Chapter 31
Coordinate Systems and Transformations

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1 INTRODUCTION

Schrödinger's Hamiltonian describing a system of N charged particles in a coordinate frame fixed in the laboratory is

$$\mathsf{H}(\mathbf{x}) = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla^2(\mathbf{x}_i) + \frac{e^2}{8\pi\epsilon_o}\sum_{i,j=1}^{N}{}' \frac{Z_i Z_j}{x_{ij}} \quad (1)$$

where the separation between particles is defined by

$$x_{ij}^2 = \sum_{\alpha}(x_{\alpha j} - x_{\alpha i})^2 \quad (2)$$

It is convenient to regard $\mathbf{x}_i$ as a column matrix of three Cartesian components $x_{\alpha i}$, $\alpha = x, y, z$ and to regard $\mathbf{x}_i$ collectively as the $3 \times N$ matrix $\mathbf{x}$. Each of the particles has mass m_i and charge $Z_i e$. The charge numbers Z_i are positive for a nucleus and -1 for an electron. In a neutral system, the charge numbers sum to zero.

When it is necessary to distinguish between electrons and nuclei, the variables may be split up into two sets, one set consisting of L variables, $\mathbf{x}_i^e$, describing the electrons and the other set of H variables, $\mathbf{x}_i^n$, describing the nuclei and $N = L + H$. It should be emphasized that the coordinates simply specify field points and cannot actually be particle coordinates because of the indistinguishability of sets of particles. However, we shall continue to designate them as if they were particle coordinates. In this usage, special care has to be taken to avoid confusion when considering permutations of identical particles.

The Hamiltonian describes any system composed of N charged particles including not only a molecule comprising H nuclei and L electrons but also H atoms, each with a number of electrons summing in all to L and so on. When we choose not to specify precisely what system we have in mind, we shall call the assembly of particles covered by the Hamiltonian a *cluster*.

The eigenstates of full problem

$$\mathsf{H}(\mathbf{x})\psi(\mathbf{x}) = E\psi(\mathbf{x}) \quad (3)$$

are not square-integrable because the Hamiltonian (1) is invariant under uniform translations in the frame fixed in the laboratory. This means that the centre of mass moves through space like a free particle, the states of a free particle are not quantized, and eigenfunctions are not square-integrable. The centre-of-mass motion must therefore be separated out to disentangle any bound states from the continuum.

The Hamiltonian is also invariant under all orthogonal transformations (rotation reflections) of the particle variables in the frame fixed in the laboratory, so it is sensible to separate as far as possible the orientational motions of the system from its purely internal motions because it is in terms of the internal motions that many aspects of cluster behaviour are visualized. The internal motions comprise dilations, contractions, and deformations of a

Handbook of Molecular Physics and Quantum Chemistry, Edited by Stephen Wilson. Volume 1: *Fundamentals*. © 2003 John Wiley & Sons, Ltd. ISBN: 0-471-62374-1.

specified configuration of particle variables. Put colloquially, the internal motions specify the cluster geometry.

The Hamiltonian is invariant under the permutation of the variable sets of all identical particles too, and it is natural to require, if possible, that the coordinates chosen to describe the system transform in a simple way under such permutations. But in any case, it is essential that the permutational properties of the various coordinates be well specified in order that trial wave functions are properly symmetric or antisymmetric, according to particle type, when spin variables are included.

The way in which translational motion can be removed from the problem is well understood from classical mechanics. However, it involves an essentially arbitrary choice of translationally invariant coordinates and there is always one such coordinate less than the original number because of the centre-of-mass coordinate. After this separation is made, it is clearly a matter of opinion and/or convention how the translationally invariant coordinates should be identified. So the role of the coordinates in specifying either electronic or nuclear motions becomes problematic.

The separation of orientation variables from internal variables is also a well-understood problem, but in order to achieve the separation, the three orientation variables have to be specified in terms of a particular way of fixing a coordinate frame in the (non-rigid) assembly of particles. This choice is, like the choice of translationally invariant coordinates, quite arbitrary. However, whatever choice is made, there will always be a configuration of the particles that causes the definition of the frame to fail. This can be appreciated by thinking of a three-particle system and imagining fixing the frame in it so as to put all three particles in a plane. This defines an axis normal to the plane, for example, the z-axis, and the x- and y-axes can then be chosen at will to form a right-handed orthogonal system of axes. But if the three particles are collinear, then the frame definition fails. In addition to this complication, the definition of three orientation variables removes a further three variables from the translationally invariant ones to leave $3N-6$ variables to describe the internal motions. The internal coordinates must be invariant to any orthogonal transformation of the translationally invariant coordinates and so must be expressible in terms of scalar products of these coordinates. The choice here is again quite arbitrary in terms of the already arbitrary choice of translationally invariant coordinates.

The internal and orientation coordinates can obviously be expressed directly in terms of the original coordinates in the laboratory frame and so there is no absolute need to consider the translational motion in a separate step. However, to do so aids clear exposition.

2 REMOVING TRANSLATIONAL MOTION

To remove the centre-of-mass motion from the full Hamiltonian, all that is needed is a coordinate transformation symbolized by

$$(\mathbf{t}\,\mathbf{X}_T) = \mathbf{x}\,\mathbf{V} \tag{4}$$

In equation (4), $\mathbf{t}$ is a $3 \times N-1$ matrix and $\mathbf{X}_T$ is a 3×1 matrix, so that the combined (bracketed) matrix on the left-hand of equation (4) is $3 \times N$. $\mathbf{V}$ is an $N \times N$ matrix that, from the structure of the left-hand side of equation (4), has a special last column whose elements are

$$V_{iN} = {M_T}^{-1} m_i, \qquad M_T = \sum_{i=1}^{N} m_i \tag{5}$$

Hence, $\mathbf{X}_T$ is the standard centre-of-mass coordinate.

$$\mathbf{X}_T = {M_T}^{-1} \sum_{i=1}^{N} m_i \mathbf{x}_i \tag{6}$$

As the coordinates $\mathbf{t}_j$, $j = 1, 2, \ldots, N-1$ are to be translationally invariant, we require on each remaining column of $\mathbf{V}$

$$\sum_{i=1}^{N} V_{ij} = 0, \quad j = 1, 2, \ldots, N-1 \tag{7}$$

and it is easy to see that equation (7) forces $\mathbf{t}_j \rightarrow \mathbf{t}_j$ as $\mathbf{x}_i \rightarrow \mathbf{x}_i + \mathbf{a}$, for all i.

The $\mathbf{t}_i$ are independent if the inverse transformation

$$\mathbf{x} = (\mathbf{t}\,\mathbf{X}_T)\mathbf{V}^{-1} \tag{8}$$

exists. The structure of the right-hand side of equation (8) shows that the bottom row of $\mathbf{V}^{-1}$ is special and, without loss of generality, we may require its elements to be

$$(\mathbf{V}^{-1})_{Ni} = 1, \quad i = 1, 2, \ldots, N \tag{9}$$

The inverse requirement on the remainder of $\mathbf{V}^{-1}$ implies that

$$\sum_{i=1}^{N} (\mathbf{V}^{-1})_{ji} m_i = 0, \quad j = 1, 2, \ldots, N-1 \tag{10}$$

When we write the column matrix of the Cartesian components of the partial derivative operator as $\partial/\partial\mathbf{x}_i$, the coordinate change (4) gives

$$\frac{\partial}{\partial \mathbf{x}_i} = \sum_{j=1}^{N-1} V_{ij} \frac{\partial}{\partial \mathbf{t}_j} + m_i {M_T}^{-1} \frac{\partial}{\partial \mathbf{X}_T} \tag{11}$$

and when it seems more convenient, this column matrix of derivative operators will also be denoted as the vector grad operator $\vec{\nabla}(\mathbf{x}_i)$.

If a second set $\mathbf{t}'$ of translationally invariant coordinates is constructed, then within the common domain of both transformations, that set is related to the original set by

$$(\mathbf{t}' \mathbf{X}_T) = (\mathbf{t} \mathbf{X}_T)\overline{\mathbf{V}}, \qquad \overline{\mathbf{V}} = \mathbf{V}^{-1}\mathbf{V}' \tag{12}$$

where $\mathbf{V}'$ defines $\mathbf{t}'$. The matrix $\overline{\mathbf{V}}$ is

$$\begin{pmatrix} \mathbf{G} & \mathbf{0} \\ \mathbf{0} & 1 \end{pmatrix}, \qquad G_{ij} = (\overline{\mathbf{V}})_{ij}, \quad i, j = 1, 2, \ldots, H-1 \tag{13}$$

It is easily seen that the form of equation (11) is preserved under a change from $\mathbf{t}$ to $\mathbf{t}'$. It is thus the case that any set of translationally invariant coordinates can be related to any other set in their common domain by means of a linear transformation. This in turn means that it will often be the case that results established for one particular choice are more generally valid.

2.1 Permutational transformation of the translationally invariant coordinates

The general permutation of identical particles can be written as

$$\mathcal{P}(\mathbf{x}^e \mathbf{x}^n) = (\mathbf{x}^e \mathbf{x}^n) \begin{pmatrix} \mathbf{P}^e & \mathbf{0} \\ \mathbf{0} & \mathbf{P}^n \end{pmatrix} \equiv \mathbf{x}\mathbf{P} \tag{14}$$

where $\mathbf{P}^e$ and $\mathbf{P}^n$ are standard permutation matrices. They are orthogonal with determinant ±1 according to whether the permutation is of even or odd parity. The matrix $\mathbf{P}^n$ will have non-zero entries only within groups of identical particles and is most conveniently visualized as having block-diagonal form, one block for each group of identical particles. The effect of this permutation on the translationally invariant coordinates is

$$\mathcal{P}(\mathbf{t}\mathbf{X}_T) = (\mathbf{t}\mathbf{X}_T) \begin{pmatrix} \mathbf{H} & \mathbf{0} \\ \mathbf{0} & 1 \end{pmatrix} \tag{15}$$

where

$$(\mathbf{H})_{ij} = (\mathbf{V}^{-1}\mathbf{P}\mathbf{V})_{ij} \quad i, j = 1, 2, \ldots, N-1 \tag{16}$$

The matrix $\mathbf{H}$ is not necessarily in standard permutational form nor is it orthogonal, even though it has determinant ±1 according to the sign of $|\mathbf{P}|$. Thus, under any permutation of like particles, the translationally invariant coordinates will transform into linear combinations of themselves. Any chosen transformed coordinate will, generally, involve both $\mathbf{P}^e$ and $\mathbf{P}^n$ in its definition. If it is desired to identify electrons with a particular set of translationally invariant coordinates, specialized coordinate choices must be made to avoid $\mathbf{P}^n$ becoming involved in the definition of their transformed forms, and even more specialized choices must be made to ensure that members of the chosen set transform only into each other under $\mathbf{P}^e$.

2.2 The translationally invariant Hamiltonian

The Hamiltonian (1) in the new coordinates becomes

$$\begin{aligned} \mathsf{H}(\mathbf{t}, \mathbf{X}_T) = &-\frac{\hbar^2}{2} \sum_{i,j=1}^{N-1} \frac{1}{\mu_{ij}} \vec{\nabla}(\mathbf{t}_i) \cdot \vec{\nabla}(\mathbf{t}_j) \\ &+ \frac{e^2}{8\pi\epsilon_o} {\sum_{i,j=1}^{N}}' \frac{Z_i Z_j}{r_{ij}(\mathbf{t})} - \frac{\hbar^2}{2M_T} \nabla^2(\mathbf{X}_T) \end{aligned} \tag{17}$$

Here

$$\frac{1}{\mu_{ij}} = \sum_{k=1}^{N} {m_k}^{-1} V_{ki} V_{kj} \quad i, j = 1, 2, \ldots, N-1 \tag{18}$$

The $N-1$-dimensional square matrix composed of all the $1/\mu_{ij}$ is denoted as $\boldsymbol{\mu}^{-1}$. It is inverse to a matrix of reduced masses $\boldsymbol{\mu}$ but in our approach it is straightforward to construct the elements of the inverse directly. The operator r_{ij} is just x_{ij} as given by equation (2) but is expressed as a function of $\mathbf{t}_i$. Thus,

$$r_{ij}(\mathbf{t}) = \left[\sum_{\alpha} \left(\sum_{k=1}^{N-1} [(\mathbf{V}^{-1})_{kj} - (\mathbf{V}^{-1})_{ki}] t_{\alpha k} \right)^2 \right]^{1/2} \tag{19}$$

In equation (17), the $\vec{\nabla}(\mathbf{t}_i)$ are grad operators expressed in the Cartesian components of $\mathbf{t}_i$ and the last term represents the centre-of-mass kinetic energy. Since the centre-of-mass variable does not enter the potential term, the centre-of-mass problem may be separated off completely so that the full solution is of the form

$$T(\mathbf{X}_T)\Psi(\mathbf{t}) \tag{20}$$

where $\Psi(\mathbf{t})$ is a solution to the problem specified by the first two terms in equation (17), which will be denoted collectively by $\mathsf{H}(\mathbf{t})$ and referred to as the *translationally invariant* Hamiltonian.

Since all possible sets of translationally invariant coordinates can be related by linear transformations, the spectrum of the translationally invariant Hamiltonian is quite independent of the choice of translationally invariant coordinates made.

It is a straightforward, if rather tedious, matter to show that the translationally invariant Hamiltonian is invariant under any permutation of particles with the same masses and the same charges.

In certain special cases, such as that of a neutral or positively charged atom, it is possible to show that the translationally invariant Hamiltonian has an infinite number of bound states (described, *a fortiori* by square-integrable wave functions) below the start of the continuum. For the general cluster Hamiltonian, few results of this kind are known but it seems reasonable to expect that the molecular Hamiltonian for a 'recognized' molecule will have at least some bound states.

2.3 The translationally invariant angular momentum operator

The total angular momentum operator may be written as

$$\mathsf{L}(\mathbf{x}) = \frac{\hbar}{i}\sum_{i=1}^{N}\hat{\mathbf{x}}_i\frac{\partial}{\partial\mathbf{x}_i} \tag{21}$$

where $\mathsf{L}(\mathbf{x})$ is a column matrix of Cartesian components and the skew-symmetric matrix $\hat{\mathbf{x}}_i$ is

$$\hat{\mathbf{x}}_{\mathbf{i}} = \begin{pmatrix} 0 & -x_{zi} & x_{yi} \\ x_{zi} & 0 & -x_{xi} \\ -x_{yi} & x_{xi} & 0 \end{pmatrix} \tag{22}$$

The matrix $\hat{\mathbf{x}}_{\mathbf{i}}$ can also be written in terms of the infinitesimal rotation generators

$$\mathbf{M}^x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \quad \mathbf{M}^y = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\mathbf{M}^z = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{23}$$

so that

$$\hat{\mathbf{x}}_i = \sum_{\alpha} x_{\alpha i}\mathbf{M}^{\alpha T} \tag{24}$$

A variable symbol with a caret over it will, from now on, be used to denote a skew-symmetric matrix as defined by equation (24). The matrices are simply representations of the antisymmetric (Levi-Civita) tensor, such that $\mathbf{M}^{\alpha}_{\beta\gamma}$ is $e_{\alpha\beta\gamma}$.

Transforming to coordinates $\mathbf{X}_T, \mathbf{t}_i$ gives

$$\mathsf{L}(\mathbf{x}) \rightarrow \frac{\hbar}{i}\sum_{i=1}^{N-1}\hat{\mathbf{t}}_i\frac{\partial}{\partial\mathbf{t}_i} + \frac{\hbar}{i}\hat{\mathbf{X}}_T\frac{\partial}{\partial\mathbf{X}_T} \tag{25}$$

and in future the first term will be denoted as $\mathsf{L}(\mathbf{t})$ and called the *translationally invariant angular momentum*. The square of this operator and its z-component commute with the translationally invariant Hamiltonian. It is therefore possible to choose the eigenfunctions (if there are any) of the translationally invariant Hamiltonian to be angular momentum eigenfunctions.

Although the translationally invariant angular momentum operator is not invariant under a general orthogonal transformation of particle coordinates, it is invariant under coordinate inversion. It is also invariant under the permutation of any of the coordinate sets, not just those of identical particles.

2.4 The translationally invariant dipole operator

The total dipole operator is

$$\mathsf{d}(\mathbf{x}) = e\sum_{i=1}^{N} Z_i\mathbf{x}_i \tag{26}$$

and simple transformation using equation (8) leads to

$$\mathsf{d}(\mathbf{t}, \mathbf{X}_T) = e\sum_{i=1}^{N-1}\tilde{Z}_i\mathbf{t}_i + eZ_T\mathbf{X}_T \tag{27}$$

where the first term in equation (27) will be denoted $\mathbf{d}(\mathbf{t})$ and where the effective charges are given by

$$\tilde{Z}_i = \sum_{j=1}^{N}(\mathbf{V}^{-1})_{ij}Z_j \qquad Z_T = \sum_{i=1}^{N} Z_i \tag{28}$$

As is to be expected, the centre-of-mass-dependent term in the dipole vanishes if the system is neutral, that is, if $Z_T = 0$.

The translationally invariant dipole operator is not invariant under a general orthogonal transformation of particle coordinates but it only changes sign under coordinate inversion. It is invariant under the permutation of the coordinate sets of particles with identical charges.

3 FIXING A FRAME IN THE BODY

For a system with more than two particles, one can transform the coordinates **t** such that the rotational motion can be expressed in terms of three orientation variables, with the remaining motions expressed in terms of variables (commonly called *internal coordinates*), which are invariant under all orthogonal transformations of the **t**. For $N = 2$, only two orientation variables are required and this case is rather special and is excluded from all subsequent discussion. To construct the frame fixed in the body, it is supposed that the three orientation variables are specified by means of an orthogonal matrix **C**, the elements of which are expressed as functions of three Eulerian angles ϕ_m, $m = 1, 2, 3$, which are orientation variables. We require that the matrix **C** is specified in terms of the translationally invariant coordinates **t**. Thus, the Cartesian coordinates **t** are considered related to a set **z** by

$$\mathbf{t} = \mathbf{C}\mathbf{z} \tag{29}$$

so the matrix **C** may be thought of as a direction cosine matrix, relating the laboratory frame to the frame fixed in the body. The laboratory frame may always be chosen as a right-handed frame but this choice might not always be available in the case of a frame fixed in the body. Since **z** are fixed in the body, not all their $3N - 3$ components are independent, for there must be three relations between them. Hence components of $\mathbf{z}_i$ must be writable in terms of $3N - 6$ independent internal coordinates $q_i, i = 1, 2, \ldots, 3N - 6$. Some of the q_i may be components of $\mathbf{z}_i$ but, generally, q_i are expressible in terms of scalar products of the $\mathbf{t}_i$ (and equally of the $\mathbf{z}_i$) since scalar products are the most general constructions that are invariant under orthogonal transformations of their constituent vectors. If only proper orthogonal transformations are considered, the scalar triple products are also invariants but they change sign under improper operations.

Equation (29) *defines* the Cartesian form of the variables in the frame fixed in the body by means of **C**. Thus, *any* orthogonal transformation of the translationally invariant coordinates (including inversion) leaves them, by definition, unchanged.

To express the translationally invariant differential operators in terms of the orientation and internal coordinates, we must obtain expressions for the partial derivatives of these coordinates with respect to the translationally invariant ones. There has been much previous work along these lines but most of it has been in the context of particular coordinate choices. However, both Chapuisat and his colleagues,$^{(1,2)}$ and Handy and his colleagues$^{(3,4)}$ among others,$^{(5-7)}$ have presented rather general and abstract accounts of the methodology. Additional references may be found in References 8,9, and 10.

To deal with the orientational variables, we note that

$$\frac{\partial}{\partial t_{\alpha i}}(\mathbf{C}^T\mathbf{C}) = \mathbf{0}_3 \tag{30}$$

because **C** is an orthogonal matrix and hence $\mathbf{C}^T\mathbf{C} = \mathbf{E}_3$. Therefore,

$$\frac{\partial \mathbf{C}^T}{\partial t_{\alpha i}}\mathbf{C} = \hat{\omega}^{\alpha i} \tag{31}$$

where $\hat{\omega}^{\alpha i}$ is a skew-symmetric matrix of the same form as equation (22), containing three independent elements $\omega_\gamma^{\alpha i}$. Using the form (24), equation (31) becomes

$$\frac{\partial \mathbf{C}}{\partial t_{\alpha i}} = \sum_\gamma \omega_\gamma^{\alpha i}\mathbf{C}\mathbf{M}^\gamma \tag{32}$$

We introduce the matrix with elements $\Omega_{\beta\gamma}^i$ such that

$$\omega_\gamma^{\alpha i} = \sum_\beta C_{\alpha\beta}\Omega_{\beta\gamma}^i \tag{33}$$

so that the elements of the matrix $\boldsymbol{\Omega}^i$ are functions of the internal coordinates only. Hence equation (32) becomes

$$\frac{\partial \mathbf{C}}{\partial t_{\alpha i}} = \sum_\beta (\mathbf{C}\mathbf{M}^\beta)(\mathbf{C}\boldsymbol{\Omega}^i)_{\alpha\beta} \tag{34}$$

Because **C** is a function of the ϕ_m only, it follows that

$$\frac{\partial \mathbf{C}}{\partial t_{\alpha i}} = \sum_{m=1}^{3} \frac{\partial \mathbf{C}}{\partial \phi_m}\frac{\partial \phi_m}{\partial t_{\alpha i}} \tag{35}$$

and by analogy with equations (30) to (32), it follows that

$$\frac{\partial \mathbf{C}}{\partial \phi_m} = \sum_\gamma (\mathbf{D}^{-1})_{m\gamma}\mathbf{C}\mathbf{M}^\gamma \tag{36}$$

where $(\mathbf{D}^{-1})_{m\gamma}$ is a function of the ϕ_m only and plays the same role in equation (36) that $\omega_\gamma^{\alpha i}$ does in equation (32).

Strictly speaking, since the elements of **C** in equation (34) are assumed to be functions of $\mathbf{t}_i$ while in equations (35) and (36) they are assumed to be functions of ϕ_m, a different symbol for **C** should be used in the second case. However, the usage is clear from the context and so no distinction will be made.

From equations (34) to (36), it follows that

$$\sum_{m=1}^{3}(\mathbf{D}^{-1})_{m\gamma}\frac{\partial\phi_m}{\partial t_{\alpha i}} = (\mathbf{C}\boldsymbol{\Omega}^i)_{\alpha\gamma}$$

so finally

$$\frac{\partial\phi_m}{\partial t_{\alpha i}} = (\mathbf{C}\boldsymbol{\Omega}^i\mathbf{D})_{\alpha m} \tag{37}$$

The process so far is, indeed, purely formal since **C** has not been specified in terms of the $\mathbf{t}_i$ or the ϕ_m.

A similar formal process establishes that

$$\frac{\partial q_k}{\partial t_{\alpha i}} = (\mathbf{C}\mathbf{Q}^i)_{\alpha k} \tag{38}$$

where the elements of $\mathbf{Q}^i$ are dependent only on internal variables because the q_k are functions only of scalar products of the $\mathbf{t}_i$.

This establishes the form for the Jacobian matrix for the transformation from the $(\boldsymbol{\phi}, \mathbf{q})$ to the $(\mathbf{t})$. In summary, the Jacobian matrix elements are

$$\frac{\partial\phi_m}{\partial t_{\alpha i}} = (\mathbf{C}\boldsymbol{\Omega}^i\mathbf{D})_{\alpha m} \tag{39}$$

$$\frac{\partial q_k}{\partial t_{\alpha i}} = (\mathbf{C}\mathbf{Q}^i)_{\alpha k} \tag{40}$$

In the foregoing equations, the elements of $\mathbf{Q}^i$ and of $\boldsymbol{\Omega}^i$ are dependent on internal variables only, whereas the elements of **C** and of **D** are functions of the Eulerian angles only.

Although not all the $z_{\beta i}$ can be linearly independent, they all possess derivatives with respect to the $t_{\epsilon j}$, which, from equations (29) and (34), have the form

$$\frac{\partial z_{\beta i}}{\partial t_{\epsilon j}} = (\mathbf{C}\boldsymbol{\Omega}^j\hat{\mathbf{z}}_i)_{\epsilon\beta} + C_{\epsilon\beta}\delta_{ij} \tag{41}$$

It is also sometimes possible to express the constraint conditions on the $z_{\beta i}$ in the form $f_m(\mathbf{z}) = 0$, $m = 1, 2, 3$ and hence as $f_m(\mathbf{C}^T\mathbf{t}) \equiv g_m(\mathbf{t}) = 0$, $m = 1, 2, 3$. In that case

$$\frac{\partial g_m}{\partial t_{\epsilon j}} = [\mathbf{C}(-\boldsymbol{\Omega}^j\mathbf{T} + \mathbf{S}^j)]_{\epsilon m} = 0$$

where

$$S^j_{\epsilon m} = \frac{\partial f_m}{\partial z_{\epsilon j}}, \qquad \mathbf{T} = \sum_{i=1}^{N-1}\hat{\mathbf{z}}_i^T\mathbf{S}^i$$

The derivative with respect to $z_{\epsilon j}$ is perfectly well defined in the usual way even though the $z_{\epsilon j}$ are not all independent variables because $f_m(\mathbf{z})$ is an explicit function of all of them. If **T** is non-singular, then one can write

$$\boldsymbol{\Omega}^i = \mathbf{S}^i\mathbf{T}^{-1} \tag{42}$$

This result was apparently first noticed by Sørensen.$^{(11)}$

The derivatives of the translationally invariant coordinates in terms of the orientation and internal coordinates are

$$\frac{\partial}{\partial\mathbf{t}_i} = \mathbf{C}\left(\boldsymbol{\Omega}^i\mathbf{D}\frac{\partial}{\partial\boldsymbol{\phi}} + \mathbf{Q}^i\frac{\partial}{\partial\mathbf{q}}\right) \tag{43}$$

where $\partial/\partial\boldsymbol{\phi}$ and $\partial/\partial\mathbf{q}$ are column matrices of 3 and $3N - 6$ partial derivatives, respectively, and $\partial/\partial\mathbf{t}_i$ are column matrices of 3 partial derivatives.

There are similar developments in the expressions associated with the inverse transformation, and the elements of the inverse Jacobian matrix are

$$\frac{\partial t_{\alpha i}}{\partial\phi_m} = (\mathbf{C}\hat{\mathbf{z}}_i\mathbf{D}^{-T})_{\alpha m} \tag{44}$$

$$\frac{\partial t_{\alpha i}}{\partial q_k} = (\mathbf{C}\tilde{\mathbf{Q}}^i)_{\alpha k} \tag{45}$$

where the elements of $\tilde{\mathbf{Q}}^i$ are functions of the internal coordinates alone.

The relationship between the Jacobian matrix and its inverse leads to the following expressions

$$\sum_{i=1}^{N-1}\hat{\mathbf{z}}_i^T\boldsymbol{\Omega}^i = \mathbf{E}_3 \qquad \sum_{i=1}^{N-1}\tilde{\mathbf{Q}}^{iT}\mathbf{Q}^i = \mathbf{E}_{3N-6}$$

$$\sum_{i=1}^{N-1}\hat{\mathbf{z}}_i^T\mathbf{Q}^i = \mathbf{0}_{3,3N-6} \qquad \sum_{i=1}^{N-1}\tilde{\mathbf{Q}}^{iT}\boldsymbol{\Omega}^i = \mathbf{0}_{3N-6,3} \tag{46}$$

and

$$\boldsymbol{\Omega}^i\hat{\mathbf{z}}_j^T + \mathbf{Q}^i\tilde{\mathbf{Q}}^{jT} = \delta_{ij}\mathbf{E}_3 \tag{47}$$

These expressions are helpful in the formal manipulations that lead to expressions for the operators in orientation and internal coordinates.

The symmetry properties of the internal and angular coordinates are not immediately apparent and they will be discussed separately from the discussion of operator forms. But it should be noted here that permutations will generally induce changes in both the internal and orientational coordinates. In particular, a change can be induced in an Eulerian angle that is expressible only in terms of the angles *and* the internal coordinates.

3.1 The angular momentum operator in a frame fixed in the body

The translationally invariant angular momentum operator becomes

$$\mathsf{L}(\mathbf{t}) = -\frac{\hbar}{i}|\mathbf{C}|\mathbf{C}\mathbf{D}\frac{\partial}{\partial\boldsymbol{\phi}} = |-\mathbf{C}|\mathbf{C}\mathsf{L}(\boldsymbol{\phi}) \tag{48}$$

where $|\mathbf{C}|$ is either $+1$ or -1 according to whether $\mathbf{C}$ corresponds to a proper rotation or to an improper rotation. This term arises because on the formal variable change (29)

$$\hat{\mathbf{t}}_i = |\mathbf{C}|\mathbf{C}\hat{\mathbf{z}}_i\mathbf{C}^T \tag{49}$$

There is at this stage an element of choice for the definition of the angular momentum in the frame fixed in the body, and in equation (48) it can be seen that we have chosen

$$\mathsf{L}(\boldsymbol{\phi}) = \frac{\hbar}{i}\mathbf{D}\frac{\partial}{\partial\boldsymbol{\phi}} \tag{50}$$

Often, indeed perhaps more usually, the negative of this operator is chosen. However, a little algebra shows that in either case $\mathsf{L}^2(\boldsymbol{\phi}) \equiv \mathsf{L}^2(\mathbf{t})$ and that $\mathsf{L}_z(\boldsymbol{\phi})$ and $\mathsf{L}_z(\mathbf{t})$ commute with L^2 so one can find a complete set of angular momentum eigenfunctions $|JMk\rangle$ such that

$$\begin{aligned}
\mathsf{L}^2(\mathbf{t})|JMk\rangle &= \mathsf{L}^2(\boldsymbol{\phi})|JMk\rangle = \hbar^2 J(J+1)|JMk\rangle \\
\mathsf{L}_z(\mathbf{t})|JMk\rangle &= \hbar M|JMk\rangle \\
\mathsf{L}_z(\boldsymbol{\phi})|JMk\rangle &= \hbar k|JMk\rangle
\end{aligned} \tag{51}$$

The functions $|JMk\rangle$ are often called *symmetric-top* eigenfunctions.

Choosing the angular momentum operator in the frame fixed in the body according to equation (50) means that the components of this operator obey the *standard* commutation conditions, so that the angular momentum eigenfunctions, $|JMk\rangle$ have the standard properties of those defined in Reference 12 or in Reference 13. Explicitly, if $\mathbf{C}$ is parameterized by the standard Euler angle choice made in these references, then

$$\begin{aligned}
|JMk\rangle &= \left(\frac{2J+1}{8\pi^2}\right)^{1/2}(-1)^k\mathcal{D}^{J*}{}_{M-k}(\boldsymbol{\phi}) \\
\mathcal{D}^{J*}{}_{M-k}(\boldsymbol{\phi}) &= \mathrm{e}^{iM\phi_1}d^J_{M-k}(\phi_2)\mathrm{e}^{-ik\phi_3}
\end{aligned} \tag{52}$$

where $\mathcal{D}^J$ is the standard Wigner matrix as defined by Brink and Satchler(12) or Biedenharn and Louck.(13) If the more usual choice of the negative of equation (50) is made, its components obey the celebrated anomalous commutation conditions, and the relevant symmetric-top functions are proportional to $\mathcal{D}^{J*}{}_{Mk}$. With the present choice, however, the step-up and step-down operators may be defined in the usual way as $L_\pm = L_x \pm iL_y$ and then

$$\begin{aligned}
\mathsf{L}_\pm(\mathbf{t})|JMk\rangle &= \hbar C^\pm_{JM}|JM\pm 1k\rangle \\
\mathsf{L}_\pm(\boldsymbol{\phi})|JMk\rangle &= \hbar C^\pm_{Jk}|JMk\pm 1\rangle
\end{aligned} \tag{53}$$

where the phase conventions are chosen as the standard Condon and Shortley ones(14) so that

$$C^\pm_{Jj} = [J(J+1) - j(j\pm 1)]^{1/2} \tag{54}$$

A more extended discussion of these matters can be found in Section 3.8 of Reference 13 and also in References 15 and 16.

It can be shown,(13,17) that, whatever the parametrization, for any $\mathbf{C}$ in $SO(3)$, the Wigner $\mathcal{D}^1$ matrix can be written as

$$\mathcal{D}^1 = \mathbf{X}^\dagger\mathbf{C}\mathbf{X} \tag{55}$$

with

$$\mathbf{X} = \begin{pmatrix} \dfrac{-1}{\sqrt{2}} & 0 & \dfrac{1}{\sqrt{2}} \\ \dfrac{-i}{\sqrt{2}} & 0 & \dfrac{-i}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix} \tag{56}$$

provided $C_{\alpha\beta}$ is ordered $\alpha, \beta = x, y, z$ and the indices on $\mathcal{D}^1$ run $+1, 0, -1$ across each row and down each column. For the present choice of operators, it may further be shown that

$$\begin{aligned}
|1Mk\rangle &= \left(\frac{3}{8\pi^2}\right)^{1/2}(-1)^k\mathcal{D}^{1*}_{M-k} = \left(\frac{3}{8\pi^2}\right)^{1/2}(\mathbf{X}^T\mathbf{C}\mathbf{X})_{Mk} \\
&= \left(\frac{3}{8\pi^2}\right)^{1/2}\mathbf{D}^1_{Mk}(\mathbf{C})
\end{aligned} \tag{57}$$

It should be emphasized that for any choice of Eulerian angle definition, it is always possible to construct another matrix $\mathbf{C}$ simply by multiplying the original choice by $-\mathbf{E}_3$. There is no choice of transformed Eulerian angles that will result in this other matrix. Thus, to specify the transformation completely, it is necessary to specify the Eulerian angles and $|\mathbf{C}|$, the parity of the transformation. If the original choice of matrix represents a proper rotation with parity $+1$, the other matrix represents a reflection with parity -1. It follows from equation (36) that both matrices give rise to the same matrix $\mathbf{D}$ so that from equation (48) $\mathsf{L}(\mathbf{t})$ is invariant under inversion, as is required. For the time being, we shall neglect this possibility and consider simply proper rotations so that attention will be confined to $SO(3)$.

3.2 The Hamiltonian in a frame fixed in the body

The complete kinetic energy operator may be written as

$$\mathsf{K}(\mathbf{q}) + \mathsf{K}(\boldsymbol{\phi}, \mathbf{q}) \tag{58}$$

The transformation of the translationally invariant kinetic energy operator from equation (17) into the coordinates $\boldsymbol{\phi}$ and $\mathbf{q}$ is long and tedious but the final result can be stated directly; as the derivation is mechanical, simply letting equation (43) operate on itself and summing over i and j, there is no need to go into details. The resulting operators are

$$\mathsf{K}(\boldsymbol{\phi}, \mathbf{q}) = \frac{1}{2}\left(\sum_{\alpha\beta} \kappa_{\alpha\beta}\mathsf{L}_\alpha \mathsf{L}_\beta + \hbar \sum_{\alpha} \lambda_\alpha \mathsf{L}_\alpha\right) \tag{59}$$

and

$$\mathsf{K}(\mathbf{q}) = -\frac{\hbar^2}{2}\left(\sum_{k,l=1}^{3N-6} g_{kl}\frac{\partial^2}{\partial q_k \partial q_l} + \sum_{k=1}^{3N-6} h_k \frac{\partial}{\partial q_k}\right) \tag{60}$$

$\boldsymbol{\kappa}$ is an inverse generalized inertia tensor defined as the 3×3 matrix

$$\boldsymbol{\kappa} = \sum_{i,j=1}^{N-1} \frac{1}{\mu_{ij}} \boldsymbol{\Omega}^{i^T} \boldsymbol{\Omega}^j \tag{61}$$

and

$$\lambda_\alpha = \frac{1}{i}\left(\nu_\alpha + 2\sum_{k=1}^{3N-6} \tau_{k\alpha}\frac{\partial}{\partial q_k}\right) \tag{62}$$

with the $3N - 6 \times 3$ matrix $\boldsymbol{\tau}$ defined as

$$\boldsymbol{\tau} = \sum_{i,j=1}^{N-1} \frac{1}{\mu_{ij}} \mathbf{Q}^{i^T} \boldsymbol{\Omega}^j \tag{63}$$

and

$$\nu_\alpha = \sum_{i,j=1}^{N-1} \frac{1}{\mu_{ij}} \left[\sum_\beta (\boldsymbol{\Omega}^{i^T} \mathbf{M}^\beta \boldsymbol{\Omega}^j)_{\beta\alpha} + \sum_{l=1}^{3N-6} \left(\mathbf{Q}^{i^T} \frac{\partial}{\partial q_l} \boldsymbol{\Omega}^j\right)_{l\alpha}\right] \tag{64}$$

The term (62) is associated with the Coriolis coupling and so no coordinate system can be found in which it will vanish.

The $3N - 6 \times 3N - 6$ matrix $\mathbf{g}$ is given by

$$\mathbf{g} = \sum_{i,j=1}^{N-1} \frac{1}{\mu_{ij}} \mathbf{Q}^{i^T} \mathbf{Q}^j \tag{65}$$

and

$$h_k = \sum_{i,j=1}^{N-1} \frac{1}{\mu_{ij}} \left[\sum_\beta (\boldsymbol{\Omega}^{i^T} \mathbf{M}^\beta \mathbf{Q}^j)_{\beta k} + \sum_{l=1}^{3N-6} \left(\mathbf{Q}^{i^T} \frac{\partial}{\partial q_l} \mathbf{Q}^j\right)_{lk}\right] \tag{66}$$

It is possible to choose a coordinate system in which this last term vanishes but, in general, it does not disappear. It might seem too that since h_k contains $\boldsymbol{\Omega}$, its precise form will depend on the way in which the embedded frame is defined. Some choice of embedding must, indeed, be made actually to construct h_k. However, h_k is independent of any particular choice of embedding.$^{(7)}$

The potential energy operator is

$$\mathsf{V}(\mathbf{q}) = \frac{e^2}{8\pi\epsilon_0} \sum_{i,j=1}^{N}{}' \frac{Z_i Z_j}{r_{ij}(\mathbf{q})}$$

while r_{ij} is defined just as in equation (19) but with $z_{\alpha k}(\mathbf{q})$ replacing $t_{\alpha k}$.

Although both $\mathsf{L}_z(\boldsymbol{\phi})$ and $\mathsf{L}_z(\mathrm{t})$ commute with L^2, only $\mathsf{L}_z(\mathbf{t})$ and L^2 commute with the Hamiltonian so that the eigenfunctions $\Psi(\mathbf{t})$ from equation (20) can be written in the form

$$\Psi(\mathbf{t}) \rightarrow \Psi^{J,M}(\boldsymbol{\phi}, \mathbf{q}) = \sum_{k=-J}^{+J} \Phi_k^J(\mathbf{q})|JMk\rangle \tag{67}$$

where the $|JMk\rangle$ are angular momentum eigenfunctions and where the internal coordinate function on the right-hand side cannot depend on M because, in the absence of a field, the energy of the system does not depend on M. Eigenfunctions of this kind form a basis for irreducible representations of $SO(3)$, as required.

3.3 The dipole operator in a frame fixed in the body

The dipole operator (26) is

$$\mathsf{d}(\mathbf{t}) = e\sum_{i=1}^{N-1} \tilde{Z}_i \mathbf{C}\mathbf{z}_i = e\mathbf{C}\mathsf{d}(\mathbf{q}) \tag{68}$$

Confining attention to $SO(3)$, it follows from equation (55) that

$$\mathbf{X}^{\dagger}\mathsf{d}(\mathbf{t}) = e\mathcal{D}^{1}\mathbf{X}^{\dagger}\mathsf{d}(\mathbf{q}) \tag{69}$$

It is not, however, the practice to work with the form $\mathbf{X}^{\dagger}\mathsf{d}$ but rather with the so-called 'spherical' form,

$$\mathsf{d}^{s} = \mathbf{X}^{T}\mathsf{d} \tag{70}$$

where, for example,

$$\mathbf{X}^{T}\mathbf{z} = \begin{pmatrix} -\dfrac{z_x + iz_y}{\sqrt{2}} \\ z_z \\ \dfrac{z_x - iz_y}{\sqrt{2}} \end{pmatrix} \tag{71}$$

Taking the complex conjugate of both sides of equation (69) gives

$$\mathsf{d}^{s}(\mathbf{t}) = \mathcal{D}^{1*}\mathsf{d}^{s}(\mathbf{q}) \tag{72}$$

with the column elements labelled $(\mathsf{d}^{s}_{+1}, \mathsf{d}^{s}_{0}, \mathsf{d}^{s}_{-1})$.

3.4 The Jacobian for the transformation to a frame fixed in the body

As the transformation (4) is linear, its Jacobian is simply a constant that can be ignored. The transformation from the $\mathbf{t}_i$ to the Eulerian angles and the internal coordinates is non-linear and has a Jacobian $|\mathbf{J}|^{-1}$ where $\mathbf{J}$ is the matrix constructed from the terms in equations (39) and (40). The non-linearity is a topological consequence of any transformation that allows rotational motion to be separated(18) and there is always some conformation of the particles that causes the Jacobian to vanish. Clearly where the Jacobian vanishes, the transformation is undefined. This failure manifests itself in the Hamiltonian by the presence of terms that diverge unless, acting on the wave function, they vanish. This can occur either by cancellation or by the wave function itself being vanishingly small in the divergent region.

The origin of these divergences is not physical: they arise simply as a consequence of the choice of coordinates. A particular choice can obviously preclude the description of a possible physical state of a system. Such states may be physically reasonable, but they simply cannot be described within the given coordinate choice.

The important point is that the non-linear transformation cannot be globally valid. As it has only local validity, one can at most derive a local Hamiltonian that is valid within a particular domain. According to general topological considerations,(18) one can construct a sequence of transformations that have common ranges of validity sufficient for passage from one to another to cover the whole space.

The volume element for integration is

$$\mathrm{d}\mathbf{t} = |\mathbf{J}|^{-1}\,\mathrm{d}\boldsymbol{\phi}\,\mathrm{d}\mathbf{q} \tag{73}$$

It is sometimes more convenient to construct the determinant of the metric derived from the terms (39) and (40), which will be equal to $|\mathbf{J}|^{-2}$ within a constant factor. The determinant is

$$|\mathbf{D}^{-1}|^{2}\begin{vmatrix} \boldsymbol{\kappa} & \boldsymbol{\tau}^{T} \\ \boldsymbol{\tau} & \mathbf{g} \end{vmatrix}^{-1} \tag{74}$$

where the matrices in the partitions are given by equations (61), (65), and (63). Within a constant factor,

$$|\mathbf{J}|^{-1} = |\mathbf{D}|^{-1}|\boldsymbol{\kappa}|^{-1/2}|\mathbf{g} - \boldsymbol{\tau}\boldsymbol{\kappa}^{-1}\boldsymbol{\tau}^{T}|^{-1/2} \tag{75}$$

It is the factor $|\mathbf{D}|^{-1}$ that is the angular part of the Jacobian, and in the standard parametrization, $|\mathbf{D}|^{-1} = \sin\phi_2$, as required for the usual interpretation of the matrix elements. The remaining terms in equation (75) are functions of q_k alone. It is perhaps worthwhile noticing that in the Podolsky approach to the construction of a frame fixed in the body, which is the approach used when moving from the classical Hamiltonian in coordinates other than the rectangular ones, directly to the quantum-mechanical Hamiltonian, it is the form of the Jacobian arising from equation (75) that is naturally used. The matter is discussed in Section 35b of Reference 19.

The choice is sometimes made to incorporate the internal coordinate part of the Jacobian (or some of it) into the definition of the Hamiltonian. This is a fairly familiar process when working in spherical polars, for example, where the radial volume element $r^2\,\mathrm{d}r$ can be reduced to $\mathrm{d}r$ by writing the trial wave function $\psi(r)$ as $r^{-1}P(r)$ and modifying the Hamiltonian to refer to $P(r)$. This modification changes the derivative terms in the operator by $\partial/\partial r \rightarrow (\partial/\partial r - 1/r)$ and so on but alters none of the multiplicative or $\partial/\partial\theta$ terms. The resulting Hamiltonian is often said to be in *manifestly Hermitian* form. Particular examples of this kind of construction can be found in References 20 and 21 while a general account is given in Section 35 of Reference 19. This process is often extremely useful in practice with specific coordinate choices; however, it does not simplify matters at the level of formal exposition, and in what follows, we shall *not* explicitly consider its incorporation. However, the fact that it can be incorporated, in whole or in part, should always be borne in mind when identifying operator forms. Thus, if the Jacobian was incorporated into the function on which the operator on the right-hand side of equation (43) was working, then it would have a changed form that is appropriate for working on what remains of the function when the Jacobian has been dealt with. Similarly, the forms of the kinetic energy operators would be modified.

The internal coordinates can be written as functions of the scalar products of the translationally invariant coordinates, and a symmetric matrix of all possible scalar products can be written as

$$\mathbf{S} = \mathbf{t}^T\mathbf{t}, \quad \text{so that} \quad S_{ij} = \mathbf{t}_i^T\mathbf{t}_j \tag{76}$$

Using equations (12) and (13), the scalar products for this set are related to the scalar products for a set $\mathbf{t}'$ by a congruent transformation

$$\mathbf{S}' = \mathbf{G}^T\mathbf{S}\mathbf{G} \tag{77}$$

It follows from this that any set of internal coordinates may be written completely in terms of any other set of internal coordinates within their common domain. It is not generally the case, however, that closed forms can be given for such a rewriting.

3.5 Alternative forms of the kinetic energy operator expressed in the frame fixed in the body

The internal coordinate part of the inverse metric matrix arising from equations (44) and (45) is

$$\begin{pmatrix} \mathbf{I} & \mathbf{y} \\ \mathbf{y}^T & \mathbf{f} \end{pmatrix} \tag{78}$$

The component matrices are

$$\mathbf{I} = \sum_{i,j=1}^{N-1} \mu_{ij}\hat{\mathbf{z}}_i^T\hat{\mathbf{z}}_j \tag{79}$$

and this matrix is clearly the form of the instantaneous inertia tensor in a frame fixed in the body, while

$$\mathbf{y} = \sum_{i,j=1}^{N-1} \mu_{ij}\hat{\mathbf{z}}_i^T\tilde{\mathbf{Q}}^j \qquad \mathbf{f} = \sum_{i,j=1}^{N-1} \mu_{ij}\tilde{\mathbf{Q}}^{iT}\tilde{\mathbf{Q}}^j \tag{80}$$

in which the matrix $\boldsymbol{\mu}$ is inverse to the matrix with elements defined in equation (18) and has elements

$$\mu_{ij} = \sum_{k=1}^{N} m_k[(\mathbf{V})^{-1}]_{ik}[(\mathbf{V})^{-1}]_{jk}, \quad i, j = 1, 2, \ldots, N-1 \tag{81}$$

By standard matrix manipulations,

$$\mathbf{f}^{-1} = (\mathbf{g} - \boldsymbol{\tau}\boldsymbol{\kappa}^{-1}\boldsymbol{\tau}^T) \qquad \mathbf{I}^{-1} = (\boldsymbol{\kappa} - \boldsymbol{\tau}^T\mathbf{g}^{-1}\boldsymbol{\tau})$$
$$\mathbf{g}^{-1} = (\mathbf{f} - \mathbf{y}^T\mathbf{I}^{-1}\mathbf{y}) \qquad \boldsymbol{\kappa}^{-1} = (\mathbf{I} - \mathbf{y}\mathbf{f}^{-1}\mathbf{y}^T) \tag{82}$$

and

$$\boldsymbol{\tau}\boldsymbol{\kappa}^{-1} + \mathbf{f}^{-1}\mathbf{y}^T = \mathbf{0}_{3N-6,3} \tag{83}$$

With these results, the kinetic energy operator is put into a form analogous to that found by Eckart$^{(22)}$ by introducing the Coriolis coupling operator

$$\boldsymbol{\pi} = \frac{\hbar}{i}\boldsymbol{\kappa}^{-1}\boldsymbol{\tau}^T\frac{\partial}{\partial\mathbf{q}} \tag{84}$$

The sum of the kinetic energy operators (59) and (60) may be rewritten as

$$\mathsf{K}_a(\boldsymbol{\phi}, \mathbf{q}) + \mathsf{K}_a(\mathbf{q})$$

with

$$\mathsf{K}_a(\boldsymbol{\phi}, \mathbf{q}) = \frac{1}{2}\left(\sum_{\alpha\beta}\kappa_{\alpha\beta}(\mathsf{L}_\alpha + \pi_\alpha)(\mathsf{L}_\beta + \pi_\beta) + \frac{\hbar}{i}\sum_{\alpha}\nu_\alpha\mathsf{L}_\alpha\right) \tag{85}$$

and

$$\mathsf{K}_a(\mathbf{q}) = -\frac{\hbar^2}{2}\left(\sum_{k,l=1}^{3N-6} f_{kl}^{-1}\frac{\partial^2}{\partial q_k\partial q_l} + \sum_{k=1}^{3N-6}\bar{h}_k\frac{\partial}{\partial q_k}\right) \tag{86}$$

in which

$$\bar{h}_k = h_k - \sum_{\beta}\left(\boldsymbol{\tau}^T\frac{\partial}{\partial\mathbf{q}}\right)_{\beta}(\boldsymbol{\kappa}^{-1}\boldsymbol{\tau}^T)_{\beta k} \tag{87}$$

3.6 Internal and orientational coordinates expressed directly in terms of the original coordinates

Clearly, any expressions for the angular and internal coordinates in terms of translationally invariant coordinates can be re-expressed using equation (4) in terms of the laboratory-fixed coordinates. Therefore, it is always possible to pass directly from laboratory-fixed coordinates to these coordinates without an explicit choice of translationally invariant coordinates. If this is done, the internal coordinate part of the Jacobian now has an extra $3N \times 3$ partition, which consists of the N 3×3

matrices, $M_T^{-1} m_i \mathbf{E}_3$ for $i = 1, 2, \ldots, N$, and there is a similar extension to the inverse Jacobian consisting of N repetitions of $\mathbf{E}_3$. The sums in equation (26) now extend up to N and the equivalent extension of reverse product form is

$$\boldsymbol{\Omega}^i \hat{\mathbf{z}}_j^T + \mathbf{Q}^i \tilde{\mathbf{Q}}^{jT} = \mathbf{E}_3(\delta_{ij} - M_T^{-1} m_i) \tag{88}$$

The extra requirements arising from the product of the enlarged Jacobian and its inverse are that the following relationships are satisfied as identities.

$$\begin{aligned} &\sum_{i=1}^{N} \boldsymbol{\Omega}^i = \mathbf{0}_3 \qquad \sum_{i=1}^{N} \mathbf{Q}^i = \mathbf{0}_{3,3N-6} \\ &\sum_{i=1}^{N} m_i \hat{\mathbf{z}}^i = \mathbf{0}_3 \qquad \sum_{i=1}^{N} m_i \tilde{\mathbf{Q}}^i = \mathbf{0}_{3,3N-6} \end{aligned} \tag{89}$$

They are easily seen to be satisfied as identities for any translationally invariant choice of angular and internal coordinates.

The metric and its inverse are constructed using $m_i^{-1}\delta_{ij}$ in place of $1/\mu_{ij}$ and $m_i \delta_{ij}$ in place of μ_{ij}, respectively. The metric matrix then becomes $3N \times 3N$ with an extra 3×3 block on the diagonal with elements M_T^{-1}, and similarly, the inverse metric has an extra 3×3 block with elements M_T. Only null blocks connect these to the rest of the matrix, and the components of the rest of the matrix generalize in an obvious way with sums over particle indices running to N rather than $N - 1$.

4 SYMMETRY PROPERTIES REALIZED IN A FRAME FIXED IN THE BODY

As noted at the end of our initial discussion of fixing a frame in the body, the symmetry properties of the angular and internal coordinates necessary for fixing are not at once apparent. Here we shall attempt to discuss these matters.

4.1 Rotation-reflection symmetry

The full rotation-reflection symmetry of the Hamiltonian is that of the orthogonal group in three dimensions, $O(3)$, but the symmetric-top functions (52) are a basis only for representations of the rotation group $SO(3)$, that is, parity is ignored. To introduce parity, we consider the appropriate extension by considering the construction of the angular functions using the orientation matrix $\mathbf{C}$. Using the elements of $\mathbf{D}^1$ from equation (57), the elements of the matrix $\mathbf{D}^2$ can be obtained by vector coupling

$$D^2_{mm'} = \sum_{ss'} \langle 11ss'|2m'\rangle D^1_{ps} D^1_{p's'}, \quad m = p + p'$$

in which $\langle 11ss'|2m'\rangle$ is a Clebsch–Gordan coefficient as defined in Reference 12. $\mathbf{D}^3$ can be constructed by coupling the elements of $\mathbf{D}^1$ and $\mathbf{D}^2$ and so on, at every stage coupling to the maximum allowed J value, the so-called *fully stretched* coupling scheme. Coupling the indices p and p' is also possible because (see Appendix 2 of Reference 17) the matrices $\mathbf{D}^J$ are strictly spherical double tensors. We do not bother to do this because we are uninterested in the z-component of angular momentum in the laboratory frame. The general matrix $\mathbf{D}^J$ can then be obtained directly in terms of the elements of $\mathbf{C}$. Hence, expressions for the angular momentum eigenfunctions for $\mathcal{D}^J$ can also be obtained (for details, see Section 6.19 of Reference 13). The relationship is

$$D^J_{mm'}(\mathbf{C}) = (-1)^{m'} \mathcal{D}^{J*}_{m\,-m'}(\mathbf{C}), \quad |\mathbf{C}| = +1$$

If the matrix $\mathbf{C}$ is replaced by the matrix product $\mathbf{CU}$ where $\mathbf{U}$ is also an orthogonal matrix, then from equation (57)

$$\begin{aligned} |1Mk\rangle &\rightarrow \left(\frac{3}{8\pi^2}\right)^{1/2} (\mathbf{X}^T\mathbf{CUX})_{Mk} \\ &= \left(\frac{3}{8\pi^2}\right)^{1/2} (\mathbf{X}^T\mathbf{CXX}^\dagger\mathbf{UX})_{Mk} \\ &= \sum_{n=-1}^{+1} |1Mn\rangle \mathcal{D}^1_{nk}(\mathbf{U}) \end{aligned} \tag{90}$$

so that the general result is

$$|JMk\rangle \rightarrow \sum_{n=-J}^{+J} |JMn\rangle \mathcal{D}^J_{nk}(\mathbf{U}) \tag{91}$$

in which $\mathcal{D}^J(\mathbf{U})$ is the matrix made up from the elements of $\mathbf{U}$ in exactly the same way that $\mathcal{D}^J$ is made up from the elements of $\mathbf{C}$. A precise account of how this is to be done is given in Section 6.19 of Reference 13. If $\mathbf{U}$ is a constant matrix, then $\mathcal{D}^J(\mathbf{U})$ is a constant matrix and equation (91) simply represents a linear combination. If $\mathbf{U}$ is a unit matrix, then $|JMk\rangle$ is invariant.

The group $O(3)$ is the direct product of the inversion group C_i with the special orthogonal group in three dimensions, $SO(3)$. The inversion group consists of the identity operator E and the inversion operator I. The operations of $SO(3)$ may be realized in three-dimensional coordinate space by proper 3×3 orthogonal matrices $\mathbf{R}$, and the inversion may be realized by $-\mathbf{E}_3$. Thus, for every matrix $\mathbf{R}$ in $SO(3)$, there is a companion matrix $-\mathbf{R}$ in $O(3)$. The matrix $-\mathbf{R}$ in general represents a reflection such that if a proper rotation by π is performed about the normal to the reflection plane and this operation is followed by the inversion, then the matrix $-\mathbf{R}$ results. From the foregoing analysis, because of the fully stretched form of the coupling, given a Wigner matrix composed from an orthogonal matrix $\mathbf{R}$,

$$\mathcal{D}^J(-\mathbf{R}) = (-1)^J \mathcal{D}^J(\mathbf{R}) \tag{92}$$

so the matrices constructed in this way provide irreducible representations of even parity for even J but of odd parity for odd J. Thus, in a colloquial sense at least, they provide only half the representations that there should be for $O(3)$, for there should as well be representations of odd parity for even J and of even parity for odd J since the group manifold consists of two disconnected but isomorphic sheets. This defect can be remedied, however, by following the work of Biedenham and Louck$^{(13)}$ and of Ezra$^{(17)}$ and defining

$$\mathcal{D}^{0J}(\mathbf{R}) = \mathcal{D}^J(\mathbf{R}) \qquad \mathcal{D}^{1J}(\mathbf{R}) = |\mathbf{R}|\mathcal{D}^J(\mathbf{R}) \tag{93}$$

where $|\mathbf{R}|$ denotes the determinant of $\mathbf{R}$. Thus, it follows that

$$\mathcal{D}^{rJ}(-\mathbf{R}) = (-1)^{r+J}\mathcal{D}^{rJ}(\mathbf{R}), \quad r = 0, 1 \tag{94}$$

The angular momentum eigenfunctions are generalized to include parity as

$$|JMkr\rangle = |\mathbf{C}|^r |JMk\rangle \tag{95}$$

then it is easily shown that under the change $\mathbf{C} \to \mathbf{CU}$, equation (91) generalizes to

$$|JMkr\rangle \to \sum_{n=-J}^{+J} |JMnr\rangle \mathcal{D}^{rJ}_{nk}(\mathbf{U}) \tag{96}$$

This establishes the position of the matrices $\mathcal{D}^{rJ}$ as representation matrices for the general orthogonal transformation in three dimensions, and, in particular, if $\mathbf{U} = -\mathbf{E}_3$, then $\mathcal{D}^{rJ}(-\mathbf{E}_3) = (-1)^{r+J}\mathbf{E}_3$, as is required.

The underlying integral for the normalization of $|JMkr\rangle$ must now extend over both sheets of $O(3)$ and is$^{(13)}$

$$\int \mathcal{D}^{r'J'*}_{M'k'}(\mathbf{C})\mathcal{D}^{rJ}_{Mk}(\mathbf{C})|\mathbf{D}|^{-1}\,\mathrm{d}\boldsymbol{\phi} + \int \mathcal{D}^{r'J'*}_{M'k'}(-\mathbf{C})\mathcal{D}^{rJ}_{Mk}(-\mathbf{C})|\mathbf{D}|^{-1}\,\mathrm{d}\boldsymbol{\phi} \tag{97}$$

where $|\mathbf{D}|^{-1}$ is the angular part of the Jacobian and the integrals are each over the whole range of the Eulerian angles. If $r' = r$, then both integrals are the same and each has the value $\delta_{J'J}\delta_{M'M}\delta_{k'k}8\pi^2/(2J+1)$, whereas if $r' \neq r$, then both integrals have the same absolute value but opposite signs and hence they cancel. Thus, the generalized rotation-reflection eigenfunctions are orthonormal according to

$$\langle J'M'k'r' \mid JMkr\rangle = \delta_{J'J}\delta_{M'M}\delta_{k'k}\delta_{r'r} \tag{98}$$

In a discussion of inversion and parity towards the end of Chapter 19 of his book '*Group Theory*',$^{(23)}$ Wigner notes that in two-body and three-body systems (and in these systems only), it is possible to realize the effect of an inversion by means of a sequence of proper rotations because each of these cases have rather special features. Thus, the matrix $\mathbf{C}$ that is used to transform to the coordinate system fixed in the body can be chosen in the three-body case such that all three particles lie in a plane. If that plane is, say, the x- y one, then the z-coordinates of the particles will all be zero and the effect of an inversion can be achieved by performing a proper rotation by π about the z-axis. Two-body systems have not been considered for reasons explained earlier but three-body systems have not, so far, been excluded. However, the only genuinely three-body systems of interest are such systems as the helium atom and the hydrogen molecule ion, and these are best dealt with by quite special methods that are specific to each problem. Thus, three-body systems can also be ignored without much loss of generality. To do so is not to ignore triatomic molecules, because in these systems there will be four or more particles and at least one electron must be present for binding. Thus, the foregoing discussion can be regarded as the general treatment of parity for our purposes.

In the discussion of internal coordinates made earlier in Section 3, it was noted that internal coordinates composed from scalar triple products of translationally invariant coordinates would not be used in the present work since it was desired that the internal coordinates should be invariant not only under rotations but under rotation reflections too. This seems the sensible thing to do because it makes the most complete separation possible between the internal and orientation parts of the wave function, but it is not a choice that is universally made.

It is now strictly necessary to extend equation (67) as

$$\Psi^{J,M}(\mathbf{t}) \to \Psi^{J,M,r}(\boldsymbol{\phi}, \mathbf{q}) = \sum_{k=-J}^{+J} \Phi^{J,r}_k(\mathbf{q})|JMkr\rangle \tag{99}$$

This form allows for the possibility that states of different parity can, in principle, have different energies. There are, however, no parity-dependent terms in the Hamiltonian, so that there is no reason to expect that the functions $\Phi_k^{J,r}(\mathbf{q})$ that differ just in r value are in any way different. Thus, the energies of such a parity pair would be degenerate. This degeneracy must however be 'accidental', in the sense that it is not due to $O(3)$ symmetry. This is because $O(3)$ is the direct product $C_i \times SO(3)$, so that there will be two distinct irreducible representations of $O(3)$ for every representation of $SO(3)$. This is precisely analogous to the way in which distinct g and u representations arise in point groups such as C_{6h} or D_{6h} that are direct products $C_i \times C_6$ or $C_i \times D_6$. The fact that the two representations are distinct means that there is no group theoretical reason to suppose that the two states $|JMkr\rangle$ for $r = 0, 1$ should be degenerate.

4.2 Rotation reflections defined in the frame fixed in the body

Any chosen set of translationally invariant coordinates can be re-expressed in terms of another choice of the matrix that fixes a frame in the body according to

$$\mathbf{t} = \mathbf{C}\mathbf{z} \rightarrow \overline{\mathbf{C}}\overline{\mathbf{z}}$$

with

$$\overline{\mathbf{C}} = \mathbf{C}\mathbf{R}^T, \qquad \overline{\mathbf{z}} = \mathbf{R}\mathbf{z} \tag{100}$$

and where $\mathbf{R}$ is an orthogonal matrix whose elements are at most functions of the internal coordinates q_k. Clearly, the matrix $\mathbf{R}$ can be chosen to produce any other frame that is desired from any given frame fixed in the body. Such a change, while changing the $\mathbf{z}$ as given earlier, will not change the internal coordinates as these depend only on scalar products of the $\mathbf{t}_i$. The changes induced in the dipole operator by these transformations are perfectly apparent and will not be explicitly considered but the derivative operators do need attention. By retaining the original choice of Eulerian angles and internal coordinates, it can readily be shown that

$$\frac{\partial}{\partial \mathbf{t}_i} = \overline{\mathbf{C}}\left(\overline{\boldsymbol{\Omega}}^i \overline{\mathbf{D}} \frac{\partial}{\partial \boldsymbol{\phi}} + \overline{\mathbf{Q}}^i \frac{\partial}{\partial \mathbf{q}}\right) \tag{101}$$

Here

$$\overline{\boldsymbol{\Omega}}^i = |\mathbf{R}|\mathbf{R}\boldsymbol{\Omega}^i\mathbf{R}^T \tag{102}$$

$$\overline{\mathbf{D}} = |\mathbf{R}|\mathbf{R}\mathbf{D} \tag{103}$$

and

$$\overline{\mathbf{Q}}^i = \mathbf{R}\mathbf{Q}^i \tag{104}$$

so that

$$\overline{\mathsf{L}}(\boldsymbol{\phi}) = \frac{\hbar}{i}|\mathbf{R}|\mathbf{R}\mathbf{D}\frac{\partial}{\partial \boldsymbol{\phi}} = |\mathbf{R}|\mathbf{R}\mathsf{L}(\boldsymbol{\phi}) \tag{105}$$

Notice that in this form the components of $\overline{\mathsf{L}}$ do not commute with $\partial/\partial q_k$ unless it happens that $\mathbf{R}$ is a constant matrix. It would be possible, in principle, to define a new set of Eulerian angles in which the angular components of $\overline{\mathsf{L}}$ can be expressed, so that they can commute with $\partial/\partial q_k$. However, the present form is the one most useful for our purposes. Carrying these changes through to the construction of the kinetic energy operator, it turns out that $\mathsf{K}(\mathbf{q})$ is invariant while $\mathsf{K}(\boldsymbol{\phi}, \mathbf{q})$ becomes

$$\frac{1}{2}\left(\sum_{\alpha\beta}\overline{\kappa}_{\alpha\beta}\overline{\mathsf{L}}_\alpha\overline{\mathsf{L}}_\beta + \hbar\sum_\alpha \overline{\lambda}_\alpha\overline{\mathsf{L}}_\alpha\right) \tag{106}$$

where

$$\overline{\boldsymbol{\kappa}} = \mathbf{R}\boldsymbol{\kappa}\mathbf{R}^T, \quad \overline{\boldsymbol{\tau}} = |\mathbf{R}|\boldsymbol{\tau}\mathbf{R}^T, \quad \overline{\boldsymbol{\nu}} = |\mathbf{R}|\boldsymbol{\nu}\mathbf{R}^T$$

and so

$$\overline{\lambda}_\alpha = |\mathbf{R}|\sum_\beta R_{\alpha\beta}\lambda_\beta$$

When $\mathbf{R} = -\mathbf{E}_3$ and so represents a simple inversion, $\mathsf{K}(\boldsymbol{\phi}, \mathbf{q})$ remains invariant as would have been expected from our earlier discussion.

Any changes induced in $\mathsf{K}(\boldsymbol{\phi}, \mathbf{q})$ by $\mathbf{R}$ are in form alone. All that has happened is that the axes about which the angular momentum is defined have been changed. But since the original choice was one of convention, the changes are of no physical significance. However, one particular choice might be much better than another for the purposes of approximate calculation.

The invariance of h_k in equation (60) is, at first sight, surprising because it apparently depends, via $\boldsymbol{\Omega}^i$, on the choice of Eulerian angles. In fact, since it arises from terms that are scalar products of derivatives, it cannot actually so depend, as has been explicitly demonstrated. That the h_k in equation (66) do not depend in any way on the embedding choice, whereas the ν_α do, is consistent with these results. This invariance has interesting consequences when considering only states with $J = 0$. One can then choose any convenient embedding to derive the $\boldsymbol{\Omega}^i$ and compute both expressions using it. Perhaps the easiest one to choose is a three-particle one, although, in general, one would have to re-express the internal coordinates chosen with this embedding in terms of the ones chosen for the actual problem. This observation is entirely consistent with the observation made by Lukka,(7) that a purely conventional choice of angular variables is sufficient to derive the rotationally invariant part of the kinetic energy operator.

While considering invariances of this kind, it is perhaps appropriate to notice here too that, in principle, once the part of the Hamiltonian independent of the Eulerian angles has been obtained in any set of internal coordinates, it may be transformed to any other chosen set of internal coordinates. However, since the relationship between the two sets of internal coordinates will usually be non-linear and not invertible in closed form, this observation is worth much less in practice than it is in theory.

4.3 Permutational symmetry

We now consider the behaviour of both the internal coordinates and the Eulerian angles under the permutation of identical particles. Using equation (16), it is seen that a permutation

$$\mathcal{P}\mathbf{t} = \mathbf{tH} = \mathbf{t}' \tag{107}$$

and using equation (76) it is seen that

$$\mathbf{S}' = \mathbf{H}^T\mathbf{SH} \tag{108}$$

where the matrices comprise the scalar products of the translationally invariant coordinate before and after permutation.

By making the functional dependencies explicit, equation (29) may be written as

$$\mathbf{t} = \mathbf{C}(\boldsymbol{\phi})\mathbf{z}(\mathbf{q}) \tag{109}$$

and using equations (107) and (108), two different expressions for the permuted translationally invariant coordinates may be obtained. The first follows at once from equations (109) and (107)

$$\mathbf{t}' = \mathbf{tH} = \mathbf{C}(\boldsymbol{\phi})\mathbf{z}(\mathbf{q})\mathbf{H} \tag{110}$$

and this gives the $\mathbf{t}'_i$ as functions of ϕ and $\mathbf{q}$.

Alternatively, the Eulerian angles and the internal coordinates can be expressed directly as functions of $\mathbf{t}$ and hence of $\mathbf{t}'$ according to

$$\phi_m(\mathbf{t}) \to \phi_m(\mathbf{tH}^{-1}) = \overline{\phi}_m(\boldsymbol{\phi}, \mathbf{q}) \tag{111}$$

and

$$q_k(\mathbf{S}) \to q_k(\mathbf{H}^{-T}\mathbf{SH}^{-1}) = \overline{q}_k(\mathbf{q}) \tag{112}$$

To avoid overloading the notation, the convention has been adopted, in which the transformed function is indicated as induced from the original function by the inverse transformation of the original variables.

Notice again that the effect of the permutation on q_k can at most produce a function of q_k. This follows from equation (77) that shows that any of the collection of scalar products in one set of translationally invariant coordinates is related by a congruent transformation to the collection of scalar products of the other set. Thus, internal coordinates of one kind must be functions of internal coordinates of the other. However, the effect of the permutation on ϕ_m can produce a function of both the ϕ_m and the q_k. If the permuted internal coordinates and Eulerian angles are now used in equation (109), the resulting expression will be for the permuted translation-free variables. Thus,

$$\mathbf{t}' = \mathbf{C}[\overline{\boldsymbol{\phi}}(\boldsymbol{\phi}, \mathbf{q})]\mathbf{z}[\overline{\mathbf{q}}(\mathbf{q})] \tag{113}$$

so that

$$\mathbf{t}' = \overline{\mathbf{C}}(\boldsymbol{\phi}, \mathbf{q})\overline{\mathbf{z}}(\mathbf{q}) \tag{114}$$

On equating equations (110) and (114), it follows that

$$\overline{\mathbf{z}} = \overline{\mathbf{C}}^T\mathbf{CzH} \tag{115}$$

Naturally, some care must be taken about the domain in which the orthogonal matrix $\overline{\mathbf{C}}^T\mathbf{C}$ exists but since the foregoing expression can be at most a function of the internal coordinates, it follows that, where it exists, its elements are, at most, functions of the internal coordinates. Denoting this matrix by $\mathbf{U}$ (and from now on, since they will always be the original ones fixed in the body, the variables will not be explicitly given), it follows that

$$\overline{\mathbf{z}} = \mathbf{UzH} \tag{116}$$

and

$$\overline{\mathbf{C}} = \mathbf{CU}^T \tag{117}$$

giving a relationship (albeit implicit) between the permuted and unpermuted variables fixed in the body. It is as well to state explicitly that there will be such a relationship for every distinct permutation, and therefore the matrices should strictly carry a designation to indicate which of the permutations is being considered. But that would be to overload the notation in a way that is not necessary here and so it will not be done.

Now that these relationships have been established, the effects of a permutation on the various parts of the wave function must now be worked out. Using the convention mentioned earlier, the variable change (116) will be

$$\mathbf{z} \to \mathbf{U}^T\mathbf{z}\mathbf{H}^{-1} \tag{118}$$

while equation (117) will be

$$\mathbf{C} \to \mathbf{CU} \tag{119}$$

when considering the change in a function upon the change of variables. Thus, the angular eigenfunctions change under permutations according to equation (96).

It is rather difficult to say anything precise about the change induced in q_k under permutation. The internal coordinates are expressible entirely in terms of scalar products and they are invariant under inversion, which simply causes the $\mathbf{t}_i$ to change sign. So it is only the permutation group and not the permutation-inversion group that is relevant here. The scalar products of $\mathbf{t}_i$ are identical to the scalar products of $\mathbf{z}_i$ and the change is that given in equation (112), namely,

$$\mathbf{q}(\mathbf{S}) \to \mathbf{q}(\mathbf{H}^{-T}\mathbf{S}\mathbf{H}^{-1}) \tag{120}$$

where the notation of equation (118) has been used and where $\mathbf{S}$ is regarded as a function of q_k. However, the result has no general form and so the best that can be said is that a permutation of particles induces a general function change

$$\Phi_k^{J,r}(\mathbf{q}) \to \Phi'^{J,r}_k(\mathbf{q}) \tag{121}$$

where the precise nature of the function change depends on the permutation, the chosen form of the internal coordinates, and on the chosen functional form. Thus, the general change induced in equation (99) by $\mathcal{P}$ is

$$\begin{aligned}\Psi^{J,M,r}(\boldsymbol{\phi}, \mathbf{q}) &\to \sum_{k=-J}^{+J} \sum_{n=-J}^{+J} \mathcal{D}^{rJ}_{nk}(\mathbf{U})\Phi'^{J,r}_k(\mathbf{q})|JMnr\rangle \\ &= \sum_{n=-J}^{+J} \overline{\Phi}^{J,r}_n(\mathbf{q})|JMnr\rangle \end{aligned} \tag{122}$$

From the discussion in Section 4.1 the function (99) should carry an additional label $\mathbf{s}$ to specify to which irreps of the various symmetric groups in the problem it belongs. If the function is such that it belongs to a one-dimensional irrep of the symmetric group containing the permutation $\mathcal{P}$, then the resulting function (122) can differ from the original one by at most a sign change. In the case of a multidimensional representation, the resulting function (122) will be at most a linear combination of the set of degenerate functions providing a basis for the irrep. So, despite possible coordinate mixing, there are no difficulties in principle. However, in practice, one must construct approximate wave functions that are not immediately adapted to the permutational symmetry of the problem and that must be explicitly adapted by, for example, the use of projections. In these circumstances, coordinate mixing can cause tremendous complications. The expression (122) will clearly be very difficult to handle for not only will a $\mathbf{U}$ be difficult to determine but it must be found for each distinct permutation of the identical particles and in a problem of any size there will be a large number of such permutations.

It should be noted here that this coupling of rotations by the permutations can mean that certain rotational states do not occur because they cannot satisfy the correct symmetry requirements under the permutation of identical particles; whether this is the case has to be determined in any particular occurrence by the changes induced according to equation (122), and this would, in general, be exceptionally tricky. However, Ezra(17) has discussed the problem in detail in some special cases. This possibility is relevant in assigning statistical weights to rotational states.

An account of the changes induced in the various operators by the permutations is much the same as that given in Section 4.2 in describing rotations in a frame fixed in the body. The only additional complications arise from the presence of $\mathbf{H}$ in equation (116) as compared with the second term in equation (100). In fact, this matrix takes care of the permutational invariance of the quantities like $\boldsymbol{\mu}^{-1}$ that arise from the translationally invariant forms; otherwise the algebra is the same as that used in Section 4.2.

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