Constructing A Body_Fixed Reference Frame For A Polyatomic Molecule

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ABSTRACT

An attempt is made to show in a straightforward way how a body-fixed frame may be constructed in classical and hence in quantum mechanics for a polyatomic mole - cule with the aid of which the vibration-rotation be - haviour of the molecule may be described.

INTRODUCTION

More than thirty years ago Ferigle and Weber pub - lished a beautiful and simple account (1) of the way in which coordinate axes could be fixed in a molecule to provide a body-fixed (BF) frame of reference such that rotational and translational motions could be des - cribed as motions of the BF frame and internal motions could be described with respect to the BF frame.

They centred their discussion on the method that Eckart(2) had proposed for constructing a BF frame for "normal molecules".Such molecules would today be called "semi-rigid"molecules (SRMs)but to quote Ferigle and Weber,"a molecule is called normal when there are no gross internal motions and when in the vibrationless state,it behaves like a rigid body (zero point energy not be considered)".They also considered briefly the

work of Sayvetz (3) in the construction of BF frames for
molecules that did exhibit gross internal motions,mole-
cules that would today be called "non-rigid" molecules
(NRMs).They worked entirely in classical mechanics and
did not consider in any detail how the quantum mecha -
nical equivalents of the classical hamiltonian equa -
tions of motion were to be constructed.

Since the appearance of their article there have
been many developments in this field and it seemed app-
ropriate now to attempt to offer an account analogous
to theirs but which took cognizance of some,at least ,
of the more recent development,which used rather more
modern notation and which was rather more explicit
about the passage to the quantum mechanical hamiltonian
from the classical one.

It is hoped that the present account will help as an
introduction to modern theoretical monographs on mole-
cular spectroscopy (such as Bunker 4 and to the more
recent literature.The account does not deal in any de-
tail with nonrigid molecules but it will,it is hoped
serve as an introduction to monographs (such as that
Ezra(5) on this subject too.

1 . Classical relations

If a collection of Coulomb-interacting particles
have cartesian coordinates R= { $R_{f\lambda}$ } with respect to a
lab-fixed (LF) coordinate system,with the conjugate
momenta { $P_{f\lambda}$ } , then the lagrangian and the hamiltonian
form of the total energy of the whole system are

$$E = \tfrac{1}{2} \sum_{f\lambda} m_{\lambda} \dot{R}^2_{f\lambda} + V(R), \qquad 1.1$$

and

$$H = \tfrac{1}{2} \sum_{f\lambda} P^2_{f\lambda}/m_{\lambda} + V(R), \qquad 1.2$$

respectively,where V(R) is the potential energy of the
entire system and consists of all the Coulomb interac-
tions between all pairs of particles.(In this work the
index λ refers to a general particle,and the indices
f,g,h, refer to a general direction of the LF frame
axes.Unit vectors will be denoted $\underset{\sim}{e}_f$ etc.)

Let the transformation equation to a new set of real

Generalized coordinates $q = \{q_\tau\}$ be of the type

$$R_{f\lambda} = R_{f\lambda}(q) \qquad\qquad 1.3$$

then eq. 1 becomes

$$E = \tfrac{1}{2} \sum_{\tau\sigma} g_{\tau\sigma} \dot{q}_\tau \dot{q}_\sigma + V(q), \qquad 1.4$$

where

$$q_{\tau\sigma} = \sum_{f\lambda} m_\lambda (\partial R_{f\lambda}/\partial q_\tau)(\partial R_{f\lambda}/\partial q_\sigma) \qquad 1.5$$

If $\{p_\tau\}$ are the conjugate momenta to the set $\{q_\upsilon\}$ (remembering that $p_\tau = \partial(T-V)\partial q_\tau$ where T is the classical kinetic energy of the system) and $g^{\tau\sigma}$ is the matrix reciprocal to $g_{\tau\sigma}$, then it is easy to show that

$$\dot{q}_\tau = \sum_\gamma g^{\tau\gamma} p_\gamma, \qquad 1.6$$

and thus that the hamiltonian form of 1.4 is

$$H = \tfrac{1}{2} \sum_{\tau\sigma} g^{\tau\sigma} p_\tau p_\sigma + V(q), \qquad 1.7$$

where the explicit form of $g^{\tau\sigma}$ is, by the chain-rule,

$$g^{\tau\sigma} = \sum_{f\lambda} m_\lambda^{-1} (\partial q_\tau/\partial R_{f\lambda})(\partial q_\sigma/\partial R_{f\lambda}). \qquad 1.8$$

In tensor language the quantities $g_{\tau\sigma}$ are the components of a symmetric covariant tensor of rank two called the tranformation metric tensor and the quantities $g^{\tau\sigma}$ are the components of a symmetric contravariant tensor of rank two, the reciprocal tensor of $g_{\tau\sigma}$.

2. Translation to quantum mechanics

The rule of correspondence in quantum mechanics valid for cartesian coordinate systems is simple and given in all elementary texts, so that the operator form of 1.2 is simply the standard form.

$$H = -(\hbar^2/2) \sum_\lambda \nabla_\lambda^2/m_\lambda + V(R), \qquad 2.1$$

and the Schrödinger equation is

$$[-\hbar^2/2)\nabla^2 + V(R)]\psi_R = E\psi_R, \qquad 2.2$$

where $\nabla^2 = \sum_\lambda \nabla_\lambda^2/m_\lambda$ and ψ_R is the wavefunction in R space. The operator form of 1.7 is a bit more difficult to derive, but it is possible to show using tensor algebra [see e.g. [6]], that the laplacian ∇^2 in a generalized coordinate system q is given by

$$\nabla^2 = g^{-\frac{1}{2}} \sum_{\tau\sigma} (\partial/\partial q_\tau) g^{\frac{1}{2}} g^{\tau\sigma}(\partial/\partial q_\sigma), \qquad 2.3$$

where $g = Det|g_{\tau\sigma}| = (Det|g^{\tau\sigma}|)^{-1}$.

If ψ_q is the wavefunction in q-space,then the norma-
lization condition for the two spaces is

$$\int \psi_q^* \psi_q \prod_\tau dq_\tau = \int \psi_R^* \psi_R \prod_{f\lambda} dR_{f\lambda} = \int \psi_R^* \psi_R g^{\frac{1}{2}} \prod_\tau dq_\tau .$$

$$2.4$$

Therefore,we may define

$$\psi_R = g^{-1/4} \psi_q. \qquad\qquad 2.5$$

In some coordinate systems volume element of the
form $\rho_g \prod_\tau dq_\tau$ is found useful,where the weight factor
ρ_q is some function of the coordinates q.In this case
we may define

$$\psi_R = (\rho_q^2/g)^{\frac{1}{2}} \psi_q. \qquad\qquad 2.6$$

Substituting for ∇^2 and ψ_R from 2.3 and 2.4 in
2.2 we arrive at the following expression,originally
derived by podolsky (7) (see also ref.8) for the hamil-
tonian operator corresponding to the classical expres-
sion 1.7 in a generalized coordinate system.

$$H = (-\hbar^2/2)(\rho_q^2/g)^{-1/4} g^{-\frac{1}{2}} \sum_{\tau\sigma} (\partial/\partial q_\tau) g^{\frac{1}{2}} g^{\tau\sigma} (\partial/\partial q_\sigma)(\rho_q^2/g)^{1/4}$$

$$+ V(q). \qquad\qquad 2.7$$

3.Classical Molecular Hamiltonian

In order to separate the translational,rotational,
vibrational and electronic variables as completely as
possible,we may transform the LF cartesian coordinates
of the nuclei and electrons in the molecule to a mo -
ving body-fixed (BF) frame(to be specified later)
through the following steps:

(i)Shift the origin of the LF frame to the molecular
center-of-mass;keeping the axes parallel,in order to
separate the translational variables.

(ii)Shifting the origin from the molecular center-of-
mass to the nuclear center-of-mass,keeping the axes
parallel,in order to separate electronic variables
from the nuclear variables.

(iii) Without shifting the origin,change to the BF
frame in order to separate the nuclear framework rota-
tional variables from the nuclear framework vibra—
tional variables.

If the position of a particle (an electron or a nucleus) is $\underset{\sim}{R}_\lambda$ in the LF frame and $\underset{\sim}{r}_\lambda$ in the BF frame, then the general transformation equation may be formulated as(fig.1):

$$\underset{\sim}{r}_\lambda = \underset{\sim}{R}_\lambda - \underset{\sim}{R} - \underset{\sim}{d} , \qquad 3.1$$

where $\underset{\sim}{R}$ is the position of the molecular center of mass with respect to the LF frame:

$$\underset{\sim}{R} = \sum_\lambda m_\lambda \underset{\sim}{R}_\lambda /M , \qquad 3.2$$

with $M = \sum_\lambda m_\lambda$ the total mass of the molecule. Here $\underset{\sim}{d}$ is a vector from the molecular center-of-mass to the nuclear center-of-mass. In this work the indices i,j refer to the nuclei: S,**t** to the electrons; k,l,m,n, to the vibra - tional variables; and u or v is a general rotational variable. Cartesian components are written as α , β γ corresponding to x,y,z and unit vectors as $\underset{\sim}{\varepsilon}_\alpha$ etc.

Since the origin of the BF frame is at the nuclear center of mass,

$$\sum_j m_j \underset{\sim}{r}_j = \underset{\sim}{0}, \qquad 3.3$$

therefore,

$$\underset{\sim}{d} = -m/M \sum_S \underset{\sim}{r}_S , \qquad 3.4$$

where m is the electronic mass. It also follows that

$$\sum_\lambda m_\lambda (\underset{\sim}{r}_\lambda + \underset{\sim}{d}) = \underset{\sim}{0}. \qquad 3.5$$

If $C_{g\gamma} = \underset{\sim}{e}_g \cdot \underset{\sim}{\varepsilon}_\gamma$ is the direction cosine matrix which determines the orientation of the BF frame axes with respect to the LF frame axes, then 3.1 can be written as

$$R_{g\lambda} = R_g + \sum_\alpha C_{g\alpha} (r_{\alpha\lambda} + d_\alpha). \qquad 3.6$$

The time derivative of 3.6 can be written as

$$\dot{R}_{g\lambda} = \dot{R}_g + \sum_\alpha (\dot{C}_{g\alpha} (r_{\alpha\lambda} + d_\alpha) + C_{g\alpha} (\dot{r}_{\alpha\lambda} + \dot{d}_\alpha)). \quad 3.7$$

To make a relationship between $C_{g\alpha}$ and the time deri - vative of the rotational variables u, we use a mathe- matical trick as follows. Since $\underset{\sim}{C}$ is an orthogonal matrix, then $C^T (\partial \underset{\sim}{C}/\partial u)$ is a skew-symmetric matrix and can be written in terms of skew-symmetric matrices $e_{\alpha\beta\gamma} = (\underset{\sim}{e}_\alpha)_{\beta\gamma}$ as follows

$$(\underset{\sim}{C}^T \partial \underset{\sim}{C}/\partial u)_{\beta\gamma} = \sum_\alpha X_{u\alpha} (\underset{\sim}{e}_\alpha)_{\beta\gamma} \qquad \text{or}$$

$$\partial C_{g\gamma}/\partial u = \sum_{\alpha\beta} X_{u\alpha} C_{g\beta} (e_{\alpha})_{\beta\gamma} . \qquad 3.8$$

where the $X_{u\alpha}$ are some coefficients (the form of mat-
rices $(e_{\alpha})_{\beta\gamma}$ and $(X^{-1})_{\alpha u}$ are given in Appendix I).
Therefore

$$\dot{C}_{g\gamma} = \sum_{u} (\partial C_{g\gamma}/\partial u)\dot{u}$$

$$= \sum_{\alpha\beta u} e_{\alpha\beta\gamma} X_{u\alpha} C_{g\beta} \dot{u} . \qquad 3.9$$

It is convenient when considering polyatomic mole-
cules to construct the direction cosine matrix $\underset{\sim}{C}$ as a
function of the rotational variables alone and to in-
troduce 3N-6 generalised variables q_k to describe the
internal motions of the nuclei. With this choice the
time derivatives of the nuclear variable in the BF
frame become.

$$\dot{r}_{\alpha i} = \sum_{k} (\partial r_{\alpha i}/\partial q_k)\dot{q}_k . \qquad 3.10$$

Clearly such choices are not possible for diatomic
molecules (N=2) and such molecules are thus excluded
from further consideration here.

The Lagrangian form of kinetic energy of the system
is from 1.1 ,given by,

$$2T = \sum_{g\lambda} m_\lambda \dot{R}_{g\lambda}^{.2} . \qquad 3.11$$

Substituting for $\dot{R}_g$ from 3.7 ,followed by insertion
of 3.9 and 3.10 and using the 3n variables $r_{\alpha t}$ to
describe the n electrons,gives the matrix expression:

$$2T = (\underset{\sim\sim\sim\sim}{Ruqr}) \begin{pmatrix} \underset{\sim}{M} & \underset{\sim}{O} & \underset{\sim}{O} & \underset{\sim}{O} \\ \underset{\sim}{O} & \underset{\sim}{X}(\underset{\sim}{I}+\underset{\sim}{W})\underset{\sim}{X}^T & -(\underset{\sim\sim}{XZ}) & -(\underset{\sim\sim}{XY}) \\ - & - & - & - \\ \underset{\sim}{O} & -(\underset{\sim\sim}{XZ})^T & \underset{\sim}{G}^{-1} & \underset{\sim}{O} \\ \underset{\sim}{O} & -(\underset{\sim\sim}{XY})^T & \underset{\sim}{O} & \underset{\sim}{D}^{-1} \end{pmatrix} \begin{pmatrix} \dot{\underset{\sim}{R}} \\ \dot{\underset{\sim}{u}} \\ \dot{\underset{\sim}{q}} \\ \dot{\underset{\sim}{r}} \end{pmatrix}$$

$$3.12$$

The matrix in 3.12 is the tensor $g_{\tau\sigma}$ expressed in mat-
rix form and its sub-matrices are defined as follows:

$$Z_{\alpha k} = \sum_{i} m_i \sum_{\beta\gamma} e_{\alpha\beta\gamma} r_{\beta i} \partial r_{\gamma i}/\partial q_k . \qquad 3.13$$

$$G^{-1}_{k\ell} = \sum_{\alpha i} m_i (\partial r_{\alpha i} \partial q_k)(\partial r_{\alpha i}/\partial q_\ell) . \qquad 3.14$$

$$I_{\alpha\beta} = \sum_{\gamma\delta\epsilon} e_{\alpha\gamma\epsilon} e_{\beta\delta\epsilon} \sum_{i} m_i r_{\gamma i} r_{\delta i} . \qquad 3.15$$

$$D^{-1}_{\gamma s,\delta t} = (-m^2/M + m\delta_{st})\delta_{\gamma\delta} . \qquad 3.16$$

$$Y_{\alpha,\delta t} = \sum_{\gamma s} D^{-1}_{\gamma s,\delta t} \sum_{\eta} e_{\alpha\eta\gamma} r_{\gamma s} . \qquad 3.17$$

$$W_{\alpha\beta} = \sum_{\gamma s,\delta t} D^{-1}_{\gamma s,\delta t} \sum_{\eta} e_{\alpha\eta\gamma} r_{\eta s} \sum_{\xi} e_{\beta\xi\delta} r_{\xi t} . \qquad 3.18$$

A little algebra shows that

$$\underset{\sim}{W} = \underset{\sim}{Y}\underset{\sim}{D}\underset{\sim}{Y}^T , \qquad 3.19$$

with

$$D_{\gamma s,\delta t} = (m^{-1}\delta_{st} + m_N^{-1})\delta_{\gamma\delta} , \qquad 3.20$$

where m_N is total mass of the nuclei.

To bring the kinetic energy expression 3.12 to hamiltonian form it is necessary (see 1.6) to invert the transformation matrix to obtain the matrix repre — sentative of $g^{\tau\sigma}$ .To do this the partioning method which is described in the Appendix II is used.The result is:

$$2T=(\underset{\sim}{p}^R \underset{\sim}{p}^u \underset{\sim}{p}^q \underset{\sim}{p}^r) \begin{bmatrix} \underset{\sim}{M}^{-1} & \underset{\sim}{0} & \underset{\sim}{0} & \underset{\sim}{0} \\ \underset{\sim}{0} & \underset{\sim}{X}^{-T}\underset{\sim}{\mu}\underset{\sim}{X}^{-1} & \underset{\sim}{X}^{-T}\underset{\sim}{\mu}(\underset{\sim}{Z}\underset{\sim}{G}) & \underset{\sim}{X}^{-T}\underset{\sim}{\mu}(\underset{\sim}{Y}\underset{\sim}{D}) \\ \underset{\sim}{0} & (\underset{\sim}{Z}\underset{\sim}{G})^T\underset{\sim}{\mu}\underset{\sim}{X}^{-1} & \underset{\sim}{G}+(\underset{\sim}{Z}\underset{\sim}{G})^T\underset{\sim}{\mu}(\underset{\sim}{Z}\underset{\sim}{G}) & (\underset{\sim}{Z}\underset{\sim}{G})^T\underset{\sim}{\mu}(\underset{\sim}{Y}\underset{\sim}{D}) \\ \underset{\sim}{0} & (\underset{\sim}{Y}\underset{\sim}{D})^T\underset{\sim}{\mu}\underset{\sim}{X}^{-1} & (\underset{\sim}{Y}\underset{\sim}{D})^T\underset{\sim}{\mu}(\underset{\sim}{Z}\underset{\sim}{G}) & \underset{\sim}{D}+(\underset{\sim}{Y}\underset{\sim}{D})^T\underset{\sim}{\mu}(\underset{\sim}{Y}\underset{\sim}{D}) \end{bmatrix} \begin{bmatrix} \underset{\sim}{p}^R \\ \underset{\sim}{p}^u \\ \underset{\sim}{p}^q \\ \underset{\sim}{p}^r \end{bmatrix}$$
$$3.21$$

in which $\underset{\sim}{p}^R,\underset{\sim}{p}^u,\underset{\sim}{p}^q,\underset{\sim}{p}^r$ are the conjugate momenta corres- ponding to the generalized velocities $\dot{\underset{\sim}{R}},\dot{\underset{\sim}{u}},\dot{\underset{\sim}{q}}$ and $\dot{\underset{\sim}{r}}$ res - pectively and the matrix $\underset{\sim}{\mu}$ is defined as:

$$\underset{\sim}{\mu}^{-1} = \underset{\sim}{I} - \underset{\sim}{Z}\underset{\sim}{G}\underset{\sim}{Z}^T , \qquad 3.22$$

and the matrix $\underset{\sim}{G}$ is the matrix inverse to $\underset{\sim}{G}^{-1}$ in 3.14

The total angular momentum for a system of parti - cles with respect to the origin of the LF frame is de- fined by

$$J_f = \sum_{\lambda} m_{\lambda} \sum_{gh} e_{fgh} R_{g\lambda} \dot{R}_h . \qquad 2.23$$

In order to express 3.24 in terms of the molecular coordinates,we substitute for $R_{g\lambda}$ from 3.6 and for $\dot{R}_h$ from 3.7 which after making use of 3.9 and 3. 10 and 3.13 - 3.18 by straightforward algebra, we obtain

$$J_f = |\underset{\sim}{C}| (\sum_{gh} e_{fgh} R_g \dot{R}_h + \sum_{\alpha} C_{f\alpha} (-(\underset{\sim}{I}+\underset{\sim}{W})^T \underset{\sim}{X}^T \dot{\underset{\sim}{u}} + \underset{\sim}{Z}\dot{\underset{\sim}{q}} + \underset{\sim}{Y}\dot{\underset{\sim}{r}})_{\alpha} \qquad 3.24$$

where the factor $|\underset{\sim}{C}|$ (+1 or-1) arises because angular momentum is an axial or pseudo-vector.

The first term in 3.24 is the angular momentum of
the center-of-mass of the molecule with respect to the
origin of the LF frame,and the second term is the total
angular momentum of the molecule about the center of
mass.We shall continue to use the notation J for the
components of the angular momentum about the center-of
-mass:

$$J_f = |\underset{\sim}{C}| \sum_\alpha C_{f\alpha} (-(\underset{\sim}{I}+\underset{\sim}{W})^T \underset{\sim}{X}^T \dot{\underset{\sim}{u}} + \underset{\sim}{Z}\dot{\underset{\sim}{q}} + \underset{\sim}{Y}\dot{\underset{\sim}{r}})_\alpha . \qquad 3.25$$

If the J_f are projected along the BF frame axes, the
column matrix of components $\underset{\sim}{J}$ is then

$$\underset{\sim}{J} = -(\underset{\sim}{I} + \underset{\sim}{W})^T \underset{\sim}{X}^T \dot{\underset{\sim}{u}} + \underset{\sim}{Z}\dot{\underset{\sim}{q}} + \underset{\sim}{Y}\dot{\underset{\sim}{r}} \qquad 3.26$$

From 1.6 the velocities may be written in terms of
the momenta with the aid of the transformation matrix
in 3.21 and after a little algebra it follows that

$$\underset{\sim}{J} = -\underset{\sim}{X}\underset{\sim}{p}^u . \qquad 3.27$$

Thus the total angular momentum is carried by the mo -
tion of the BF frame and does not involve the q_k or
the $r_{\alpha s}$.

   At this stage it is possible to write down a formal
expression for the Hamiltonian in either classical form
1.7 or quantum mechanical form 2.3 or 2.7 .Such an
expression would however be of the little value without
explicit expression for the molecular variables and it is
such expressions that are considered in the next section.

4.Vibrational variables
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   So far the molecular variables have not been spe -
cified in detail but it has been assumed that there
exist 3N-6 vibrational variables,q_k,that can be written
in terms of the 3N cartesian variables,$r_{\alpha i}$ of the BF
frame.

$$q_k = q_k(\underset{\sim}{r}_1, \underset{\sim}{r}_2 \cdots \underset{\sim}{r}_N) . \qquad 4.1$$

This implies that the $r_{\alpha i}$ cannot all be independent
variables but that there must be six relations among
them corresponding to the translational and rotational
invariance requirements.

   The three relations that correspond to the require-
ment of translational invariance follow at once from
3.3 .They effectively define the centre mass variable

and are

$$O = \sum_i m_i r_{\alpha i}, \quad \alpha = X, y \text{ or } Z. \qquad 4.2$$

The three relations that correspond to the require -
ments of rotational invariance can be written generally
as

$$f_m(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \ldots \underset{\sim}{r}_N) = O, \quad m = 1, 2, 3. \qquad 4.3$$

where the functional form of the f_m can be chosen in
many different ways. From 3.6 it is easily seen that
the three relations 4.3 effectively determine the
elements of the direction cosine matrix $\underset{\sim}{C}$ as functions
of $(R_{g\lambda} - R_g)$ and hence that they determine the rota -
tional variables, u, of the problem (which are often ta-
ken to be three Euler angles). It is not however usu -
ally necessary to obtain explicit expressions for the
rotational variables since, as will be seen, it is po -
ssible to express the hamiltonian in terms involving
only the components of angular momentum whose properties
are well known, and to avoid explicit reference to the
angular variables themselves. Nevertheless the choice
of constraints 4.3 is a matter of some delicacy since
it must be made with a view to the explicit inversion
4.1 to give.

$$r_{\alpha i} = r_{\alpha i} (q_1, q_2, \ldots, q_{3N-6}), \quad \begin{array}{l} \alpha = X, y, z \\ i = 1, 2, \ldots, N, \end{array} \qquad 4.4$$

if the hamiltonian is actually to be expressed in terms
of the q_k. The issues involved are probably best ex -
plained by giving and account of the way in which Eckart(2)
first successfully solved the problem (see also 9,10).

Eckart supposed that for most ordinary molecules it
was possible to find a BF frame in which the nuclei had
equilibrium positions r_i^o about which their motions
were localized. These positions defined a molecular
framework or geometry about which the actual nuclear
positions could be represented in terms of displace -
ment coordinates, $\rho_{\alpha i} = r_{\alpha i} - r_{\alpha i}^o$, such that the q_k could be
written as

$$q_k = \sum_{\alpha i} B_{k\alpha i} \rho_{\alpha i} \equiv \sum_i \underset{\sim}{s}_{ki} \underset{\sim}{\rho}_i \qquad 4.5$$

where the $B_{k,\alpha i}$ (the components of the vector $\underset{\sim}{s}_{k,i}$) were

constants.Eckart then expressed the three rotational constraints by means of the equation

$$o = \sum_i m_i (r^o_{\sim i} \times r_{\sim i})_\alpha \quad , \quad \alpha = x,y,z \qquad 4.6$$

These relations are easily seen to correspond to the requirement that the nuclei,when at their equili - brium positions,have no angular motion with respect to the BF frame. Because the $r_{\alpha i}$ satisfy 4.2 and,by de - finition, 4.6 it is possible to rewrite equations 4. 2 , 4.6 and 4.5 in matrix form as

$$\begin{pmatrix} O \\ \sim \\ O \\ \sim \\ q \\ \sim \end{pmatrix} = \begin{pmatrix} B^1 \\ -\sim- \\ B^2 \\ -\sim- \\ B \\ \sim \end{pmatrix} \rho = \bar{B}\rho \qquad 4.7$$

with

$$B^1_{\alpha \beta i} = \delta_{\alpha \beta} m_i$$

$$B^2_{\alpha \beta i} = \sum_\gamma \epsilon_{\alpha \beta \gamma} r^o_{\gamma i} m_i, \qquad 4.8$$

and the elements of $\underset{\sim}{B}$ as given by 4.5 .

If the matrix $\underset{\sim}{B}$ in 4.7 is non-singular then its inverse gives the required explicit form for the $r_{\alpha i}$ in terms of the q_k alone.

The explicit inversion of $\bar{B}$ is not a trivial matter but it may be shown that an inverse exists if the 3N-6 rows of B are linearly independent and if the elements of B satisfy the relations,

$$\sum_i s_{\sim ki} = o_{\sim} \quad , \quad \sum_i r^o_{\sim i} \times s_{\sim ki} = o_{\sim} \quad , \text{ all } k, \qquad 4.9$$

where the alternative notation for the elements of $\underset{\sim}{B}$ given in 4.5 has been used.It was first shown by Wil- son that it was possible to find prescriptions for choosing sets of S_{ki} that satisfy the above require - ments and which yield physically significant internal coordinates.Rules for choosing such S_{ki} are given at some length in Wilson,Decius and Cross (11).If such a set is chosen then it may be shown that

$$o_{\alpha i} = \sum_k A_{\alpha i,k} q_k,$$

$$A_{\sim} = m^{-1}_{\sim} B^T_{\sim} (B m^{-1}_{\sim} B^T_{\sim})^{-1} \qquad 4.10$$

where m is a diagonal matrix of the nuclear masses.

The internal coordinates as defined by 4.5 must seem to a chemist or physicist somewhat artificial.The natural internal coordinates in which to describe a molecule are surely felt to be the bond lengths and bond angles,or displacements from the equilibrium values of these quantities.But if such quantities had been used to define a set of internal coordinates then the relationship between the q_k and the $r_{\alpha i}$ would have been a non-linear one so that explicit inversion of the equation would have been at best very difficult and at worst impossible,while maintaining the conditions 4.6 Of course in principle it is possible to choose another set of conditions to replaco 4.6 and which allow for explicit inversion but in practice this is very diffi- cult to do except in certain special cases.It is also the case that the conditions 4.6 lead to a particular- ly simple and physically appealing form of the hamil - tonian,as will be seen,so that it is desirable to keep the form.

It should perhaps be noticed at this point that if the chosen equilibrium geometry is linear then equation 4.6 supplies only one constraint while if the geometry is planar it supplies only two constraints.In both these cases,therefore,the definition of constraints fails and special steps have to be taken to supply the extra cons trains. It is not necessary to consider these in more detail here (but see refs.12,13)and it is enough to say that what follows in respect of the Eckart hamiltonian does not apply to linear systems at all but it does apply to planar systems if it is understood that the onе (BF) axis is perpendicular to the molecular plane and the three (BF) axes constitute a right-handed set.

It is of course possible to express any interal coordinate (such as a bond-length) as a power series in the displacement coordinates,or indeed as a power series in a chosen set of q_k.Thus for example a general interal coordinate $\mathcal{q}_k$ may be written as

$$\mathcal{R}_k = \sum_{\alpha i} B_{k\alpha i}\, \rho_{\alpha i} + \tfrac{1}{2} \sum_{\alpha i \beta j} B^{\alpha i \beta j} \rho_{\alpha i} \rho_{\beta j} + \dots \qquad 4.11$$

where the coefficients are the first, second and so on derivatives of $\mathcal{R}_k$ with respect to the $\rho_{\alpha i}$ evaluated at $\rho_{\alpha i} = 0$. By taking 4.11 to any chosen order, explicit expressions can be obtained for the $\mathcal{R}_k$ and for the inverse expression to that order, so that it is possible to use arbitrary internal coordinates to whatever accuracy is desired and this has been the subject of much recent interest (14).

In this context the linear internal coordinates defined by Eckart may be regarded as approximations for small displacements of the nuclei. The Eckart form of the hamiltonian is thus often considered to describe only vibrational motions of infinitesimal amplitude but this is not a correct view. Precisely the same physical occurrences are described by the hamiltonian whether expressed in terms of the q_k or the $\mathcal{R}_k$. Which set is chosen is a matter for judgement in any particular problem. Thus Hoy Mills and Strey (15) make out a convincing argument for choosing a particular set of curvi - linear coordinates, $\mathcal{R}_k$, because they offer advantages in the construction of a force-field (see later) that is transferable from one isotopic form of a molecule to another.

Whatever form of coordinates are chosen however it is easily seen that the Eckart form of the hamiltonian breaks down if the amplitude of the vibration is so large as to make the constraints 4.6 incapable of satisfaction and hence the direction cosine matrix undefined. Thus the hamiltonian of Eckart is not a satisfactory hamiltonian for describing large amplitude internal motions (such as internal rotation) in a molecule and both the constraint conditions and the definition of internal coordinates must be modified to construct a hamiltonian which allows for such motions. Such modification was first attempted by Sayvetz (3) shortly after the initial work of Eckart but this work will not be

considered further here.

To return now to the form of the Eckart Hamiltonian
for "normal"mollcules.It is easily seen on using 4.10
to evaluate 3.14 that

$$\underset{\sim}{G}^{-1} = (\underset{\sim}{B}\ \underset{\sim}{m}^{-1}\ \underset{\sim}{B}^T)^{-1} \qquad\qquad 4.12$$

so that

$$G_{k\ell} = (\underset{\sim}{B}\ \underset{\sim}{m}^{-1}.\underset{\sim}{B}^T)_{k\ell} \equiv \sum_i\ m_i^{-1}\underset{\sim}{s}_{k,i}.\underset{\sim}{s}_{\ell,i} \qquad 4.13$$

G is thus the familiar Wilson G-matrix,which expre-
sses a portion of the internal kinetic energy of the
molecule in the bi-linear form $\sum_k\ G_{k\ell}p_k^q p_\ell^q$.Clearly it
would be advantageous in terms of manipulation to make
this bilinear form diagonal and this is indeed possible
for it is seen from 4.9 that a linear combination
(over i) of the s_{ki} that satisfy 4.9 also satisfies
4.9 .It is,therefore,possible to define a new set of
internal coorrinates Q_k (which may be thought of as a
linear combination of the q_k),

$$Q_k = \underset{\alpha i}{\sum}\ m_i^{\frac{1}{2}}l_{\alpha ik}\rho_{\alpha i}, \qquad\qquad 4.14$$

such that

$$\underset{\alpha i}{\sum}\ l_{\alpha ik}l_{\alpha i\ell} = \delta_{k\ell}. \qquad\qquad 4.15$$

With this choice it is seen that the elements of
$m_i^{\frac{1}{2}}l_{\alpha ik}$ define the Q_k in the same way that the elements
$B_{k\alpha i}$ define the q_k and so on making the appropriate
correspondences in 4.13 it follows that G becomes a
(3N-6) by (3N-6) unit matrix and from 4.10 that

$$\rho_{\alpha i} = m_i^{-\frac{1}{2}}\underset{k}{\sum}\ l_{\alpha ik}Q_k. \qquad\qquad 4.16$$

A particular case of the orthogonal coordinates intro-
duced above are the normal coordinates for the problem.
These coordinates are appropriate when the potential
energy of the molecule ·can be' well represented by the
power series expansion about the equilibrium geometry.

$$V(\underset{\sim}{\rho}) = V(\underset{\sim}{0}) + \tfrac{1}{2}\underset{\alpha i,\ \beta j}{\sum}\ V_{\alpha i\beta j}^{(2)}\rho_{\alpha i}\rho_{\beta j}. \qquad 4.17$$

The constant term in 4.17 may be treated as the origin
of vibrational energy and the linear term in the expan-
sion is absent because the first derivatives of V eval-

uated at the equilibrium geometry vanish.Substituting
4.16 into 4.17 yields

$$V(\underset{\sim}{Q}) = V(\underset{\sim}{O}) + \tfrac{1}{2} \underset{\sim}{Q}^T F \underset{\sim}{Q}, \qquad\qquad 4.18$$

where $\underset{\sim}{Q}$ is a column matrix of the Q_k and

$$F_{k\ell} = \sum_{\substack{\alpha i \\ \beta j}} m_i^{-\frac{1}{2}} m_j^{-\frac{1}{2}} l_{\alpha i k} V_{\alpha i \beta j}^{(2)} l_{\beta j \ell}. \qquad 4.19$$

$\underset{\sim}{F}$ is clearly a constant symmetric matrix that can be
diagonalized by means of an orthogonal transformation
$\underset{\sim}{U}$ such that

$$\underset{\sim}{U}^T \underset{\sim}{F} \underset{\sim}{U} = \underset{\sim}{f}, \quad \underset{\sim}{U}^T \underset{\sim}{U} = \underset{\sim}{E}_{3N-6} \qquad\qquad 4.20$$

where $\underset{\sim}{f}$ is a diagonal matrix.Introducing the coordi
nates

$$\bar{\underset{\sim}{Q}} = \underset{\sim}{U}^T \underset{\sim}{Q}, \qquad\qquad 4.21$$

enables (4.18) to be written in the form

$$V(\bar{\underset{\sim}{Q}}) = V(\bar{\underset{\sim}{O}}) + \tfrac{1}{2} \bar{\underset{\sim}{Q}}^T \underset{\sim}{f} \bar{\underset{\sim}{Q}}. \qquad\qquad 4.22$$

Substituting 4.14 into 4.21 gives an expression
for the $\bar{Q}_k$ in terms of the $\rho_{\alpha i}$ with the coefficients
playing the part of the $B_{k\alpha i}$ for the new coordinates.
If the resulting $\underset{\sim}{B}$ matrix is used in 4.13 it is easi-
ly seen that $\underset{\sim}{G}$ remains a unit matrix.Thus is the new
coordinates $\bar{Q}_k$ that diagonalize both $\underset{\sim}{F}$ and $\underset{\sim}{G}$ are the
required normal coordinates.

In practice it is usual to obtain expressions for $\underset{\sim}{G}$
and for $\underset{\sim}{F}$ in terms of the non-orthogonal coordinates q_k
and then to construct directly a transformation that
diagonalizes both $\underset{\sim}{G}$ and $\underset{\sim}{F}$ in this basis,hence obtain -
ing the normal coordinates in terms of the q_k and thus
in terms of the $\rho_{\alpha i}$ using 4.5 This is the celebrated
Wilson FG matrix method described in detail in the text
of Wilson,Decius and Cross (11).

The matrix $\underset{\sim}{F}$ is often called the <u>force constant</u> mat-
rix and is said to represent the molecular force-field
in the quadratic or harmonic approximation.The term
harmonic approximation is used because,as will be seen,
in first approximation the vibrational part of the Ec-
kart hamiltonian,when expressed in normal coordinates,
simply becomes a sum of harmonic-oscillator like hamil-

tonians.

5. The complete classical hamiltonian in the Eckart formulation

If it is supposed that a set of orthogonal internal coordinates (perhaps normal coordinates) has been found for a problem so that the $l_{\alpha i k}$ in 4.12 and 4.15 are actually known, it is now easy to show 3.13 becomes

$$z_{\alpha k} = \sum_{\ell} \xi^{\alpha}_{\ell k} Q_{\ell} , \qquad\qquad 5.1$$

with

$$\xi^{\alpha}_{\ell k} = \sum_{i} (\underline{l}_{ik} \times \underline{l}_{i\ell})_{\alpha} . \qquad\qquad 5.2$$

where the constants $\xi^{\alpha}_{\ell k}$ are usually called the Coriolis coupling constants. Using this form 5.1 in 3:22 it follows after some algebra that

$$(\underset{\sim}{\mu}^{-1})_{\alpha\beta} = I_{\alpha\beta} - \sum_{k\ell m} \xi^{\alpha}_{km} \xi^{\beta}_{\ell m} Q_{k} Q_{\ell} . , \qquad 5.3$$

where $I_{\alpha\beta}$ is an element of the usual instantaneous inertia tensor as defined by 3.15 , expressed in terms of the Q_{k}. It is possible to show after some further algebra (see eg.ref.9) that $\underset{\sim}{\mu}$ may be written explicitly as

$$\underset{\sim}{\mu} = (\underset{\sim}{I}")^{-1} \underset{\sim}{I}^{O} (\underset{\sim}{I}")^{-1}, \qquad\qquad 5.4$$

where $\underset{\sim}{I}^{O}$ is the equilibrium geometry inertia tensor and where

$$I"_{\alpha\beta} = I^{O}_{\alpha\beta} + \tfrac{1}{2} \sum_{k} a^{\alpha\beta}_{k} Q_{k} , \qquad\qquad 5.5$$

with

$$a^{\alpha\beta}_{k} = 2 \sum_{\gamma\delta\epsilon} e_{\alpha\gamma\epsilon} e_{\beta\delta\epsilon} \sum_{i} m_{i}^{\frac{1}{2}} r^{O}_{\gamma i} l_{\delta i k}. \qquad 5.6$$

Remembering that $\underset{\sim}{D}$ is given by 3.20 and that $\underset{\sim}{G}$ is a unit matrix, we now have explicit expressions for all the sub-matrices in the transformation matrix 3.21 , with the exception of the matrix $\underset{\sim}{X}$. This last matrix, as is seen from its definition 3.8 , depends only on the angular variables and from 3.27 it is seen simply to define the angular momentum of the problem. Thus if the hamiltonian is expressed in terms of the problem. Thus if the hamiltonian is expressed in terms of the angular momentum components, whose properties are anyway known,

explicit reference to the angular variables in the hamiltonian may be avoided.

In order to express the hamiltonian now derivable from 1.7 , 3.21 and the above explicit forms it is convenient to define the variables.

$$G_\alpha = \sum_{k\ell} \xi^\alpha_{k\ell} Q_k p^Q_\ell , \qquad\qquad 5.7$$

and

$$L_\alpha = \sum_{s\eta\gamma} e_{\alpha\eta\gamma} r_{\eta s} p^r_{\gamma s}. \qquad\qquad 5.8$$

The hamiltonian now follows on making the appropriate substitutions and is (ignoring the center-of-mass term):

$$H = \tfrac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta}(J_\alpha - G_\alpha - L_\alpha)(J_\beta - G_\beta - L_\beta) + \tfrac{1}{2} \sum_k (p^Q_k)^2 + \tfrac{1}{2}$$

$$\sum_{\alpha s, \beta t} (m^{-1}\delta_{st} + m^{-1}_N)\delta_{\alpha\beta} p^r_{\alpha s} p^r_{\beta t} + V(r,Q) \qquad 5.9$$

and the determinant g, (see 2.3 is just (ignoring constant factors)

$$|\underset{\sim}{X}|^2 |\underset{\sim}{\mu}|^{-1} \qquad\qquad 5.10$$

6. The quantum mechanical hamiltonian in the Eckart formulation

Although, in principle, it is a straightforward matter to use 2.7 to form the quantum mechanical hamiltonian the actua algebra involved is, in fact, extremely complicated. It was shown by ref.9 that the most compact form and the form most like the classical form 5.9 could be obtained by choosing ρ_q 2.6 to be $|\underset{\sim}{X}|$ and intro - ducing operators analagous to 5.8 and 5.9 .

$$\hat{G}_\alpha = \hbar/i \sum_{k\ell} \xi^\alpha_{k\ell} Q_k \, \partial/\partial Q_\ell \qquad\qquad 6.1$$

$$\hat{L}_\alpha = \hbar/i \sum_{s\eta\gamma} e_{\alpha\eta\gamma} r_{\eta s} \, \partial/\partial r_{\gamma s} \qquad\qquad 6.2$$

and by observing that both these operators commute with $\mu_{\alpha\beta}$ for any choice of β.

With these choices the quantum mechanical form of 5.9 is

$$\hat{H} = \tfrac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta}(\hat{J}_\alpha - \hat{G}_\alpha - \hat{L}_\alpha)(\hat{J}_\beta - \hat{G}_\beta - \hat{L}_\beta) - \hbar^2/2 \sum_k \partial^2/\partial Q^2_K$$

$$- \hbar^2/2m \sum_s \nabla_s^2 - \hbar^2/2m_N \sum_{s,t} \nabla_s \cdot \nabla_t + \hat{U}(Q) + \hat{v}(r,Q)$$

6.3

where

$$\hat{U}(Q) = - \hbar^2/8 \sum_\alpha \mu_{\alpha\alpha}$$

6.4

The term $\hat{U}(Q)$ (often called the Watson term) arises from
the reduction of the kinetic energy expression although
its form is that of an addition to the potential energy.

From 2.4 it is easily seen that the correct form
of the normalization integral for solutions $\psi(r,Q,u)$ of
6.3 is just

$$\int |\psi(r,Q,u)|^2 (|X| \prod_u du)(\prod_{\alpha s} dr_{\alpha s})(\prod_k dQ_k)$$

6.5

In fact the integral over the angular variables in 6.5
can always be done explicitly. This is because the eigen-
functions, $|Jk\rangle$ of the quantum mechanical angular mo-
mentum operator, form a complete set so that the ge -
neral solution must be writable as

$$\psi(r,Q,u) = \sum_{k=-J}^{+J} C_k \psi_{Jk}(r,Q) |Jk\rangle \, ,$$

6.6

and

$$\int J'k'\rangle^+ |Jk\rangle |X| \prod_u du = \delta_{J'J} \delta_{k'k}.$$

6.7

In fact some care must be taken with the angular mo-
mentum operators in 6.3 for it can be shown by choo -
sing an explicit set of angular variables and constru-
cting X in terms of them, that the components, J_α, of the
quantum mechanical operator defined by putting 3.27
in operator form, do not obey the standard commutation
relations but rather the anomalous ones.

$$\left[\hat{J}_\alpha, \hat{J}_\beta\right] = -i\hbar \sum_\gamma e_{\alpha\beta\gamma} \hat{J}_\gamma \, .$$

6.8

which differ in the sign of the right hand side from the
standard ones. This difficulty can easily be circumven-
ted however by defining the operators $K_\alpha = -J_\alpha$, which do
obey the standard commutation relations and in terms of
the operators the first term in 6.3 becomes:

$$\tfrac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta}(\hat{K}_\alpha + \hat{G}_\alpha + \hat{L}_\alpha)(\hat{K}_\beta + \hat{G}_\beta + \hat{L}_\beta).$$

6.9

However it is the form involving the $\hat{J}_\alpha$ operators which
is the usual one in the literature.

In attempting solution of the quantum mechanical
problem specified by the hamiltonian 6.3 it is usual
to make the Born-Oppenheimer approximation and to
assume that the total wavefunction for the problem may
be written as product of an electronic and a nuclear
motion part.Calculating the expectation value of the
hamiltonian with respect to the electronic motions only
and neglecting certain terms,leads to a hamiltonian for
nuclear motion of the form

$$\hat{H} = \tfrac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} (\hat{J}_\alpha - \hat{G}_\alpha)(\hat{J}_\beta - \hat{G}_\beta)$$
$$-\hbar^2/2 \sum_k \partial^2/\partial Q_k^2 + \hat{U}(\underset{\sim}{Q}) + \hat{E}(\underset{\sim}{Q}), \qquad 6.10$$

where $\hat{E}(\underset{\sim}{Q})$ is the potential formed by integrating out
the electronic variables.It is easily seen that this
potential is,to a first approximation,the sum of the
electronic energy and the nuclear repulsion energy at
any set of nuclear positions and for the Eckart axis
choice to be useful it must have a deep minimum at $\underset{\sim}{Q}=0$.

7. Expansion of the tensor $\underset{\sim}{\mu}$ and the vibrational poten-
   tial energy

If the vibrational amplitudes are small compared to
the inter-nuclear distances,expansion of the tensor $\underset{\sim}{\mu}$
and of the vibrational potential energy V as a Taylor
series in the normal coordinates usually converges ra-
pidly justifying the use of higher order terms in hamil-
tonian expansion as perturbations.

The Taylor expansion of the tensor $\underset{\sim}{\mu}$ can be written
as

$$\underset{\sim}{\mu} = \underset{\sim}{\mu}^0 + \sum_k (\partial\underset{\sim}{\mu}/\partial Q_k)Q_k + \tfrac{1}{2} \sum_{kl} \partial^2\underset{\sim}{\mu}/\partial Q_k \partial Q_l)Q_k Q_l +\cdots \qquad 7.1$$

where $\underset{\sim}{\mu}^0 = (\underset{\sim}{I}^0)^{-1}$ is the inverse of the moment of inertia
matrix for the nuclear framework in its equilibrium
configuration.Using 5.4 , 5.5 and the rule for differen-
tiation of an inverse matrix

$$d/dt \underset{\sim}{A}^{-1}(t) = -\underset{\sim}{A}^{-1}(t)(d/dt \underset{\sim}{A}(t))\underset{\sim}{A}^{-1}, \qquad 7.2$$

we can easily obtain:

$$\underset{\sim}{\mu} = \underset{\sim}{\mu}^{o} - \sum_{k} (\underset{\sim}{\mu}^{o} \underset{\sim}{a}_{k} \underset{\sim}{\mu}^{o}) Q_{K} + 3/4 \sum_{kl} (\underset{\sim}{\mu}^{o} \underset{\sim}{a}_{k} \underset{\sim}{\mu}^{o} \underset{\sim}{a}_{l} \underset{\sim}{\mu}^{o}) Q_{k} Q_{l} + \cdots$$

7.3

If the equilibrium configuration is referred to the principal-axis system, that is $I_{\alpha\beta}^{o} = I_{\alpha\alpha}^{o} \delta_{\alpha\beta}$, then   7.3 can be written as

$$\mu_{\alpha\beta} = \mu_{\alpha\alpha}^{o} \delta_{\alpha\beta} - \sum_{k} (u_{\alpha\alpha}^{o} a_{k}^{\alpha\beta} \mu_{\beta\beta}) Q_{k}$$

$$+ 3/4 \sum_{kl\delta} (\mu_{\alpha\alpha}^{o} a_{k}^{\alpha\delta} \mu_{\delta\delta}^{o} a_{l}^{\delta\beta} \mu_{\beta\beta}^{o}) Q_{k} Q_{l} \cdot$$

7.4

Defining the dimensionless normal coordinates q_{k}' by

$$Q_{k} = (\hbar^{2}/f_{k})^{1/4} q_{k}' .$$

7.5

where $f_{k} = (2\pi c \omega_{k})^{2}$, and ω_{k} (in cms^{-1}) is the normal frequency associated with Q_{k} and the rotational constants B_{α} and $B_{k}^{\alpha\beta}$ (both in cm^{-1}) as

$$B_{\alpha} = \mu_{\alpha\alpha}^{o} (\hbar^{2}/2hc) ,$$

$$B_{k}^{\alpha\beta} = (\hbar^{2}/2hc)(\partial\mu_{\alpha\beta}/\partial q_{k}')$$

$$= - [\hbar^{3}/2(hc)^{3/2}] \mu_{\alpha\alpha}^{o} a_{k}^{\alpha\beta} \mu_{\beta\beta}^{o} \omega_{k}^{-\frac{1}{2}} ,$$

7.6

then we may write 7.3 as

$$\frac{1}{2} \mu_{\alpha\beta} = B_{\alpha} \delta_{\alpha\beta} + \sum_{k} B_{k}^{\alpha\beta} q_{k}' + 3/4 \sum_{kl\delta} (B_{\delta}^{-1} B_{k}^{\alpha\delta} B_{l}^{\delta\beta}) q_{k}' q_{l}' .$$

7.7

The expansion of the vibrational potential energy in terms of dimensionless normal coordinates q_{k}' is written as

$$(V/hc) = \frac{1}{2} \sum_{k} \omega_{k} q_{k}'^{2} + 1/6 \sum_{klm} \phi_{klm} q_{k}' q_{l}' q_{m}'$$

$$+ 1/24 \sum_{klmn} \phi_{klmn} q_{k}' q_{l}' q_{m}' q_{n}' + \ldots$$

7.8

where ϕ_{klm} and ϕ_{klmn} are the cubic and quartic potential constants.

Introducing 7.5 and 7.7 into 6.10 and making use of the notation $\hat{H}_{nm}$ where the first subscript is the degree in the vibrational operators (coordinates and momenta) and the second subscript is the degree in the components of the total angular momentum operator J_{α}'

then we obtain

$$\hat{H} = \sum_{mn} \hat{H}_{nm} \qquad\qquad 7.9$$

with

$$\hat{H}_{02} = \sum_{\alpha} B_{\alpha} \hat{J}_{\alpha}^{2} \ , \qquad \hat{H}_{22} = 3/4 \sum_{\alpha\beta\delta} \sum_{k l} (B_{\delta}^{-1} B_{k}^{\alpha\delta} B_{l}^{\delta\beta}) \hat{q}_{k}' \hat{q}_{l}' \hat{J}_{\alpha} \hat{J}_{\beta}$$

$$\hat{H}_{12} = \sum_{\alpha\beta} B_{k}^{\alpha\beta} q_{k}' \hat{J}_{\alpha} \hat{J}_{\beta} \ , \hat{H}_{21} = -2 \sum_{\alpha} B_{\alpha} \hat{G}_{\alpha} \hat{J}_{\alpha} \ , \qquad 7.10$$

and so on for the rotational part.

For the vibrational part of the vibration-rotation hamiltonian using $\hat{P}_{k}$ to denote $\hbar/i \partial/\partial q_{k}'$, we obtain

$$\hat{H}_{20} = 1/2 \sum_{k} (\hbar f_{k}^{\frac{1}{2}})(\hat{p}_{R}^{2} + \hat{q}_{R}'^{2})$$

$$\hat{H}_{30} = (hc/6) \sum_{k l m} \phi_{k l m} q_{k}' q_{l}' q_{m}' \ ,$$

$$\hat{H}_{40} = (hc/24) \sum_{k l mn} \phi_{k l mn} q_{k}' q_{l}' q_{m}' q_{n}' \ , \qquad 7.11$$

and so on. $\hat{H}_{02}$ is the rigid rotator operator, $\hat{H}_{12}$ and $\hat{H}_{22}$ are the centrifugal distortion operators, $\hat{H}_{20}$ is the harmonic oscillator operator, $\hat{H}_{30}$ and $\hat{H}_{40}$ describe the anharmonicity of molecular vibrations.

Thus to a first approximation the hamiltonian in the Eckart choice of the BF frame is just the sum of $\hat{H}_{02}$ and $\hat{H}_{20}$, the assymetric rigid rotor and harmonic oscillator hamiltonians. It follows then that in this approximation its solutions are of the form

$$\Phi(q') \underset{\sim}{\sum_{k=-J}^{+J}} C_{k} |Jk> \qquad\qquad 7.12$$

where $\Phi(q')$ is simply a product of harmonic oscillator eigenfunctions one for each oscillator defined by a normal coordinate. The total energy is therefore a sum of a rotational energy and a vibrational energy. The vibrational energy is of the form

$$E_{V} = \sum_{k=1}^{3N-6} \varepsilon_{k}, \varepsilon_{k} = (n_{k} + \tfrac{1}{2})\hbar c \omega_{k}, n_{k} = 0,1,2,\dots \quad 7.13$$

and the precise form of the rotational energy depends on the equilibrium geometry of the nuclear framework and hence the relationship between the rotational cons-tants. If two of the rotational constants are equal for

example and equal to B then the molecule is a symmetric
top and the form of the rotational energy is

$$E_k = h(BJ(J+1) - (C-B)k^2),\qquad 7.14$$

where C is the unique rotational constant.The expres -
sion for the asymmetric top is somewhat more compli -
cated than this and will not be considered here,for
sufficient has been done,it is hoped,to enable contact
to be made with the treatment of vibration-rotation
given in elementary spectroscopic texts and for entry
to be affected to the more extensive research on this
subject.

Appendix I:The matrices $(e_\alpha)_{\beta\gamma}$ and (X^{-1})

The definition of the permutation symbol or unit
antisymmetric tensor $e_{\alpha\beta\gamma}$:

$$e_{\alpha\beta\gamma} = +1;\ \alpha,\beta,\gamma\ \text{in cyclic order,}$$
$$= 1;\ \alpha,\beta,\gamma\ \text{not in cyclic order,}$$
$$= 0;\ \text{two indices alike}\qquad (A1)$$

implies that

$$e_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$e_y = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$e_z = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\qquad (A2)$$

These matrices are also introduced in ref.14.

Taking the eulerian angles θ,ϕ,χ as the rotational
variables and using the convention of Wilson et al,(9)
for these angles, then from 3.8 and the above matri-
ces,it is straightforward to show that

$$X^{-1} = - \begin{pmatrix} \sin\chi & -\csc\theta\cos\chi & \cot\theta\cos\chi \\ \cos\chi & \csc\theta\sin\chi & -\cot\theta\sin\chi \\ 0 & 0 & 1 \end{pmatrix}$$

Appendix II:

Inverse by partitioning:

let the matrix $\underset{\sim}{A} = (a_{ij})$ of order m and its inverse
$\underset{\sim}{B} = (b_{ij})$ be partitioned into submatrices of indicated
order:

$$
\begin{pmatrix}
\underset{\sim}{A}_{11} & \underset{\sim}{A}_{12} \\
(p \times p) & (p \times y) \\
- - - - - - - - \\
\underset{\sim}{A}_{21} & \underset{\sim}{A}_{22} \\
(y \times p) & (y \times y)
\end{pmatrix}
\quad \text{and} \quad
\begin{pmatrix}
\underset{\sim}{B}_{11} & \underset{\sim}{B}_{12} \\
(p \times p) & (p \times y) \\
- - - - - - - - \\
\underset{\sim}{B}_{21} & \underset{\sim}{B}_{22} \\
(y \times p) & (y \times y)
\end{pmatrix}
$$

where $p + y = n$. Since $\underset{\sim}{A}\underset{\sim}{B} = \underset{\sim}{B}\underset{\sim}{A} = \underset{\sim}{E}_n$, we have

$$
\begin{aligned}
&\underset{\sim}{B}_{11} = \underset{\sim}{H}^{-1} & &\underset{\sim}{B}_{22} = \underset{\sim}{D}^{-1} + \underset{\sim}{A}_{22}^{-1} \underset{\sim}{A}_{21} \underset{\sim}{H}^{-1} \underset{\sim}{A}_{12} \underset{\sim}{A}_{22}^{-1} \\
&\underset{\sim}{B}_{12} = -\underset{\sim}{H}^{-1} \underset{\sim}{A}_{12} \underset{\sim}{A}_{22}^{-1} & &\underset{\sim}{B}_{21} = -\underset{\sim}{A}_{22}^{-1} \underset{\sim}{A}_{21} \underset{\sim}{H}^{-1} \\
&\underset{\sim}{B}_{22} = -\underset{\sim}{A}_{22}^{-1} \underset{\sim}{A}_{21} \underset{\sim}{H}^{-1}
\end{aligned}
$$

where

$$
\underset{\sim}{H} = \underset{\sim}{A}_{11} - \underset{\sim}{A}_{12} \underset{\sim}{A}_{22}^{-1} \underset{\sim}{A}_{21}
$$

also, since

$$
\begin{pmatrix}
\underset{\sim}{A}_{11} & \underset{\sim}{A}_{12} \\
\underset{\sim}{A}_{21} & \underset{\sim}{A}_{22}
\end{pmatrix}
\begin{pmatrix}
\underset{\sim}{E}_p & \underset{\sim}{O} \\
-\underset{\sim}{A}_{22}^{-1} \underset{\sim}{A}_{21} & \underset{\sim}{I}_q
\end{pmatrix}
=
\begin{pmatrix}
\underset{\sim}{H} & \underset{\sim}{A}_{12} \\
\underset{\sim}{O} & \underset{\sim}{A}_{22}
\end{pmatrix}
$$

then,

$$
\det|\underset{\sim}{A}| = \det|\underset{\sim}{A}_{22}| . \det|\underset{\sim}{H}| . \qquad\qquad A4
$$
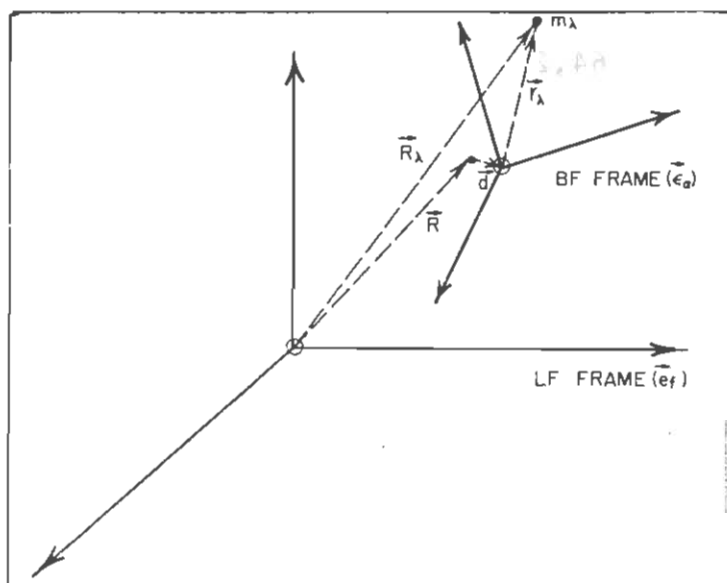
Fig. 1. TRANSFORMATION
TO BF FRAME

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