Lecture Notes in Chemistry

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Acknowledgments

Introduction

The aim of the present article is to give a critical exposition of the theory of the symmetry properties of rigid and nonrigid molecules. Despite the fact that several accounts of the subject, both technical and didactic, are now available, and despite the extensive discussion of nonrigid molecule symmetry that has been going on since the classic papers of Hougen and Longuet-Higgins, there remains a need for a unifying survey of the problem. Previous treatments have tended to emphasize one or the other particular viewpoint at the expense of a broader view.

Renewed interest in the details of the symmetry classification of rotation-vibration states of highly symmetric (octahedral) molecules has led to a reexamination of the relation between conventional point group operations and permutations of identical nuclei in rigid molecules, together with a clarification of the fundamental role of the Eckart constraints and associated Eckart frame. As is shown below, analogous insights can also be obtained in the case of nonrigid molecule symmetry, where the Eckart-Sayvetz conditions provide a natural generalization of the Eckart constraints.

The importance of particular definitions of the 'molecule-fixed' frame in the theory of molecular symmetry can be better appreciated by examining their dynamical origin. Chapter 1 is therefore devoted to a description of the derivation of the usual Wilson-Howard-Watson form of the molecular Hamiltonian, together with its generalization to nonrigid molecules. Particular attention is given to the introduction of molecular models and use of the Eckart and Eckart-Sayvetz constraints. Some other approaches to nonrigid molecule dynamics are also examined.

After a brief review of the fundamental symmetries of the complete molecular Hamiltonian, Chapter 2 gives a treatment of the symmetry properties of rigid molecules based upon the static molecular model, following closely that of Louck and Galbraith. Both the interpretation of feasible nuclear permutations and the invariance group of the Eckart frame are discussed in detail. The important problem of a correct definition of the parity of rotational wavefunctions, and hence of molecular systems, is also considered. The formal theory is illustrated by application to the symmetry classification of states of diatomic molecules.

Chapter 3 then develops a unified approach to the symmetry properties of nonrigid molecules. The formalism is based explicitly upon the properties of the semi-rigid molecular model, and is a straightforward generalization of the theory given for rigid molecules in Chapter 2. A symmetry group of the semi-rigid model is defined, and identified as the nonrigid molecule group. Induced transformations of Born-Oppenheimer variables result in feasible permutations of nuclei. It is shown that previous approaches can thereby be encompassed within a unified scheme.

Having dealt with fundamental matters concerning the nature of symmetry operations in nonrigid molecules, attention is turned to the related technical problem of handling the large symmetry groups involved. An investigation of the structure of nonrigid molecule symmetry groups is clearly important for the practical implementation of the theory. The formalism developed in Chapter 3 is well suited to the recognition and exploitation of nontrivial structure in nonrigid molecule groups. As recognized early on by McIntosh and by Altmann, these groups can often be written as semi-direct products. The systematic theory of semi-direct products is briefly reviewed in an appendix, while Chapter 4 applies the theory to derive character tables for various nonrigid molecule groups. Recognition of semi-direct product structure allows a straightforward correlation to be made between the irreducible representations of rigid and nonrigid molecule symmetry groups. Such correlations can be exploited in the general theory of vibrations in nonrigid molecules, but the details of this application have yet to be worked out.

The appendices develop in detail several important topics touched upon in the text. A glossary of mathematical symbols and abbreviations has been included for the convenience of the reader.

Table of Contents

Chapter 1. The Molecular Hamiltonian

We begin by considering the formulation of Hamiltonians for molecules both
rigid and nonrigid. Although we are primarily concerned with molecular symmetry
groups and their structure, an excursion into the theory of molecular dynamics is
necessary for several reasons. First of all, while it is true that notions of
molecular symmetry ultimately derive from the essential indistinguishability of
identical micro-particles (nuclei), which is a non-dynamical concept, in practice
our point of view is of necessity dynamics dependent. Thus, the <u>feasibility</u> of a
particular transformation [1] - in other words, the extent to which a given symmetry
is manifest in a given experiment - is obviously entirely contingent upon the forces
acting within the molecule, for a finite experimental resolution/observation time.
Conversely, since it is not possible at present to set up and solve nontrivial many-
particle (nuclear or molecular) problems using a set of coordinates displaying <u>all</u>
permutational symmetries in a simple fashion [2,3], the very way in which we
approach the dynamics is directly determined by intuitive ideas concerning feasi-
bility. One of the points we shall seek to emphasize throughout our work is the
close relation between descriptions of symmetry and dynamics. Again, a knowledge of
the transformation from cartesian to molecular (Born-Oppenheimer) coordinates used
to rewrite the Hamiltonian is essential when we come to the important practical
problem of determining the induced action of permutations of identical nuclei upon
molecular wavefunctions.

The general problem of the derivation of the quantum-mechanical molecular
Hamiltonian operator expressed in Born-Oppenheimer coordinates has recently been
reviewed by Makushkin and Ulenikov [4] and we will not trace the history of this
subject here. For the details of the procedure, we have chosen to follow the recent
account by Sørensen [5], which has, in our view, several attractive features. Thus,
Sørensen's work emphasizes the fact that it is possible to develop a treatment of
nonrigid molecule (NRM) dynamics entirely analogous to that for quasi-rigid species,
by introducing the concept of the semi-rigid molecular model (§1.4). In addition,
the stress laid upon the Eckart and Eckart-Sayvetz conditions reflects the import-

ance we shall ascribe to them in our discussions of molecular symmetry in Chapters 2 and 3. Hence, a careful discussion of the molecular Hamiltonian from this viewpoint is useful preparation for our later work, in which we shall draw on many of the ideas introduced here.

In this chapter, we are therefore concerned with the passage from the classical expression for the molecular energy in lab-fixed cartesian coordinates (§1.1) to the Wilson-Howard-Watson form of the quantum-mechanical Hamiltonian (§1.3) and its natural generalization to nonrigid systems (§1.4). A brief discussion of some other approaches to the dynamics of highly nonrigid systems is also given (§1.5).

1.1 The Molecular Kinetic Energy

Classically, the total non-relativistic energy of an isolated molecule consisting of N nuclei and N_ε electrons can be written

$$E_{mol} = \frac{1}{2} \sum_\alpha m_\alpha^{-1} \overset{\circ}{R}_i^\alpha \overset{\circ}{R}_i^\alpha + (\frac{1}{2} m) \sum_\varepsilon \overset{\circ}{R}_i^\varepsilon \overset{\circ}{R}_i^\varepsilon + V_{NN}(\underset{\sim}{R}^\alpha) + V_{NE}(\underset{\sim}{R}^\alpha; \underset{\sim}{R}^\varepsilon) + V_{EE}(\underset{\sim}{R}^\varepsilon) \quad 1.1$$

where we introduce the following notation: $\{\underset{\sim}{\hat{\ell}}_i; i = x,y,z\}$ is the laboratory coordinate frame, right-handed by definition; $\underset{\sim}{R}^\alpha \equiv$ position of nucleus α, charge z_α, mass m_α, $1 \leqslant \alpha \leqslant N$, $R_i^\alpha \equiv \underset{\sim}{\hat{\ell}}_i \cdot \underset{\sim}{R}^\alpha$, $\overset{\circ}{R}_i^\alpha \equiv d/dt_{lab} R_i^\alpha$; $\underset{\sim}{R}^\varepsilon \equiv$ position of electron ε, mass m, $1 \leqslant \varepsilon \leqslant N_\varepsilon$, $R_i^\varepsilon \equiv \underset{\sim}{\hat{\ell}}_i \cdot \underset{\sim}{R}^\varepsilon$, $\overset{\circ}{R}_i^\varepsilon \equiv d/dt_{lab} R_i^\varepsilon$; V_{NN}, V_{NE} and V_{EE} are the nucleus/nucleus, nucleus/electron and electron/electron coulomb potential energies, respectively and there is a summation convention for repeated indices i,j etc.

Our task now is to adopt some suitable set of 'molecule-fixed' coordinates, to express the molecular energy in terms of these new coordinates, to obtain a Hamiltonian form for the energy, and finally to quantize the classical Hamiltonian using a suitable quantization rule (this is the traditional route: cf. [6], Chapter 11; note, however, that a more direct approach is taken in [4,7]).

The starting point is the coordinate transformation shown in Figure 1.1 [5,8]

$$R_i^\alpha = R_i + C_{ij} r_j^\alpha(q_\lambda) \quad\quad 1.2a$$

$$R_i^\varepsilon = R_i + C_{ij} r_j^\varepsilon \quad\quad 1.2b$$
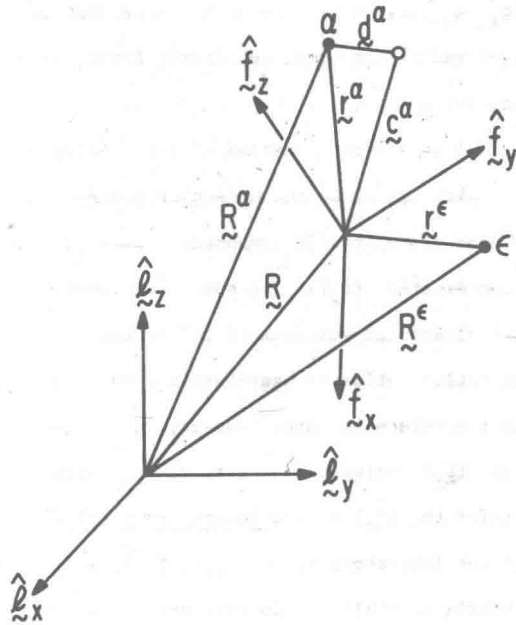
Figure 1.1   The transformation from lab-fixed to
molecular (Born-Oppenheimer) coordinates

where $R \equiv (\sum_\alpha m_\alpha R^\alpha + m \sum_\varepsilon R^\varepsilon)/(\sum_\alpha m_\alpha + mN_\varepsilon)$ is the molecular centre of mass,
$R_i \equiv \hat{\ell}_i \cdot R$, $\{q_\lambda; \lambda = 1...3N-6\}$ are 3N-6 independent internal coordinates, $\{\hat{f}_i\}$ is
the 'molecule-fixed' orthonormal coordinate frame, and $C_{ij} \equiv \hat{\ell}_i \cdot \hat{f}_j$ are elements of
the direction-cosine matrix C.

Equation 1.1 is a transformation of the electronic and nuclear coordinates into
a frame $\{\hat{f}_i\}$ with origin at the molecular centre of mass, 'rotating with the
molecule' in some sense; the 3N components $\{r_j^\alpha\}$ depend on the 3N-6 independent
generalized coordinates $\{q_\lambda\}$. The specification of a non-inertial frame carrying
the total orbital angular momentum of the system is a major problem in the general
theory of collective motion in many-particle systems (cf. [2] and references
therein). In the molecular case, however, it is often appropriate to define the
orientation of $\{\hat{f}_i\}$ using the Eckart [9] or Eckart-Sayvetz [10] conditions, so
that we can refer to $\{\hat{f}_i\}$ as the Eckart frame (§1.2).

Although the laboratory frame $\{\hat{\ell}_i\}$ is by definition right-handed, the direc-
tion-cosine matrix C is allowed to have determinant +1 or -1, so that the sense of
the molecule-fixed frame can be opposite to that of the laboratory frame, i.e.,
left-handed. The matrix C is therefore an element of the orthogonal matrix group
O(3)

$$C \in O(3) : C_{ij}C_{ij'} = \delta_{jj'}, \det C = \pm 1. \qquad 1.3$$

We set

$$C \equiv (\det C)C' \qquad 1.4a$$

where C' is a proper rotation matrix

$$C' \in SO(3), \det C' = +1 \qquad 1.4b$$

and is a function of 3 independent parameters such as the Euler angles (Appendix 1).

The only consequence of C being an element of O(3) for the derivation of the
Hamiltonian is that some care is necessary when projecting the components of axial
vectors, such as vector products, from the laboratory frame onto $\{\hat{f}_i\}$ (as pointed
out by Husson [12]). The resulting factors of (det C) are however omitted in the
rest of this chapter for the sake of clarity.

The extra freedom in the rotational coordinates is motivated by several considerations. First, as discussed in §1.2, the phenomenon of 'Eckart frame inversion' [13] shows that when large-amplitude nuclear motions are taken into account the Eckart frame does not necessarily have the same handedness as the laboratory frame. Also, Louck [7] has shown that the 'internal' and 'external' angular momenta appearing in the molecular problem can be expressed directly in terms of the direction-cosine matrix C. Not only are these expressions independent of any specific parametrization of C', but they are also invariant, as is the corresponding Hamiltonian, under the inversion $\mathcal{J}: C \rightarrow -C$ (cf. Appendix 2). As will be seen in Chapter 2, the problem of determining the transformation properties of rotational wavefunctions under improper rotations of axes is important for a detailed understanding of molecular symmetry. Using simple vector-coupling arguments (given in Appendix 2), it is possible to write rotational wavefunctions as homogeneous polynomials in the elements of the matrix C. There is then no ambiguity concerning either the parity of rotational wavefunctions, and hence of molecular systems, or the induced action of improper rotations.

Returning to the coordinate transformation 1.2, it should be emphasized that at this point the 3N-6 independent internal coordinates $\{q_\lambda\}$ are entirely general in nature, and do not necessarily describe displacements of nuclei from notional 'equilibrium positions'. In fact, it is only required that the transformation 1.2 be invertible, and that variation of the $\{q_\lambda^-\}$ should leave the nuclear centre of mass invariant [8].

In the work to follow we identify the molecular centre of mass $\underset{\sim}{R}$ with the nuclear centre of mass $\underset{\sim}{R}^{nuc}$

$$\underset{\sim}{R} \sim \underset{\sim}{R}^{nuc} \equiv \left(\sum m_\alpha \underset{\sim}{R}^\alpha\right)/\sum m_\alpha . \qquad 1.5$$

This is a conventional approximation [18], which has not however been made by Howard and Moss [19], who have explicitly derived the small (mass-polarization or recoil) correction terms arising from the fact that $\underset{\sim}{R} \neq \underset{\sim}{R}^{nuc}$. We also ignore the motions of the electrons completely. It is therefore assumed that the nuclei move in a translation/rotation invariant potential field $V(q_\lambda)$, corresponding to the

'potential energy surface' associated with a particular electronic state. This is the viewpoint of the conventional Born-Oppenheimer approximation [20, 21], and means that the Hamiltonian we shall derive should be regarded as an _effective_ molecular Hamiltonian corresponding to a given electronic state [22,23].

We shall not be particularly concerned with the details of quantizing the molecular Hamiltonian [7, 24-26] or of obtaining hermitian operators [27], and so work mainly within the framework of classical mechanics.

From equation 1.2, the velocity of nucleus α is

$$d/dt_{lab}\, \underset{\sim}{R}^{\alpha} = d/dt_{lab}\, \underset{\sim}{R} + \underset{\sim}{\omega} \wedge \underset{\sim}{r}^{\alpha} + \sum_{\lambda} \frac{\partial \underset{\sim}{r}^{\alpha}}{\partial q_{\lambda}} \dot{q}_{\lambda} \qquad 1.6$$

where the angular velocity vector $\underset{\sim}{\omega}$ is defined by

$$d/dt_{lab}\, \hat{\underset{\sim}{f}}_{i} \equiv \underset{\sim}{\omega} \wedge \hat{\underset{\sim}{f}}_{i} \qquad 1.7$$

so that

$$\underset{\sim}{\omega} \wedge \underset{\sim}{r}^{\alpha} = \underset{\sim}{\omega} \wedge \hat{\underset{\sim}{f}}_{j} r_{j}^{\alpha} . \qquad 1.8$$

The sense of the vector product is determined in the lab frame, and

$$\underset{\sim}{\omega} \wedge \underset{\sim}{r}^{\alpha} = (\hat{\underset{\sim}{f}}_{j} \wedge \hat{\underset{\sim}{f}}_{k}) \omega_{j} r_{k}^{\alpha} = (\det C) \hat{\underset{\sim}{f}}_{i} \varepsilon_{ijk} \omega_{j} r_{k}^{\alpha} \qquad 1.9$$

with

$$\omega_{j} \equiv \hat{\underset{\sim}{f}}_{j} \cdot \underset{\sim}{\omega} . \qquad 1.10$$

Defining the 3N-dimensional velocity vector

$$(v_{1}, v_{2}, \ldots, v_{3N}) \equiv (\dot{R}_{x}, \dot{R}_{y}, \dot{R}_{z}, \omega_{x}, \omega_{y}, \omega_{z}, q_{1}, \ldots, q_{3N-6}) \qquad 1.11$$

we can write

$$\underset{\sim}{\dot{R}}^{\alpha} \equiv \sum_{\nu=1}^{3N} \underset{\sim}{t}_{\alpha,\nu} v_{\nu} = \sum_{\nu} \hat{\underset{\sim}{\ell}}_{i} t_{\alpha i,\nu} v_{\nu} \qquad 1.12$$

where the transformation coefficients $[t_{\alpha i,\nu}]$ form a 3N by 3N matrix **t**. In detail, from 1.6 the t-vectors are

Translation $\qquad \underset{\sim}{t}_{\alpha,Ti} = \hat{\underset{\sim}{\ell}}_{i} \qquad\qquad i = x,y,z \qquad$ 1.13a

Rotation $\qquad \underset{\sim}{t}_{\alpha,Ri} = (\hat{\underset{\sim}{f}}_{i} \wedge \underset{\sim}{r}^{\alpha}) \qquad\quad i = x,y,z \qquad$ 1.13b

Internal $\qquad \underset{\sim}{t}_{\alpha,\lambda} = \partial \underset{\sim}{r}^{\alpha}/\partial q_{\lambda} . \qquad\qquad\qquad\qquad$ 1.13c

The nuclear kinetic energy is then

$$2T = \sum_{\alpha} m_{\alpha} \dot{R}^{\alpha}_i \dot{R}^{\alpha}_i = \sum_{\nu,\nu'} K_{\nu\nu'} v_{\nu} v_{\nu'} \qquad 1.14$$

with the matrix

$$K_{\nu\nu'} \equiv \sum m_{\alpha} \underset{\sim}{t}_{\alpha,\nu} \cdot \underset{\sim}{t}_{\alpha,\nu'} \qquad 1.15$$

i.e., $\qquad\qquad K = \tilde{t} \; m \; t \qquad m = \text{mass matrix.} \qquad 1.16$

In the assumed absence of nuclear velocity dependent potentials, we introduce generalized momenta and 'quasi-momenta' in the usual fashion (recall that the components of the angular velocity vector are not conjugate to any coordinates — the relation between the angular velocities and the time derivatives of, for example, the Euler angles, is non-integrable [29]).

$$P_{\nu} \equiv \partial T/\partial v_{\nu} = \sum_{\nu'} K_{\nu\nu'} v_{\nu'} \qquad 1.17$$

and obtain $\qquad\qquad 2T = \sum_{\nu} P_{\nu} v_{\nu} \qquad 1.18$

which is the form-invariant expression for the kinetic energy. Defining the inverse of K

$$G \equiv K^{-1} \qquad 1.19$$

we have $\qquad\qquad v_{\nu} = \sum_{\nu'} G_{\nu\nu'} P_{\nu'} \qquad 1.20$

which yields the Hamiltonian form

$$2T = \sum G_{\nu\nu'} P_{\nu} P_{\nu'} \; . \qquad 1.21$$

At this point it is possible to 'quantize' the classical molecular Hamiltonian. In essence, this involves using the formula for the 3N-dimensional Laplace-Beltrami operator in generalized coordinates (corresponding to the nuclear kinetic energy) expressed in terms of the elements of the matrix G appearing in 1.21 — this is known as the Podolsky [24] quantization procedure. Careful attention has to be given to problems concerning volume elements for integration of wavefunctions, and the presence of quasi-momenta in 1.21 [27].

To sum up, the kinetic energy 1.21 is obtained in 3 steps [5]:

    a) Form the elements of the matrix [t] as functions of the generalized coordinates $\{q_\lambda\}$ (1.13).

    b) Multiply matrices to obtain K (1.16).

    c) Invert K to obtain the important matrix G (1.19).

It is the last operation of inversion that is difficult to perform explicitly, since K is, in general, q-dependent (although see [44]).

In the light of this, Sørensen has suggested the following procedure involving <u>momentum transformation</u>:

    a') Obtain the expression for the nuclear momentum

$$\underset{\sim}{P}^\alpha \equiv \partial T/\partial \underset{\sim}{\overset{\bullet}{R}}{}^\alpha \equiv \sum_\nu \; P_\nu \underset{\sim}{s}_{\nu,\alpha} \equiv \sum_\nu P_\nu \underset{\sim}{s}_{\nu,\alpha j}\, \hat{\underset{\sim}{\ell}}_j \qquad\qquad 1.22$$

    b') Write the nuclear kinetic energy as

$$2T = \sum_\alpha m_\alpha^{-1}\, \underset{\sim}{P}^\alpha \cdot \underset{\sim}{P}^\alpha \cdot = \sum_{\nu\nu'} G_{\nu\nu'} P_\nu P_{\nu'} \qquad\qquad 1.23$$

where the G-matrix is now given <u>directly</u> in terms of the s-vectors as

$$G_{\nu\nu'} = \sum_\alpha m_\alpha^{-1}\, \underset{\sim}{s}_{\nu,a} \cdot \underset{\sim}{s}_{\lambda',\alpha} \cdot \qquad\qquad 1.24$$

As the notation suggests, this is a direct generalization of the method used to obtain the <u>vibrational</u> kinetic energy in the Wilson FG-formalism [6]; however, here it is possible to deal with all nuclear degrees of freedom, not just the vibrational, together on the same footing, in the absence of any restriction to 'small-amplitude' motions.

Noting that

$$2T = \sum_\alpha \underset{\sim}{P}^\alpha \cdot \underset{\sim}{\overset{\bullet}{R}}{}^\alpha = \sum_{\alpha\nu,\nu'} P_\nu\, \underset{\sim}{s}_{\nu,\alpha} \cdot \underset{\sim}{t}_{\alpha,\nu'} v_{\nu'} \qquad\qquad 1.25$$

we must have from 1.18

$$\sum_\alpha \underset{\sim}{s}_{\nu,\alpha} \cdot \underset{\sim}{t}_{\alpha,\nu'} = \delta_{\nu\nu'} \qquad\qquad 1.26$$

i.e., the coefficients $[s_{\nu,\alpha j}]$ form a 3N by 3N matrix which is the left-inverse of t. The orthogonality relations 1.26 are very important in the development of the Hamiltonian. Thus, from the expressions for the translational and rotational t-vectors we note that

$$\sum_\alpha \underset{\sim}{s}_{\lambda,\alpha} \cdot \underset{\sim}{t}_{\alpha,Ti} = 0 \qquad \text{for all } \lambda, i \qquad\qquad 1.27a$$

implies

$$\sum_\alpha \underset{\sim}{s}_{\lambda,\alpha} = \underset{\sim}{0} \qquad \text{for all } \lambda \qquad\qquad 1.27b$$

and that

$$\sum_\alpha \underset{\sim}{s}_{\lambda,\alpha} \cdot \underset{\sim}{t}_{\alpha,Ri} = 0 \qquad \text{for all } \lambda,i \qquad\qquad 1.28a$$

implies

$$\sum_\alpha \underset{\sim}{r}^\alpha \wedge \underset{\sim}{s}_{\lambda,\alpha} = \underset{\sim}{0} \qquad \text{for all } \lambda \qquad\qquad 1.28b$$

The relations 1.27b and 1.28b are <u>generalized Malhiot-Ferigle conditions</u> [5,8,29], and show that the internal coordinates $\{q_\lambda\}$ are invariant under translations and rotations of the nuclear configuration $\{\underset{\sim}{R}^\alpha\}$, as required [8,30].

The outstanding problem is the evaluation of the s-vectors. From the relations (cf. 1.12)

$$\dot{\underset{\sim}{R}}_i = \sum_\alpha \underset{\sim}{s}_{Ti,\alpha} \cdot \dot{\underset{\sim}{R}}^\alpha \qquad\qquad 1.29a$$

$$\dot{q}_\lambda = \sum_\alpha \underset{\sim}{s}_{\lambda,\alpha} \cdot \dot{\underset{\sim}{R}}^\alpha \qquad\qquad 1.29b$$

it follows immediately that

Translation $\qquad \underset{\sim}{s}_{Ti,\alpha} = (m_\alpha/M)\, \hat{\underset{\sim}{e}}_i \qquad\qquad\qquad 1.30a$

Internal $\qquad \underset{\sim}{s}_{\lambda,\alpha} = \underset{\sim}{\nabla}^\alpha q_\lambda \equiv \hat{\underset{\sim}{e}}_j\, \partial q_\lambda / \partial R_j^\alpha \qquad\qquad 1.30b$

where, for a geometrically-defined internal coordinate q_λ we can evaluate the derivative $(\partial q_\lambda/\partial R_j^\alpha)$ as a function of the instantaneous nuclear configuration $\{R_j^\alpha\}$. In §1.2, a more convenient expression for $\underset{\sim}{s}_{\lambda,\alpha}$ is obtained through use of <u>rectilinear</u> coordinates for rigid molecules.

How, then, to evaluate the rotational s-vectors $\underset{\sim}{s}_{Ri,\alpha}$? Consideration of the orthogonality condition

$$\sum_\alpha \underset{\sim}{s}_{Ti,\alpha} \cdot \underset{\sim}{t}_{\alpha,\lambda} = 0 \qquad \text{for all } \lambda,i \qquad\qquad 1.31$$

together with 1.13c and 1.30a shows that

$$\sum_\alpha m_\alpha(\partial \underset{\sim}{r}^\alpha/\partial q_\lambda) = \underset{\sim}{0} \qquad \text{for all } \lambda. \qquad\qquad 1.32$$

However, as recognized by Sørensen [5], this is just a differential consequence of the centre of mass condition (translational constraint)

$$\sum_\alpha m_\alpha \underset{\sim}{r}^\alpha = \underset{\sim}{0} . \qquad\qquad 1.33$$