Some Studies Concerning Rotating Axes and Polyatomic Molecules

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The theory of small vibrations when the potential energy is invariant under the rotation-displacement group is developed. The results are compared with the Brester-Wigner theory of the normal coordinates, and it is shown that the use of these coordinates implies the use of a particular (normal) system of rotating axes whose construction is given. It is shown that when the motion of a normal molecule is referred to these axes, those terms of the Hamiltonian which are linear in the angular momenta will be especially small and of the same order of magnitude as the quadratic terms (Casimir's condition). When the amplitude of one or more of the normal vibrations becomes large, this is no longer true of the normal axes; this will always be the case when one of the normal frequencies is small compared to the others, as has been noted by other writers. The normal axes are not the principal axes of inertia of the instantaneous configuration of the system, and certain conclusions recently published by the author are wrong for that reason.

1. INTRODUCTION

IN the theory of polyatomic molecules, free use is made of the possibility of referring the positions of the individual atoms to rotating axes. It has become conventional to suppose that these axes satisfy two conditions, but, so far as I am aware, no investigation has shown that these two conditions are compatible, nor has any construction been given for finding the axes which satisfy them. The present paper will give a construction for finding these axes for normal molecules; it is doubtful if such axes exist for anomalous molecules.

The first of the two conditions was formulated by Casimir[1] and depends on the fact that the Hamiltonian will always be a quadratic function of the components of the total angular momentum along the moving axes. This function will always have terms of the zeroth, first and second degrees in these components. If the molecule is quasi-rigid, and the quantum conditions are taken into account, the division into terms of zeroth, first and second orders for the purpose of a perturbation calculation will ordinarily coincide with the division into degrees just mentioned. Casimir showed that it was plausible to suppose that a particular coordinate system could be found such that the terms of the first degree were exceptionally small and of the same order of magnitude as the quadratic terms.

The second condition on the coordinate axes has entered the theory in a somewhat casual manner. It is automatically imposed by the ordinary use of those normal coordinates introduced by Wigner[2] and Brester,[3] and can be avoided only by extraordinary care. The normal coordinates may be defined as linear functions of the cartesian coordinates in a particular set of rotating axes. Conversely, the coordinates in this set of axes are linear functions of the normal coordinates, the coefficients of which have been tabulated by Brester. If another set of rotating axes is used, the cartesian coordinates will not in general be linear functions of the normal coordinates, or if this should accidentally be the case, the coefficients will not be those tabulated by Brester. Another set of considerations enters to obscure this rather simple relation: the normal coordinates are supposed to have infinitesimal values in those cases where they are actually used. Then Taylor's theorem is invoked to make it plausible to suppose that the functions mentioned will be linear in every case. This does not alter the fact that their coefficients will have Brester's values only in rare cases. Furthermore, it is a troublesome fact that the functions (direction cosines) involved in the transformation from one set of cartesian axes to another will have branch points; it is therefore not clear that the use of Taylor's theorem is justified. To summarize: it may be said that the use of the normal coordinates practically implies the use of one definite set of rotating axes. The question

[1] H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics*, Chap. V. Dissertation, Leyden (1931).

[2] E. Wigner, *Göttinger Nachrichten*, p. 133 (1930).

[3] C. J. Brester, *Kristallsymmetrie und Restrahlen*. Dissertation, Utrecht (1923).

arises: is Casimir's condition fulfilled by this set? This will be shown to be the case provided only that none of the normal frequencies is unusually small, or what amounts to the same thing, that none of the normal vibrations has an unusually large amplitude.

A survey of the literature discloses no previous investigation of this problem, but seems to indicate that different authors have held divergent opinions as to the probable outcome of such an investigation. Many of these opinions are not clearly expressed but must be deduced from the analytic procedure adopted. In a recent paper, I have studied the use of the principal axes of inertia as the rotating axes.[4] I was led to this by the erroneous belief that it was this system that is associated to the normal coordinates, and that Casimir's condition would be fulfilled provided only that the molecule is quasi-rigid. After publication, it was noticed that this belief was wrong, and that therefore the usual methods of calculation need modification when used with this system of axes. Professors Casimir and Van Vleck have both considered these modifications and shown that one of my conclusions was wrong. The latter has recently published an account[5] of his calculations which contains an excellent explanation of the matter. Apparently no one noticed that the axes are not those associated to the normal coordinates, but a comment from Professor W. V. Houston led directly to a recognition of this fact.

2. The General Transformation to Rotating Axes

When the motion of a system of particles is referred to a moving set of cartesian axes, the latter may be defined in several ways: (1) As an explicit function of the time only; (2) as an explicit function of the instantaneous positions of the particles only; (3) in more general ways. The first method of definition is treated fully in the standard texts on dynamics, but is quite irrelevant to the molecular problem. In this section it is proposed to give an account of the second.

Let the mass of the ath atom ($a=1, 2\cdots N$) be m_a and its coordinate vector (from a fixed origin) be $\mathbf{x}_a$. If the unit vectors along fixed axes are $\mathbf{e}_i$ ($i=x, y, z$) then

$$\mathbf{x}_a=\sum_i \mathbf{e}_i x_{ia}. \tag{1}$$

Suppose that a moving system of axes has been defined in some way which need not be specified further at the moment than to say that its origin is at the point $\mathbf{X}=\sum_i \mathbf{e}_i X_i$ and that unit vectors along its axes are $\boldsymbol{\varepsilon}_j$. It is convenient to suppose at the outset that the origin $\mathbf{X}$ is at the center of mass of the molecule and that both fixed and moving systems are right-handed. Then the Eq. (1) may also be written

$$\mathbf{x}_a-\mathbf{X}=\sum_j \boldsymbol{\varepsilon}_j y_{ja}$$

or

$$x_{ia}-X_i=\sum_j c_{ij} y_{ja}, \tag{2}$$

where

$$c_{ij}=\mathbf{e}_i\cdot\boldsymbol{\varepsilon}_j$$

are the direction cosines of the moving axes and the y_{ja} are the components of the vectors $\mathbf{x}_a-\mathbf{X}$ along the moving axes.

The specification of the instantaneous position of the moving axes requires six numbers, which may be taken to be the three X_i and the Eulerian angles of $\boldsymbol{\varepsilon}_j$. There being $3N$ of the quantities x_{ia}, it follows that at most $3N-6$ of the y_{ja} are independent and that they may be expressed as functions of $3N-6$ generalized coordinates q_λ. The y_{ja} will thus satisfy six equations identically in the q_λ; three of these will be

$$\sum_a m_a y_{ja}=0, \tag{3}$$

and the others will be left in the undetermined form

$$Y_i(y_{ja})=0. \tag{4}$$

These last equations constitute the definition of the moving system.

The vectors $\boldsymbol{\varepsilon}_j$ are functions of the Eulerian angles only, and through these, of the time. As they vary, they remain of unit length and mutually perpendicular; from this it follows that

$$d\boldsymbol{\varepsilon}_j/dt=\Omega\times\boldsymbol{\varepsilon}_j, \tag{5}$$

where Ω is the angular velocity of the moving axes. It is a linear function of the time-derivatives of the Eulerian angles but depends on the angles themselves in a somewhat complicated way,

[4] C. Eckart, Phys. Rev. **46**, 383 (1934).
[5] J. H. Van Vleck, Phys. Rev. **47**, 487 (1935).

described in all standard texts. From Eq. (5) it follows that

$$d(\mathbf{x}_a-\mathbf{X})/dt=\sum_j(\Omega\times\boldsymbol{\varepsilon}_j y_{ja}+\boldsymbol{\varepsilon}_j\dot{y}_{ja}),$$

and hence that the angular momentum about the center of mass is

$$\mathbf{M}=\sum_a\sum_i\sum_j m_a(\boldsymbol{\varepsilon}_i y_{ia})\times(\Omega\times\boldsymbol{\varepsilon}_j y_{ja}+\boldsymbol{\varepsilon}_j\dot{y}_{ja}). \quad (6)$$

It is important to note at the outset that when $\Omega=0$, $\mathbf{M}$ is not zero but equal to

$$\Lambda=\sum_a m_a\{\boldsymbol{\varepsilon}_x(y_{ya}\dot{y}_{za}-y_{za}\dot{y}_{ya})+\cdots\}. \quad (7)$$

Λ can be defined by the same formula when $\Omega\neq0$ and is then the angular momentum of the atoms relative to the moving axes. It is necessary to distinguish this from the components of the total angular momentum in the moving system, which are M_j and defined by $\mathbf{M}=\sum_j\boldsymbol{\varepsilon}_j M_j$. Similar equations define the components of Λ and Ω in the moving system; in terms of these, Eq. (6) may be written

$$M_i=\sum_j A_{ij}\Omega_j+\Lambda_i, \quad (8)$$

where

$$A_{xx}=\sum_a m_a(y_{ya}^2+y_{za}^2),$$

$$A_{xy}=-\sum_a m_a y_{xa}y_{ya}, \quad \text{etc.}$$

are the components of the moment of inertia tensor in the moving system. Eq. (7) may also be written

$$\Lambda_i=\sum_\lambda\dot{q}_\lambda B_{\lambda i}, \quad (9)$$

where

$$B_{\lambda x}=\sum_a m_a[y_{ya}(\partial y_{za}/\partial q_\lambda)-y_{za}(\partial y_{ya}/\partial q_\lambda)], \quad \text{etc.} \quad (10)$$

The kinetic energy, T (after ignoring the energy of the center of mass) is given by

$$2T=\sum_a m_a[d(\mathbf{x}_a-\mathbf{X})/dt]^2$$
$$=\sum_i\sum_j A_{ij}\Omega_i\Omega_j+2\sum_i\sum_\lambda\dot{q}_\lambda B_{\lambda i}\Omega_i+\sum_\lambda\sum_\mu C_{\lambda\mu}\dot{q}_\lambda\dot{q}_\mu,$$

where $C_{\lambda\mu}=\sum_i\sum_\mu m_a(\partial y_{ia}/\partial q_\lambda)(\partial y_{ia}/\partial q_\mu)$.

From this it follows that the momentum conjugate to q_λ is

$$p_\lambda=\sum_\mu C_{\lambda\mu}\dot{q}_\mu+\sum_i B_{\lambda i}\Omega_i. \quad (11)$$

It is to be noted that $p_\lambda\neq0$ when $\dot{q}_\lambda=0$; the general analogy between the Coriolis forces and a magnetic field becomes apparent in these equations. To find the Hamiltonian kinetic energy it is necessary to solve Eqs. (8), (9) and (11) for Ω_i and $\dot{q}_\mu$ in terms of M_i and p_λ. The solution will be given only for the case $C_{\lambda\mu}=\delta_{\lambda\mu}$, which is sufficiently general to illustrate the important points:

$$\Omega_i=\sum_j\alpha_{ij}M_j-\sum_\lambda p_\lambda\beta_{\lambda i},$$

$$\dot{q}_\lambda=\sum_\mu\gamma_{\lambda\mu}p_\mu-\sum_i\beta_{\lambda i}M_i,$$

where

$$A_{ij}-\sum_\lambda B_{\lambda i}B_{\lambda j}=(\alpha^{-1})_{ij},$$

$$\beta_{\lambda i}=\sum_j B_{\lambda j}\alpha_{ji},$$

$$\gamma_{\lambda\mu}=\delta_{\lambda\mu}+\sum_i B_{\lambda i}\beta_{\mu i}.$$

From this the Hamiltonian kinetic energy is obtained as

$$2T=\sum_i\sum_j\alpha_{ij}M_iM_j-2\sum_\lambda\sum_i p_\lambda\beta_{\lambda i}M_i+\sum_\lambda\sum_\mu\gamma_{\lambda\mu}p_\lambda p_\mu. \quad (12)$$

It will at once occur to the reader that a sure way of satisfying Casimir's condition is to require $\beta_{\lambda i}=0$ for all q_λ, which amounts to requiring $B_{\lambda i}=0$. These are $3N-6$ differential equations for the, as yet undefined, y_{ja}. However, it is probable that these equations possess more than six integrals independent of q_λ, and it has been seen that only this number of identities in the y_{ja} is permissible. The probability of this event becomes apparent on noting that the condition is equivalent to $\Lambda_i=0$, and the possibility of securing this for all q_λ and $\dot{q}_\lambda$ by a definition depending only on the positions of the particles is not reasonable. It is, however, always possible to require that $B_{\lambda i}=0$ for one definite set of values of q_λ. This no longer restricts the definition of the y_{ja} to an impossible extent. It is then reasonable to suppose that those terms of the kinetic energy which are linear in M_i will be especially small for those values of q_λ near the chosen set. If this is also the region in which the motion of the system takes place, a first step in the direction of fulfilling Casimir's condition will have been taken. This matter will be considered in greater detail at the end of the next section.

3. The Theory of Small Vibrations when the Potential Energy is Invariant under the Rotation-Displacement Group

The usual theory of small vibrations considers only two cases:[6] (1) All coordinates vary only by infinitesimal amounts; (2) those coordinates which vary by finite amounts are ignorable. Neither case is realized by the polyatomic molecule; the Eulerian angles vary by finite amounts and are not ignorable, since the kinetic energy depends on the components of the total angular momentum in the moving system, which are not integrals of the motion. The potential energy is independent of these angles, however, so the most general case is not yet at hand. It is none the less necessary to build the theory from first principles, and little reliance may be placed on analogies with the results proven in the standard texts.

The invariance of the potential energy U under the rotation-displacement group results in

$$U(x_{ia}') = U(x_{ia})$$

whenever $$x_{ia}' = \sum_j R_{ij} x_{ja} + \xi_i,$$

where R_{ij} is an arbitrary rotation matrix and ξ_i the components of an arbitrary vector. According to the general postulate of the theory of small vibrations, U is supposed to have a minimum for some configuration $x_{ia} = z_{ia}$; because of the invariance, it will have this same minimum value for a six-dimensional continuum of other configurations, and any one of these might be chosen for the following considerations. It is well to make the choice somewhat carefully, and to require z_{ia} to be a configuration whose center of mass is at the origin, and whose principal axes are parallel to the fixed coordinate axes.

Since U is supposed not to have a singularity at z_{ia} it may be expanded in the form

$$U(z_{ia} + \delta z_{ia}) = U(z_{ia}) + A \sum_\lambda (\omega_\lambda \delta q_\lambda)^2, \quad (13)$$

where $$\delta q_\lambda = \sum_i \sum_a q_{\lambda ia} \delta z_{ia} \quad (14)$$

are linearly independent functions. The quantities A and ω_λ are positive constants not equal to zero, but whose values are as yet quite arbitrary. The coefficients $q_{\lambda ia}$ are also arbitrary to a certain extent: to see this, note that Eq. (13) remains quite unchanged if the quantities $(\omega_\lambda \delta q_\lambda)$ are subjected to an orthogonal substitution. This may be utilized later to normalize the definition of the δq_λ. The $q_{\lambda ia}$ are not entirely without restriction, however; the most important arises from the invariance of U: the most general infinitesimal rotation-displacement is given by

$$\delta z_{xa} = \delta \xi_x + \delta \Omega_y z_{za} - \delta \Omega_z z_{ya}, \quad \text{etc.}, \quad (15)$$

where $\delta\xi$ and $\delta\Omega$ are six arbitrary infinitesimals. If these values of δz are substituted into Eq. (14) the δq must vanish, since otherwise $U(z+\delta z) \neq U(z)$. This results in the equations

$$\sum_a q_{\lambda ia} = 0, \quad \sum_a (z_{ia} q_{\lambda ja} - z_{ja} q_{\lambda ia}) = 0. \quad (16)$$

These will be linearly independent unless all N of the points z_a lie in a straight line, i.e., unless the equilibrium configuration of the molecule is linear. This case will be excluded from further consideration. It follows that there are at most $3N-6$ of the δq_λ; it will also be supposed that this maximum is reached. There will thus be many solutions of Eq. (14), all of the form

$$\delta z_{ia} = \sum_\lambda \delta q_\lambda z_{\lambda ia}.$$

The difference between any two of these will have the form of the right side of Eq. (15), $\delta\xi$ and $\delta\Omega$ now representing linear functions of the δq, determined by the two solutions in question. It is thus seen that the $z_{\lambda ia}$ are arbitrary to a greater extent than the $q_{\lambda ia}$.

To remove this additional arbitrariness, it is necessary to impose six linear equations on the $z_{\lambda ia}$ for every value of λ. These may be taken to be

$$\sum_a m_a z_{\lambda ia} = 0, \quad (17)$$

$$\sum_j \sum_a Y_{ija} z_{\lambda ja} = 0, \quad (18)$$

where the Y_{ija} are $9N$ numbers restricted only by the requirement that a certain determinant shall not vanish. This determinant has the matrix

$$Z_{ix} = \sum_a (Y_{iya} z_{za} - Y_{iza} z_{ya}), \quad \text{etc.}$$

These equations are all invariant under a change of normalization, and this may now be carried out so that

$$\sum_i \sum_a m_a z_{\lambda ia} z_{\mu ia} = A \delta_{\lambda\mu}, \quad (19)$$

[6] See, e.g., E. T. Whittaker, *Analytical Mechanics*, Chap. VII; 3rd ed., Cambridge (1927).

provided that the ω_λ are given certain values determined by the form of the potential energy function and called the normal frequencies. The constant A in Eq. (19) must have the same value as in Eq. (13), but is otherwise arbitrary. If it is given the dimensions of a moment of inertia, the δq will be dimensionless and $z_{\lambda ia}$ will have the dimensions of a length.

It will now be shown that it is always possible to define a system of rotating axes such that

$$y_{ja}=z_{ja}+\sum_\lambda q_\lambda z_{\lambda ja}. \tag{20}$$

For Eq. (3) is fulfilled because of the choice of the z_{ia} and Eq. (17). The definition of the axes is obtained by eliminating the q from Eq. (20) and is

$$\sum_j\sum_a Y_{ija}(y_{ja}-z_{ja})=0. \tag{21}$$

The quantities determining the kinetic energy are readily computed and have the form

$$\begin{aligned} A_{ij}&=A_i\delta_{ij}+\sum_\lambda q_\lambda A_{\lambda ij}+\sum_\lambda\sum_\mu q_\lambda q_\mu A_{\lambda\mu ij},\\ B_{\lambda i}&=B_{\lambda i}^{(0)}+\sum_\mu q_\mu B_{\lambda\mu i}, \qquad (22)\\ C_{\lambda\mu}&=A\,\delta_{\lambda\mu}. \end{aligned}$$

The coefficients of these equations are functions of z_{ia} and $z_{\lambda ia}$ only; all of the A's are symmetric in i and j, while $B_{\lambda\mu i}=-B_{\mu\lambda i}$.

It is now possible to consider the relation between the coordinate systems just defined (they will be called linear systems, since their defining equations are linear) and more general systems, defined by Eqs. (4). It is supposed that these latter are satisfied by $y_{ja}=z_{ja}$; then for small values of $y_{ja}-z_{ja}$ they are approximately the same as Eqs. (21) with

$$Y_{ija}=\text{const.}\times(\partial Y_i/\partial y_{ja})_{y=z}. \tag{23}$$

In general there is thus a linear system which differs from a given system only by quantities of the second order in $(y_{ja}-z_{ja})$. This approximate set of axes is uniquely determined by the original definition, and other linear systems differ from it by quantities of the first order. Occasionally, however, no such approximate linear system exists: this is true whenever the Z-determinant vanishes.

These matters may be illustrated by the principal axes, for which

$$Y_x(y_{ja})=\sum_a m_a y_{ya}y_{za},\quad \text{etc.},$$

and the approximate set is defined by

$$\sum_a m_a(y_{ia}z_{ja}+y_{ja}z_{ia})=0,\quad i\neq j. \tag{24}$$

In this case, the Eqs. (22) are somewhat simplified because Eqs. (24) are equivalent to $A_{\lambda ij}=0$. The Z-determinant is $(A_x-A_y)(A_y-A_z)\times(A_z-A_x)$, so that no approximate set exists when two or more of the principal moments of inertia are equal at equilibrium.

It is also possible to carry the considerations of the end of the preceding section to a conclusion: let it be required to find a linear set of axes for which $B_{\lambda i}=0$ when $q_\lambda=0$. This can be done by choosing the Y_{ija} so that Eq. (18) reduces to $B_{\lambda i}^{(0)}=0$, which is explicitly

$$\sum_a m_a(z_{ia}z_{\lambda ja}-z_{ja}z_{\lambda ia})=0. \tag{25}$$

This requires that

$$Y_{xxa}=0,\quad Y_{xya}=-Y_{yxa}=m_a z_{za},\quad \text{etc.}$$

The Z-determinant is now simply $A_xA_yA_z$, and cannot vanish since the linear molecules have been excluded. Eq. (21) becomes

$$\sum_a m_a(z_{ia}y_{ja}-z_{ja}y_{ia})=0,$$

or, because of Eq. (2)

$$\sum_k(F_{ki}c_{kj}-F_{kj}c_{ki})=0, \tag{26}$$

where $$F_{ki}=\sum_a m_a(x_{ka}-X_k)z_{ia}.$$

These results can be given a geometric interpretation: defining the three vectors $\mathbf{F}_i=\sum_k \mathbf{e}_k F_{ki}$, Eq. (26) becomes

$$\mathbf{F}_i\cdot\boldsymbol{\varepsilon}_j=\mathbf{F}_j\cdot\boldsymbol{\varepsilon}_i. \tag{27}$$

The vectors $\mathbf{F}_i$ can be determined before the rotating axes are known; Eq. (27) states that these are defined so that the projection of $\mathbf{F}_x$ on the y axis is equal to the projection of $\mathbf{F}_y$ on the x axis, etc. The analytical procedure for finding them is not much more complicated than that for finding the principal axes: Eq. (27) is equivalent to

$$\mathbf{F}_i=\sum_j f_{ij}\boldsymbol{\varepsilon}_j,\quad f_{ij}=f_{ji}$$

and the symmetric matrix f_{ij} can be determined from

$$\mathbf{F}_i\cdot\mathbf{F}_j=\sum_k f_{ik}f_{kj}.$$

It is thus the square root of the Gram matrix of the vectors $\mathbf{F}$. Its elements will always be real, since the characteristic values of the Gram matrix can never be negative. If none of these are zero, the $\mathbf{F}$ will not be coplanar, and the solution of Eq. (27) will be simply

$$\boldsymbol{\varepsilon}_i = \sum_j f_{ij}[\mathbf{F}_j],$$

where the $[\mathbf{F}_j]$ are the vectors reciprocal to the $\mathbf{F}_i$. For the important special case of molecules having a plane configuration, one of the vectors $\mathbf{F}$ will vanish identically. It can be shown that in this case two of the vectors $\boldsymbol{\varepsilon}$ are in the plane of the non-vanishing $\mathbf{F}$ and the third perpendicular to it.

This system of axes will be called the normal system, and its associated q_λ the normal coordinates; this does not conflict with established custom, since it will be shown in Section 5 that these are the coordinates studied by Brester and Wigner.

4. Casimir's Condition

It will now be shown that the normal axes satisfy Casimir's condition except in the case of molecules which are not really to be considered as rigid. In doing so, free use will be made of a proposition which is strictly true only in classical mechanics, and whose extension to quantum mechanics involves assumptions which have not been adequately studied. This is the proposition that, when the energy of the system is small only those values of y_{ja} need be considered which differ from z_{ja} by small amounts. If the arbitrary constant A be chosen to have a value of the order of magnitude of the A_i, this is equivalent to considering only values of q_λ which are much less than unity.

The Eqs. (8) and (11) may be written, in the case of the normal axes,

$$M_i = A_i\Omega_i + \sum_j\sum_\lambda q_\lambda A_{\lambda ij}\Omega_j + \sum_j\sum_\lambda\sum_\mu q_\lambda q_\mu A_{\lambda\mu ij}\Omega_j + \sum_\lambda\sum_\mu \dot{q}_\lambda q_\mu B_{\lambda\mu i},$$

$$p_\lambda = A\dot{q}_\lambda + \sum_\mu\sum_i q_\mu B_{\lambda\mu i}\Omega_i.$$

The A's and B's are all independent of the q_λ and the Eulerian angles and all have the order of magnitude of A. The solution of these equations may be written

$$\dot{q}_\lambda = (p_\lambda - \sum_i\sum_\mu q_\mu B_{\lambda\mu i}\Omega_i)/A,$$

$$\Omega_i = (M_i - \Lambda_i')/A + \sum_j(\sum_\lambda q_\lambda a_{\lambda ij} + \cdots)(M_j - \Lambda_j'),$$

$$\Lambda_j' = \sum\sum_{\lambda>\mu}(p_\lambda q_\mu - p_\mu q_\lambda)B_{\lambda\mu i}/A.$$

Here Λ_i' must not be confused with the previous Λ_i, from which it differs by terms of the order of pq^2; the dots in the second equation indicate quantities of the order of magnitude q^2/A or smaller, and the constants $a_{\lambda ij}$ have the magnitude $1/A$ and can easily be calculated explicitly. The expression for the kinetic energy is

$$2T = \sum_\lambda p_\lambda^2/A + \sum_i(M_i - \Lambda_i')^2/A_i + \sum_\lambda\sum_i\sum_j q_\lambda a_{\lambda ij}(M_i - \Lambda_i')(M_j - \Lambda_j') + \cdots. \tag{28}$$

It is now necessary to investigate the order of magnitude of the terms entering into this expression. It may be supposed that

$$q_\lambda \sim (\hbar/A\omega_\lambda)^{\frac{1}{2}}, \quad p_\lambda \sim (\hbar A\omega_\lambda)^{\frac{1}{2}}.$$

Furthermore, $M_i \sim \hbar$ and it is easily seen that

$$p_\lambda q_\mu \sim \hbar(\omega_\lambda/\omega_\mu)^{\frac{1}{2}}. \tag{29}$$

If all the normal frequencies are of the same order of magnitude, it follows that $\Lambda_i' \sim \hbar$. The quantity $\epsilon \sim (\hbar/A\omega_\lambda)^{\frac{1}{2}}$ may be taken as the perturbation parameter, and the three sums of Eq. (28) are of the order $\hbar\omega$, $\epsilon^2\hbar\omega$ and $\epsilon^3\hbar\omega$, respectively. Casimir's condition is thus fulfilled.

It may happen that one of the normal frequencies is much smaller than the others, in which case Eq. (29) indicates that some of the terms in Λ_i' will have an undesirably large value. This situation has come to be known as the "phenomenon of slip." In this case also, the amplitude of variation of the corresponding normal coordinate will no longer be small, and the molecule can no longer be called quasi-rigid. It may thus be said that the normal system satisfies Casimir's condition for all quasi-rigid molecules, this being really a definition of quasi-rigidity. It is doubtful whether it will ever be necessary to consider any other linear system of axes in connection with the molecular problem, for when the normal axes are not suited for its discussion, it is not clear that any other linear system will be better adapted to the purpose.

5. The Symmetry of the Normal Coordinates

The discussion of the normal coordinates given by Brester and Wigner[2, 3] differs from that given here in certain formal respects, and it must be shown that the two lead to identical definitions. In the quadratic form of Eq. (13), the ω_λ have here been supposed not to be zero, and as a consequence, there are only $3N-6$ of the δq's. Brester and Wigner, on the other hand, require the form to depend on $3N$ δq's, and consequently must admit the value zero as possible for ω_λ. This is always permissible, but there is then an arbitrariness in the six additional δq's which corresponds exactly to the arbitrariness in the $z_{\lambda ia}$ described in Section 3. This additional arbitrariness is not considered further by them, but is removed by the device of requiring the additional $q_{\lambda ia}$ to satisfy the same Eq. (16) which are satisfied by the others. There being now $3N$ of the Eq. (14), the $z_{\lambda ia}$ are completely determined except for normalization; this may be carried out so that Eq. (19) are valid for all $3N$ values of λ. The number of these equations is thus increased from $(3N-6)(3N-5)/2$ to $3N(3N+1)/2$; the new equations, insofar as they do not merely determine constant factors, prove to be precisely the Eqs. (17) and (25). The former has here been made common to all linear systems, the latter expresses the characteristic property of the normal system. It is interesting to note that the six additional δq's obtained in this way are essentially the $\delta\xi$'s and $\delta\Omega$'s of Eq. (15).

The elegant device of the null-frequencies thus leads directly to the normal system, without the necessity of considering the other linear systems. Its only disadvantage is that it does not make it clearly evident that a rotating system of axes has been defined, and that the symmetry of the q_λ depends as much on the choice of the axes as on the symmetry of the equilibrium configuration. This can be most clearly seen from the present point of view: the relation between the q's and the cartesian coordinates (either x_{ia} or y_{ja}) will depend on the Y_{ija} as well as on the z_{ia}. If the former are chosen in a very unsymmetric manner, no amount of symmetry of the latter will avail to make the q's symmetric functions of the cartesian coordinates. It is thus not permissible to define a system of rotating axes in an unsymmetric manner, then approximate them by a linear system, and suppose the resulting q_λ to be the normal coordinates.

This has frequently been done in the literature, and it is not always easy to determine whether a serious error has resulted or not. Fortunately there are certain quantities which are invariant under a change of the Y_{ija}: the normal frequencies are such quantities. Hence conclusions concerning the degeneracy of these, obtained from a consideration of the normal system, will be equally valid in any linear system. There must also be some way to show that the determination of their activity in emission and in the Raman effect is invariant. If it should ever prove to be really necessary to use the general linear systems, it will be useful to precede it by the development of the theory of these invariants. For the present it appears sufficient to use only the normal system.

Confining the attention to this, certain possibilities for the further application of symmetry considerations become apparent. Since Λ_i' must have the character of a vector product (it must behave like M_i), it follows that its components and also the $B_{\lambda\mu i}$ and $B_{\lambda i}$ must have certain determinate symmetry properties. These may be discussed in the same way as the properties of the dipole and quadrupole moments, and it is often possible to show that they must vanish. In other cases, they are related by linear equations, and in still others, the matrix elements of Λ_i' which enter into the secular equation may be shown to vanish. A very interesting elementary treatment of these matters has been given by Teller.[7]

Professor Wigner has kindly read the manuscript of this paper.

[7] E. Teller, Hand- und Jahrbuch d. chemischen Physik 9, 125 (1934).