigid constraints, $F_k(a_{\mu})$, become

$$F_{ia} = m_a \mathbf{1} (\mathbf{R} + z_{ia}) \cdot e_i,$$

where $z_{ia} (= \Sigma \alpha e_i e_i)$ specifies the equilibrium position of the $a$th atom in the moving axes.

It will now be shown that, for this case, the method can be reduced to the method of rotating axes. Adopting the notation of reference 1, let the $f_{\lambda}$ of Eq. (1) have the form

$$f_{\lambda} = (\Sigma \alpha e_i e_i) e_i,$$

where $j = x, y, z$, and the $z_{ja}$ are constants to be determined by Eqs. (4), (5) and (6). Eq. (1) becomes

$$x_{ia} = [m_a \mathbf{1} (\mathbf{R} + \Sigma_j (m_a \mathbf{1} e_{ja} + \Sigma_{\alpha j} \theta_{ja} \mathbf{e}_j) e_i) \cdot e_i.$$

If $y_{ia}$ stands for the cartesian coordinates of the $a$th atom in the moving axes, multiplied by $m_a$, it is also true that

$$y_{ia} = [m_a \mathbf{1} (\mathbf{R} + \Sigma_j y_{ja} e_j) \cdot e_i.$$

Hence, by comparison with Eq. (8),

$$y_{ja} = m_a \mathbf{1} e_{ja} + \Sigma_{\alpha j} \alpha_{ja} e_i,$$

which is the conventional transformation of coordinates. It remains to be proved that the six equations, $B_{\alpha}(0) = 0$, are precisely the ones used to define the rotating axes.

Notice, first, that for $a_{\mu} = X, Y, Z$, $B_{\mu}(0) = 0$, so that $B_{\alpha}(0) = 0$ implies $B_{\mu} = 0$. But since this is the condition that the kinetic energy of translation be separable, the three equations $B_{\lambda \mu} = 0$, etc., must be equivalent to

$$\Sigma_a m_a x_a = 0,$$

where $x_a$ is the position vector in the moving axes, i.e., the origin of these axes is always at the centroid of the molecule. That the equations do have this form can also be proved. The remaining three equations may now be found. For $a_{\mu} = e_i$, for example,

$$\partial F_{ia}/\partial \theta = m_a [z_{xa} e_i e_x - z_{xa} s_i c_i e_y + (z_{xa} s_i c_i - z_{xa} s_i c_i) e_z] \cdot e_i.$$

In this expression, and in what follows, $s, c = \sin, \cos \theta; s', c' = \sin, \cos \phi; s'', c'' = \sin, \cos \psi$. Thus, $\partial F_{ia}/\partial \theta$ and $f_{\lambda\alpha}$ (Eq. (7)) are the $i\alpha$th components of the fixed axes of certain vectors whose components in the moving system are the coefficients of $e_i$ in the respective expressions for $\partial F_{ia}/\partial \theta$ and $f_{\lambda\alpha}$. Since the $B_{\alpha}(0)$ are the sums of scalar products of these vectors resolved along $e_i$, they can be written in terms of the other components as well, giving:

$$B_{\alpha} = \Sigma_a m_a [z_{xa} z_{xa} s_i c_i'' - z_{xa} z_{xa} s_i c_i'''] + \Sigma_{\alpha j} (z_{xa} s_i c_i'' - z_{xa} s_i c_i''').$$

On rearrangement, this becomes:

$$\Sigma_a m_a (s'' z_{xa} d_{\alpha i} e_y + c'' z_{xa} d_{\alpha i} e_y),$$

where $d_{\alpha i} = \Sigma\alpha j e_{ja} e_i$. In like manner,
\[ B_{\phi i}(0) = \sum_{m} m_{i} \left( \mathbf{w}_{m} \cdot \mathbf{e}_{z} - s s^* \mathbf{w}_{m} \cdot \mathbf{e}_{y} \right) \]

\[ B_{\phi i}^{(0)} = \sum_{m} m_{i} \mathbf{w}_{m} \cdot \mathbf{e}_{z} = 0, \]

in which \( w_{m} = z_{a} \times d_{a} \). These three equations imply that

\[ \sum_{m} m_{i} z_{a} \times d_{a} = 0, \]

which is Casimir's condition in vector form,\(^6\) since \( d_{a} \) has the dimensions \( m^{1} \times \text{length} \).

The normal coordinate problem may likewise be reduced to the conventional one. The \( b_{x} (\text{Eq. (2)}) \) are simply constants and all the \( A_{x} \) can thus be set equal to the same normalization constant, \( A \).

**Linear molecules**

If the equilibrium configuration of the molecule is linear, only five coordinates are necessary to specify its rigid motion: \( X, Y, Z, \theta \) and \( \phi \), and there must be \( (3N-5)q_{a} \). Hence, there are only five of the Eqs. (4), which are insufficient to define a set of moving axes uniquely. If, now, the transformation (8) is made exactly as in the preceding section, the angle \( \psi \) enters as an arbitrary parameter, which may therefore be set equal to zero, completing the definition of the axes.

The choice of the two Eulerian angles, \( \theta \) and \( \phi \), as "rigid constraint" variables implies that \( e_{z} \) passes through the equilibrium configuration, which can always be required to have its center of mass at the origin, so that

\[ z_{a} = z_{a} = 0 \]

\[ \sum_{m} m_{i} z_{a} \times d_{a} = 0. \]

In the next section, this method is applied to a general tetratomic linear molecule; the results obtained there may be of use in the interpretation of the rotational band structure of the acetylene molecule.

**Tetratomic Linear Molecule**

In order to compute the kinetic energy, the \( f_{i o b} \), and hence the \( z_{a o b} \), must be found explicitly by solving Eqs. (5), (6), (9) and (10). Written in scalar form, Eqs. (9) and (10) are:

\[ \sum_{m} m_{i} z_{a o b} = 0 \]

\[ \sum_{m} m_{i} z_{o a b} = 0, \]

while Eq. (6), which is also invariant under a rotation of the axes, takes the form

\[ \sum_{m} m_{i} z_{a o b} = A \delta_{b a}. \]

The \( 3N-5 = 7 \) linearly independent solutions of (11) can then always be chosen normalized and orthogonal so as to satisfy (12), in which \( A \) is conveniently taken to be the equilibrium moment of inertia, \( \sum_{m} m_{a} z_{a}^{2} \). To find particular solutions, set \( z_{a} = z_{a} = 0 \); the one remaining equation has three independent solutions: \( z_{1} = g_{1}(1), z_{2} = g_{1}(2), z_{3} = h_{a} \). Two of these are also solutions for \( z_{a} = z_{a} = 0 \) (\( \lambda = 4, 5 \)), and for \( z_{a} = z_{a} = 0 \) (\( \lambda = 6, 7 \)). Thus, \( q_{1}, q_{2}, q_{3} \) describe the parallel vibrations, \( q_{4} \) and \( q_{6} \) one perpendicular mode, and \( q_{5} \) and \( q_{7} \), the other.

The potential energy must now be considered. On account of the rotational symmetry of the equilibrium configuration, and the choice of the \( z_{a o b} \), it must have the form:

\[ 2U_{0} = \sum_{m, \mu} B_{m \mu} g_{\mu} + b_{44}(q_{4}^{2} + q_{6}^{2}) + b_{55}(q_{5}^{2} + q_{7}^{2}) + 2b_{45}(q_{4}q_{5} + q_{6}q_{7}), \]

where \( \lambda, \mu = 1, 2, 3 \). Since there are four non-diagonal terms, there are four of Eqs. (5), and in order to satisfy these, it is necessary to form more general solutions of (11) without altering the character of the \( q \)'s. This may be accomplished by taking separate orthonormal linear combinations of the solutions numbered 1, 2, 3, and of those numbered 4 and 5, which provides the four independent constants needed to diagonalize the potential energy. Because of the degeneracy of the perpendicular vibrations, the same combinations used for solutions 4 and 5 must be employed for solutions 6 and 7. The complete solution may therefore be written:

\[ z_{a} = \alpha_{1} g_{a}^{(1)} + \alpha_{2} g_{a}^{(2)} + \alpha_{y} h_{a} \]

\[ z_{a} = \beta_{1} g_{a}^{(1)} + \beta_{2} g_{a}^{(2)}, \]

and \( \alpha_{1}, \alpha_{2}, \beta_{1}, \beta_{2} \) describe the parallel vibrations, \( \alpha_{y} \) one perpendicular mode, and \( \beta_{y} \) the other.

**The Hamiltonian**

The Hamiltonian kinetic energy, readily computed by the method of Wilson and Howard,\(^7\)
turns out to be
\[ 2AT = f^{-2}[M_z - \Lambda_z]^2 + (M_y - \Lambda_y)^2 + \Sigma \rho_k^2, \]
where \( \rho_k \) is conjugate to \( q_k \), \( M = M_x \varepsilon_x + M_y \varepsilon_y + M_z \varepsilon_z \) is the total angular momentum about the center of mass, and
\[ f = 1 + \alpha_{13} q_1 + \alpha_{23} q_2 + \alpha_{33} q_3. \]

The calculation also yields the result that
\[ M_z - \Lambda_z = 0. \]

The quantities \( \Lambda \) are identical (except for a normalization factor) with Wilson and Howard's \( \rho_z, \rho_y, \rho_z \), and are given by
\[ \Lambda_x = (1/A) \Sigma X_k \rho_k; \quad \Lambda_y = (1/A) \Sigma Y_k \rho_k; \quad \Lambda_z = (1/A) \Sigma Z_k \rho_k, \]
in which
\[ X_k = \sum_{n} \sum_{\alpha} \sum_{m} (z_{k\alpha} a_{n\alpha} q_\alpha) \rho_k \]
\[ Y_k = \sum_{n} \sum_{\alpha} \sum_{m} (z_{k\alpha} a_{n\alpha} - z_{k\alpha} a_{n\alpha} q_\alpha) \rho_k \]
\[ Z_k = \sum_{n} \sum_{\alpha} \sum_{m} (z_{k\alpha} a_{n\alpha} + z_{k\alpha} a_{n\alpha} q_\alpha) \rho_k. \]

Finally, the relations of \( M_x \) and \( M_y \) to the momenta conjugate to \( \theta, \phi \), and \( q_\alpha \) are:
\[ M_x = -(1/s) P_\phi + (c/s) \Lambda_x \]
\[ M_y = P_\phi. \]

It should be noted that the \( \Lambda \)'s, which always appear in the Hamiltonian of a rotating vibrator, are not the same as the components of the vibrational or internal angular momentum. The latter are defined as \( 2X_k \rho_k \), etc., rather than as \( 2X_k \rho_k \).

The calculation of the characteristic values of the Hamiltonian operator is entirely analogous to that performed by Weinberg and Eckart for the triatomic linear molecule, so that only the important steps will be described here.

**The perturbation calculation**

The approximation,
\[ f = 1, \]
is equivalent to neglecting terms of third order and higher, while Casimir's condition ensures the absence of first-order terms. There remain only terms of zero and second order, and these are:
\[ 2AT = \Sigma \rho_k^2 \]
\[ T_2 = T - T_0. \]

If polar coordinates are introduced,
\[ q_1 = \rho_1 \cos \chi_1; \quad q_2 = \rho_2 \cos \chi_2 \]
\[ q_3 = \rho_1 \sin \chi; \quad q_2 = \rho_2 \sin \chi, \]

the zero-order wave functions are, in Dennison's notation,
\[ \psi_0 = \psi(\theta, \phi) \psi^*_1(q_1) \psi^*_2(q_2) \psi^*_3(q_3) \]
\[ \times R^i_{\lambda}(\mu) e^{i \lambda} X_1 R^j_{\mu}(\nu) e^{i \mu} X_2, \]
in which \( l_1 = V_4, V_4 - 2, \ldots 1 \) or 0, etc. and \( \psi(\theta, \phi) \) is an undetermined coefficient. This can also be written:
\[ \psi_0 = \psi(\theta, \phi) \mu_n \chi N(q, \rho, \chi), \]
where \( N \) is an abbreviation for the quantum numbers \( V, n \) ranges over all the combinations \( l_1l_2 \), and \( g \) may have the values +++, +-, --, etc. The zero-order energy,
\[ W_0 = \sum_i (V_i + \frac{1}{2}) \hbar \omega_i + (V_{i+1} + 1) \hbar \omega_i + (V_i + 1) \hbar \omega_i, \]
is therefore of weight \( \pi_n = (V_i + 1)(V_i + 1) \). In this and all following summations in this section, the index \( i \) has the range 1, 2, 3. Since the first-order energy corrections, \( W_1 \), due to the addition of cubic terms in the potential energy, are all zero, the degeneracy is unaltered to this approximation, and the correct zero order combinations for the second-order calculation are
\[ \Sigma_n \Sigma_{\nu} \psi_{n\nu} \mu_{n\nu}. \]

If the operators \( T \) are defined by
\[ T_{n\nu \nu'} = \int u^*_{n' \nu'} T \psi_{n\nu} \mu_{n\nu} dq_1 \cdots dq_7, \]

the secular equations have the form:
\[ \sum_n \sum_{\nu} T_{n\nu \nu'} \psi_{n\nu} = W'' \psi_{n' \nu}, \]
in which \( W'' \) is that part of the second-order energy correction, \( W_2 \), arising from \( T_2 \) alone. This "separability" of \( W_2 \) is possible only because the matrix elements of the first-order potential energy have the property:
\[ (U_1)_{n\nu} \mu_{\lambda} = 0 \quad (\mu \neq n), \]
where \( \mu h \) has the same significance as \( ng \) but

---

*\(^9\) The operators must be transformed correspondingly: \( \rho_1 = \cos \chi_1 \rho_\psi - \sin \chi_1 \rho_\theta \), etc.; \( \Lambda_x \) becomes simply: \( \rho_{x1} + \rho_{x2} \).

*\(^{10}\) D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).
refers to a wave-function for any state other than \( W_0 \). The kinetic energy operators themselves have the form:

\[
T_{n_0 n_0'} = T_{n_0} \delta_{n_0, n_0'}
\]

and are

\[
T_{\pm \pm} = \left( \frac{1}{2A} \right) \left[ P_{\pm} P_{\pm} - \hbar c (\pm l_1 \pm l_2) \right]^2 + C.
\]

The characteristic values are immediately available:

\[
W_\gamma = \left( \frac{\hbar^2}{2A} \right) \left[ J(J+1) - K^2 \right] + C,
\]

where \( K = (\pm l_1 \pm l_2) \), \( J = |K| \), \( |K| + 1, \ldots \). The first part is essentially the energy of a linear symmetric top, while the energy of interaction is

\[
\frac{C}{2} = \left( \frac{\hbar^2}{2A} \right) \left[ (V_4 + 1) \left( \sum r_i^2 (V_i + \frac{1}{2}) (\omega_1/\omega_4 + \omega_4/\omega_1) \right) + (V_6 + 1) \left( \sum l_i^2 (V_i + \frac{1}{2}) (\omega_1/\omega_5 + \omega_5/\omega_1) \right) \right] - 21,
\]

in which the integer 2 appears because there are two degenerate perpendicular vibrations, and

\[
\begin{align*}
\alpha_i & = \alpha_i \beta_1 + \alpha_{12} \beta_2, \\
\alpha_i & = \alpha_i \beta_1 + \alpha_{21} \beta_2.
\end{align*}
\]

This is analogous to Weinberg and Eckart's result for the triatomic case, and the generalization to an \( n \) atomic linear molecule is obvious.

For the symmetric molecule \( XX_3 \), the following simplifications occur:

\[
\begin{align*}
r_1 & = 1; \quad r_2 = r_3 = 0 \\
t_1 & = 0; \quad t_2 = -(1 - t_3)\frac{1}{3}.
\end{align*}
\]

Thus, one constant, in addition to the normal frequencies, remains to be determined by the potential energy.

**Anomalous Molecules**

These are molecules possessing internal motions with amplitudes too large to be treated as normal vibrations, as, for example, the free internal rotation of an ethane-like molecule. Another example, to be discussed here, is a model of the ammonia molecule, in which it is supposed that the nitrogen atom, in an excited vibrational state, can surmount a relatively low potential barrier and vibrate between two extreme positions on opposite sides of the plane of the hydrogen atoms.

**YYX**

The rigidly constrained configuration, \( YYX \), is taken to be a tetrahedron of variable height with the \( Y \) nucleus at the apex, on the \( z \) axis of a moving system of axes, while the \( X \) nuclei form an equilateral triangle parallel to the \( x-y \) plane. The anomalous coordinate, \( \alpha'' = z \), is thus the \( z \) coordinate of the \( Y \) atom. The remaining coordinates are, as before, the three cartesian coordinates of the origin, three Eulerian angles, and five normal coordinates.

If the \( X \) nuclei, of mass \( m \), are numbered 1, 2, 3 and the axes are the principal axes of the equilibrium configuration, the vectors \( z_a \) are:

\[
\begin{align*}
z_1 & = -(S/2)e_x - (\sqrt{3}/6)S e_y - (M/3m)e_z, \\
z_2 & = (S/2)e_x - (\sqrt{3}/6)S e_y - (M/3m)e_z, \\
z_3 & = (\sqrt{3}/3)S e_y - (M/3m)e_x, \\
z_4 & = z e_z,
\end{align*}
\]

where \( M \) is the mass of the \( Y \) nucleus, and \( S \) represents the side of the equilateral triangle. Note that the lengths of the \( z_a \) are not constant, as for a normal molecule, but vary with the time.

The position vectors for the elastically constrained motion are given by

\[
r_a = z_a + m_a \delta_{a},
\]

where \( \delta_{a} \), the mass-adjusted displacement from equilibrium, is defined as

\[
\delta_{a} = \sum_{l \alpha} q_{l \alpha} d_{a \alpha},
\]

\[
= \sum_{l\alpha} z_{l \alpha} d_{a \alpha} q_{l \alpha} e_{l \alpha}.
\]

Finally, the seven equations, \( B_{\lambda \alpha}^{(0)} = 0 \), may be written:

\[
\begin{align*}
\sum m_{a} \delta_{a} & = 0 \\
\sum m_{a} z_{a} \times \delta_{a} & = 0 \\
\delta_{a} \cdot e_{z} & = 0.
\end{align*}
\]

The seventh equation states that no normal vibration involves motion of the \( Y \) atom along the \( z \) axis, or that all \( z_{a \neq 4} = 0 \).

The potential energy,

\[
U = U(q_1 \cdots q_5, z),
\]

when expanded about the point \( q_{\lambda} = 0, z = z \), takes the form:

\[
U = U(z) + \sum \sum b_{l \alpha} z_{l \alpha} g_{a} q_{a} + \cdots.
\]

This assumes that for \( q_{a} = 0 \), the \( X \) atoms are in equilibrium for all values of \( z \), which is, of course,
an approximation. The normal vibrations are given by the five orthonormal solutions of (13) which diagonalize the quadratic part of the potential energy. Three of these, \( \lambda = 1, 2, 3 \), are identical with the normal vibrations of three equal atoms at the corners of an equilateral triangle, the \( Y \) atom being unaffected. The coefficients describing the remaining double vibration, \( \lambda = 4, 5 \), are:

\[
\begin{align*}
    z_{4,x} &= z_{5,x} = 0 \\
    z_{4,y} &= z_{5,y} = -\frac{1}{3}(M/m)d \\
    z_{4,z} &= z_{5,z} = Kdz \\
    z_{6,1} &= z_{6,2} = -\frac{1}{2}Kdz \\
    z_{6,2} &= 0,
\end{align*}
\]

where \( K \) is a constant, but \( d \) is a function of \( z \) determined by the requirement that the normalization factor be independent of \( z \). What is sometimes referred to as the sixth “normal vibration,” namely; the \( z \) motion of the \( Y \) atom, is determined by \( U(z) \). Furthermore, since the amplitudes of some of the other vibrations depend on \( z \), this variable enters the interaction terms of the kinetic energy in a rather complicated manner. If the experimental data warrants it, it would be interesting to investigate the contribution of such terms to the energy levels.

**Hamiltonian kinetic energy**

It is now possible to calculate the second-order terms in the Hamiltonian of our model with complete generality. The Lagrangian kinetic energy is:

\[
2T = \Sigma m_a(R + \dot{r}_a)^2
\]

and

\[
\dot{r}_a = \omega \times r_a + \dot{z}_a + m_a^{-1}\dot{\delta}_a.
\]

Taking account of Eqs. (13) and their time derivatives, and neglecting terms quadratic in \( \dot{q}_a \), since these give rise to terms of third or higher order, one gets:

\[
2T = \Sigma \Sigma I_{ij}(\dot{\omega}_i, \dot{\omega}_j) + 2\omega_j(\Sigma \dot{\delta}_j \dot{\delta}_j + R_1 \dot{z})
+ 2\omega_j(\Sigma \dot{\delta}_j \dot{\delta}_j + R_2 \dot{z}) + 2\omega_j \Sigma \dot{\delta}_j \dot{\delta}_j
+ \mu M\dot{z}^2 + A \Sigma \dot{\delta}_j^2,
\]

in which the \( I_{ij} \) are the instantaneous moments and products of inertia, and

\[
\begin{align*}
    \mu &= (M/m) + 1 \\
    R_1 &= 2\mu M\dot{q}_4 \dot{q}_4 \\
    R_2 &= -2\mu M\dot{q}_5 \dot{q}_5.
\end{align*}
\]

Notice that the zero-order term in \( z \), which is separable, involves \( \mu M \) rather than \( M \).

The Hamiltonian kinetic energy takes the form:

\[
2T = \Sigma_i (M_i - \Lambda_i)^2/I_i \dot{q}_i^2 + P_i^2/M\mu + (1/A) \Sigma \dot{p}_j^2,
\]

where \( I \) is an equilibrium moment of inertia, and depends on \( z \). As before, \( M_i = \partial T/\partial \omega_i \) and \( P_i = \partial T/\partial \delta_i \) but the \( \Lambda_i \) are now defined by

\[
\begin{align*}
    \Lambda_i &= (1/A) \Sigma \dot{\delta}_j \dot{p}_j + (R_1/M\mu) P_z \\
    \Lambda_j &= (1/A) \Sigma \dot{\delta}_j \dot{p}_j + (R_2/M\mu) P_z \\
    \Lambda_z &= (1/A) \Sigma \dot{\delta}_j \dot{p}_j.
\end{align*}
\]

**Ethane**

This molecule has been studied in detail by Howard,\(^{11}\) and it will be sufficient to mention that the equations by which he removes the degrees of freedom corresponding to “incipient translations, over-all rotations, and internal rotation” are the seven equations, \( B_{\alpha\beta}(0) = 0 \), appropriate to his choice of the seven rigid constraint variables. Six of these variables are identical with those chosen here for normal molecules, as are the corresponding six equations (our Eqs. (9) and (10)); the seventh coordinate, which describes the internal motion, is taken to be the angle between the two methyl groups, considered as rotating relative to each other about a common axis, (the \( z \) axis of the moving system).

The seventh equation turns out to be:

\[
\Sigma_{\alpha\beta}\dot{q}_\alpha \times d_{\alpha\beta} \cdot \dot{z} = 0,
\]

where the summation extends over the atoms of one methyl group only. This means that, in first approximation, the \( z \) component of the angular momentum of each methyl group vanishes separately.

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