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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, Advances in Chemical Physics, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
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MOLECULAR PROPERTIES
OBSERVED AND COMPUTED

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I. INTRODUCTION

Atoms and molecules are the building blocks of all matter: solid, liquid, or gaseous. If we are to understand bulk matter, its property, and its reactions in detail, we need to know explicitly the static and dynamic structure of molecules. To be sure, explicit knowledge of the properties and interactions of molecules, although essential, is not enough if we are to understand bulk matter in detail. We consider here the electronic, vibrational, and rotational energy structure of isolated molecules, including their fine and hyperfine structure, as well as the interactions of molecules with external electric and magnetic fields. We base our treatment on the extensive theory that has been developed for the interpretation of molecular spectra,\(^1\) and hope to develop analogous expressions amenable to computation from first principles.

1
Much information about the rovibronic and fine structure of molecules has been obtained through extensive spectroscopic studies. Qualitative theoretical understanding of the observed effects has advanced enormously and has contributed significantly to the development and refinement of quantum mechanics, the fundamental theory for our understanding of atomic and molecular phenomena. Equally great strides have been made recently, with the advent of electronic computers, in obtaining detailed molecular structure information through \textit{ab initio} quantum-mechanical calculations. Nevertheless, there is still a great gap between the detail observed and the information obtained directly from theory, where heretofore the major effort had been focused on the calculation of electronic wave functions. The complexity of the problem to compute accurate, correlated electronic wave functions and energies has tended to obscure the importance of using such wave functions and energies in the evaluation of various molecular properties. Even the development of the theoretical basis for such calculations, which is fraught with many intricate complexities, seems rather incomplete, in spite of some notable, isolated efforts. We hope to give an extensive and consistent treatment in the direction of such a development.

To be sure, there is little need for computing molecular properties if they have been determined spectroscopically or are easily accessible to observation, except for gauging a theory, a computational method, or the accuracy of a computed wave function. However, there is a host of information about the structure of molecules, important to the understanding of their interactions and reactions, which is difficult or impossible to obtain from experiment. Spectroscopy is and will remain superior in yielding quantitative information about the structure, the potential energy surface, and the coupling terms of stable isolated molecules in the vicinity of their nuclear equilibrium conformation in the electronic ground state. Highly reactive molecules, free radicals, or electronically excited species, many of which are important in molecular interactions and reactions, are much more difficult to investigate experimentally. It is almost impossible experimentally to obtain information about the potential energy surface or coupling terms for repulsive electronic states (i.e., energy surfaces which have no strong minima); equally inaccessible is information for structures far removed from their equilibrium conformation. However, these quantities play a significant role in molecular interactions and reactions. It is here where a quantitative theoretical study is of extreme value and yields information complementary to that obtainable experimentally. To this end we hope to contribute by detailing formulas for the computation of various molecular properties analogous to the different spectroscopic constants. Even in those cases where spectra can be observed readily, quantitative studies of
the coupling effects are of value in aiding interpretation of the observed energy differences.

To accomplish and structure the task ahead, we present in Section II our understanding of the adiabatic approximation. This puts the electronic Schrödinger equation and potential surface into context; Section III gives a brief review of the state of the art of obtaining solutions to this part of the problem. In Section IV we discuss symmetry aspects of the potential energy surface, Jahn–Teller and Renner–Teller splittings, classification of electronic wave functions, and eigenfunctions of the angular momentum operator. In addition, we introduce, with the Eckart conditions, internal, normal coordinates. With this the stage is set to deal explicitly in Section V with the separation of translation, rotation, vibration, and electronic motion on the basis of the adiabatic formulation, which permits us to trace in detail the origin and form of the various coupling terms. Section VI gives a brief overview of general aspects used in the interpretation and assignment of high-resolution molecular spectral data.

General aspects needed for the theoretical derivation of molecular properties are presented in Section VII, with the details given in Appendixes 2 and 3. Here we consider the symmetry classifications of the coupling terms and perturbations, which leads naturally to the introduction of symmetry-group coupling coefficients and reduced matrix elements. These are analogous to Clebsch–Gordan coefficients and reduced matrix elements of tensor operators for the infinite rotation group. With this the theoretical background is prepared to present in Section VIII explicit formulas for the calculation of molecular properties as they are derived from the relativistic Hamiltonian of the whole molecule. This Hamiltonian and its formal separation is detailed in Appendix 1. The formulas presented give the properties in analogy to the experimentally determined spectroscopic constants. The latter, however, are state-dependent, while the formulas for the properties derived here are obtained as a function of the internal coordinates. This is theoretically more sound and should be advantageous for detailed computations. The fundamental differences that arise between the linear and nonlinear cases are pointed out separately in the places where such differences occur. Finally, in Section IX we review briefly the possibilities of calculating the properties for which we have detailed the formulas and reference some of the computations already carried out successfully.

II. ADIABATIC SEPARATION

The stationary state \( I \) of a molecule in its quantum-mechanical description is completely characterized by the wave function \( \Psi_I(\mathbf{Q}, \mathbf{q}) \), which is a
solution of the time-independent Schrödinger equation

$$\{ \mathcal{H}(\mathcal{Q}, q) - E_I \} \Psi_I(\mathcal{Q}, q) = 0 \quad (\text{II.1})$$

Here the Hamiltonian and the wave function depend on all nuclear and electronic coordinates, $\mathcal{Q}$ and $q$, respectively, including spin, in a space fixed frame. The Hamiltonian may contain static external electric and magnetic fields as well as relativistic couplings between electrons and nuclei, at least in a Pauli-type approximation. To achieve a separation of nuclear and electronic motion, we reduce the problem of solving (II.1) using, following Born, the ansatz

$$\Psi_I(\mathcal{Q}, q) = \sum_n \psi_n(\mathcal{R}, r) \theta_{nl}(\mathcal{R}, \mathcal{Q}) \quad (\text{II.2})$$

which requires some explanation. The sum is over electronic states represented by $n$, the collection of electronic quantum numbers and characterized through the electronic wave function $\psi_n(\mathcal{R}, r)$, which depends explicitly on the collection of electron coordinates $r$ and parametrically on the internal nuclear coordinates $\mathcal{Q}$. This function is a solution of the electronic Schrödinger equation

$$\{ \mathcal{H}_e(\mathcal{R}, r) - V_n(\mathcal{R}) \} \psi_n(\mathcal{R}, r) = 0 \quad (\text{II.3})$$

which may include relativistic as well as external electric and magnetic field effects. However, it depends on coordinates (and spin) in a molecular fixed frame, and the $\mathcal{R}$ dependence is parametric (i.e., there are at most multiplicative operators of $\mathcal{R}$ in $\mathcal{H}_e$). The function $\theta_{nl}(\mathcal{R}, \mathcal{Q})$ is less straightforward. It is the function component in the electronic state $n$ of the nuclear motion function corresponding to state $I$ of the molecule. It is independent of the electronic coordinates. Its dependence on the molecular fixed frame internal coordinates $\mathcal{R}$ as well as on the space fixed coordinates of the nuclei $\mathcal{Q}$ is to signify that it contains the translation of the center of mass as well as the rotation of the coordinate frame, which affords transformation from the space fixed to the molecular fixed frame.

We postpone to Section V a more detailed and specific discussion and substitute the right-hand side of (II.2) for $\Psi_I$ in (II.1), left-multiply with $\psi_*^*(\mathcal{R}, r)$ and integrate over the electronic coordinates. We obtain, considering (II.3),

$$(X_{mm} + V_m - E_I) \theta_{nl} = - \sum_n X_{mn} \theta_{nl} \quad (\text{II.4})$$
for all \( m \). This separation is exact, inasmuch as the sum in (II.2) is complete; however, it is rather formal. All the coupling between electronic and nuclear motion is hidden in the matrix elements, which may be written formally as

\[
X_{mn} = \langle \psi_m(\mathbf{R}, \mathbf{r})| \hat{\mathcal{H}}(\mathbf{Q}, \mathbf{q}) - \hat{\mathcal{H}}_e(\mathbf{R}, \mathbf{r})| \psi_n(\mathbf{R}, \mathbf{r}) \rangle_r
\]

with the integration implied over the electronic coordinate, \( r \), in the molecule fixed frame. Obviously, neither the integration nor the operator difference can be carried out without first transforming \( \hat{\mathcal{H}}(\mathbf{Q}, \mathbf{q}) \) to the molecular fixed frame; that is, \( \hat{\mathcal{H}}(\mathbf{Q}, \mathbf{q}) \) needs to be transformed first with those parts of \( \theta_{nj}(\mathbf{R}, \mathbf{Q}) \) that effect this transformation and which should be independent of \( n \), depending only on the instantaneous nuclear coordinate \( \mathbf{R} \) and the state quantum numbers collected in \( I \), especially translational energy, the total angular momentum, and its projection on a space fixed axis. This transformation will depend on the particular basis chosen and will be discussed in detail in Section V.

The conventional adiabatic approximation is obtained from (II.4) by neglecting the right-hand side and by using in \( X_{mn} \) only the operator for the nuclear kinetic energy in a molecule fixed frame. Then \( \theta_{nj} \) will be a function of \( \mathbf{R} \), the internal nuclear coordinates only; however, the potential may then be amended by a centrifugal term. We will not elaborate on this.

Since we will desire the coupling terms, we need (II.4) fully or at least with a truncated sum of type (II.2).

**III. THE ELECTRONIC EQUATION**

The solutions to the electronic Schrödinger equation, (II.3), are the basis for the adiabatic approximation; they define the potential in which the nuclei move. The potentials, as well as the electronic wave functions, are required to solve the problem for the nuclear motion in general. In order to define the terms needed later we detail here briefly the electronic Schrödinger equation and sketch structure and methods for solving it approximately.

For a molecule with \( N \) nuclei and \( n \) electrons, the electronic Hamiltonian of (II.3) may be expressed in general as a constant term plus a sum of one- and two-electron operators:

\[
\hat{\mathcal{H}}_e(\mathbf{R}, \mathbf{r}) = K(\mathbf{R}) + \sum_i^n h(\mathbf{R}, \mathbf{r}_i) + \sum_{i<j}^n g(\mathbf{r}_i, \mathbf{r}_j)
\]

(III.1)

where the constant term, which represents the nuclear–nuclear repulsion,
and the one-electron terms, which contain the electron–nuclear attraction, depend parametrically on the internal coordinates represented by \( \mathcal{R} \).

The individual terms in \((111.1)\) may still include contributions due to static external electric or magnetic fields as well as relativistic effects. The nuclear and electronic position vectors \( \mathcal{R} \) and \( r \), respectively, should then be thought of as containing the spin coordinate in addition to the spatial coordinate in a molecular fixed frame. In general, however, the field-free, nonrelativistic equation is solved explicitly (the other effects to be added later perturbatively), so we will focus for the moment on it and have in atomic units

\[
h(\mathcal{R}, r) = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} Z_\alpha r_{\alpha}^{-1}
\]

and

\[
g(r_i, r_j) = r_{ij}^{-1}
\]

The nuclear–nuclear repulsion term

\[
K(\mathcal{R}) = \sum_{\alpha < \beta} Z_\alpha Z_\beta r_{\alpha \beta}^{-1}
\]

is independent of the electronic coordinates. It remains constant and can be disregarded here, to be added whenever appropriate to the electronic energy, \( \epsilon(\mathcal{R}) \), to give the potential

\[
V(\mathcal{R}) = K(\mathcal{R}) + \epsilon(\mathcal{R})
\]

in which the nuclei move.

The electronic energy is obtained by solving

\[
\left[ \mathcal{H}_e(\mathcal{R}, r) - \epsilon_n(\mathcal{R}) \right] \psi_n(\mathcal{R}, r) = 0
\]

for various nuclear conformations. Here \( \mathcal{H}_e \) is the electronic Hamiltonian, \((111.1)\) without the nuclear–nuclear repulsion term \( K \).

With the advent of electronic computers a major effort has been focused upon solving \((111.6)\) approximately, and highly efficient and computationally sophisticated techniques have been developed to obtain correlated wave functions and energies of desired accuracy. These methods, which have become standard by now, have been reviewed extensively and expertly, \(^{2,5}\) so that we can confine ourselves here to a brief outline.
Variational as well as perturbation techniques may and are being used to solve (III.6) approximately. The computational effort required to obtain solutions of comparable accuracy determines by and large the specific method chosen, and variational methods, which seem to be more standard, appear to have a slight edge. To be sure, highly accurate energies can be obtained using perturbation theory. However, to obtain compact and accurate wave functions in this way is much more difficult. Since for the computation of molecular properties the evaluation of expectation values and transition matrix elements is required and for this electronic wave functions are needed, we restrict our discussion to the form of variational procedures. Except for two-electron systems, where it is more effective to include the interelectronic distance explicitly, the electronic wave function for a state $n$, which can be characterized by a symmetry species $\nu$ and an identification index $I$, is in general written as a superposition of configurations

$$\psi_n(\mathcal{R}, r) \equiv \psi_{\nu I}(\mathcal{R}, r) = \sum_j \Phi_{\nu j}(\mathcal{R}, r) C_{jI}$$

(III.7)

where the configuration state functions (CSF's) $\Phi_{\nu j}(\mathcal{R}, r)$ are minimal linear combinations of Slater determinants (SD's)

$$\Phi_{\nu j}(\mathcal{R}, r) = \sum_K \phi_K(\mathcal{R}, r) B_{K, \nu j}$$

(III.8)

such that they transform as symmetry species $\nu$. The SD's are antisymmetric determinantal product functions

$$\phi_K(\mathcal{R}, r) = n!^{-1/2} \det \{ \varphi_{i_1}(r_1) \cdots \varphi_{i_n}(r_n) \}$$

(III.9)

of the orbitals $\varphi_i(r)$, which are generally chosen to be orthonormal; that is,

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

(III.10)

and such that they transform according to the symmetry species of the system. The dependence of the orbitals on the nuclear conformation has been suppressed here. The set

$$K = \{ i_1, i_2, \ldots, i_n \} \quad \text{with} \quad i_1 < i_2 < \cdots < i_n$$

(III.11)

together with the orbitals specifies the SD, $\phi_K$, uniquely, while the $B_{K, \nu j}$ in (III.8) are determined by the coupling chosen and the demand that the CSF, $\Phi_{\nu j}$, transform according to symmetry species $\nu$. 
Substituting for $\psi_n$ in (III.6) the right-hand side of (III.7) for a given symmetry and varying with respect to the expansion coefficients yields the standard configuration mixing eigenvalue equation

$$\quad (H - \varepsilon)C = 0 \quad \text{(III.12)}$$

which may be solved by direct diagonalization\textsuperscript{6} of $H$ or by obtaining with iterative methods\textsuperscript{7} the lowest few roots $\varepsilon_i$ and the corresponding eigenvectors $C_i$.

The energy matrix $H$ is defined here with the elements

$$\quad H_{ij} = \langle \Phi_j | \hat{\sigma}_e | \Phi_i \rangle \quad \text{(III.13)}$$

which are obtained as specific combinations of one- and two-electron integrals of the operators of (III.2) and (III.3) with the orbitals. The specific combinations are determined through the CSF's and SD's used. It should be mentioned here that direct methods,\textsuperscript{8} which solve (III.12) iteratively, using the orbital integrals directly, without explicitly constructing $H$ appear rather promising, permitting very large configuration mixing expansions of type (III.7).

It is well known that the configuration mixing expansion is slowly convergent at best and major emphasis has been placed on the selection of important CSF's in constructing $H$. Clearly, the choice of the single-particle functions, the orbitals, is of central importance for the convergence of (III.7). The orbitals are therefore determined self-consistently, either by solving iteratively the standard Hartree–Fock equations\textsuperscript{9} or the Fock-like MCSCF equations.\textsuperscript{10} Since it would lead us too far here to review these methods, it may suffice to state that although in principle the MCSCF method would be able to yield all the orbitals needed to construct the CSF's in (III.7) and thus give an adequate wave function directly, this is in general computationally inefficient. In the SCF method, by definition, and in the MCSCF method by design, only the most important configuration and orbitals are included, while the remaining orbitals and configurations in (III.7), necessary for an adequate representation of the electronic wave function, have to be chosen differently. The virtual orbitals of SCF-type calculations are in general inappropriate unless some configuration selections are performed.\textsuperscript{11} In general, such a selection is based on a second-order perturbation theory estimate of the energy contribution of the CSF's, and extrapolation techniques have been developed to estimate the total error introduced by such selections.\textsuperscript{12} However, in the direct methods,\textsuperscript{8} which permit the calculation with a much larger number of SCF's than the conventional methods, such a selection does not seem to be possible. Here
the procedures to obtain better orbitals than the virtual SCF orbitals for
the configuration mixing (CM) calculation become of utmost importance.
Such procedures involve the approximate determination of natural
orbitals\(^{13}\) either using CM calculations iteratively,\(^{14}\) yielding the iterative
natural orbitals (INO's), or using second-order perturbation theory,\(^{15}\) yield-
ing the perturbation natural orbitals (PNO's). Naturally, these techniques,
using a conventional CM, can be used in conjunction with CSF selection
and extrapolation mentioned above. Much of this has been reviewed re-
cently\(^{2}\) and need not be elaborated further here. However, before we turn
to the use of electronic wave functions for the calculation of various
molecular properties, we should mention that the orbitals themselves are
generally expressed as linear combinations of either Slater-type functions
(STF's)

\[
\varphi_i = \sum_p x_p c_{pi} \quad (111.14)
\]

with

\[
x_p = r^n \exp(-\xi r) Y_{lm}(\theta, \phi) \quad (111.15)
\]

where \(p\) characterizes the origin, \(l, m, n, \) and \(\xi, \) or Gaussian-type functions
(GTF's)

\[
x_p = x^l y^m z^n \exp(-\xi r^2) \quad (111.16)
\]

where \(p\) characterizes the origin, \(l, m, n, \) and \(\xi.\) Of these, STF's can repre-
sent the proper long-range behavior as well as the cusps at the nuclei, both
of which are impossible with a finite number of GTF's. However, the
calculation of the necessary integrals with STF's is much more cumber-
some than with GTF's, except in atoms or linear molecules; therefore,
GTF's are used frequently for polyatomic molecules. Compendia of results
of such electronic structure calculations have been compiled.\(^{2b}\)

The first few steps in using such wave functions for the calculation of ex-
pectation values or transition matrix elements of operators other than the
energy would be quite analogous to those used in an energy-wave-function
calculation. First it is necessary to evaluate the one- and two-electron in-
tegrals over the appropriate operators and the basis functions defined by
(111.15) and (111.16). These integrals are transformed with the orbital ex-
pansion coefficients of (111.14) from the basis space into the orbital space.
The matrix elements over the \(n\)-electron functions are then obtained, akin
to those of (III.13), as specified sums of these one- or two-electron integrals, with the terms in the sum determined by the configuration mixing coefficients in (III.7), the type of CSF's and SD's used, and the symmetry of the operator involved.

IV. SYMMETRY—INTERNAL COORDINATES

In our attempt to understand the stationary states of molecules, symmetry is an extremely useful concept. Symmetry considerations allow a classification of states of the wave function as a whole and of individual parts of the wave function according to the irreducible representations of the group spanned by the symmetry operators. Group theory and the symmetry classification of states tell us the degeneracy of a particular state and whether this degeneracy will be split, and between which type of states interactions are possible, depending on the transformation properties of a perturbation.

The usefulness of the symmetry concept is based on the theorem that commuting operators in quantum mechanics have common sets of eigenfunctions, or more specifically, if

\[ \Lambda \mathcal{H} = \mathcal{H} \Lambda \]  

(IV.1)

and

\[ \Lambda \Psi = \lambda \Psi \]  

(IV.2)

where the operator \( \Lambda \) commutes with the Hamiltonian and where \( \Psi \) is an eigenfunction in the space of \( \mathcal{H} \), then \( \Psi \) can also be an eigenfunction of \( \Lambda \) with eigenvalue \( \lambda \), a constant of motion. Relations (IV.1) and (IV.2) can be used with the total Hamiltonian for the classification of the total wave function or with parts of the Hamiltonian to classify the corresponding parts of the wave function, with the symmetry classification of the total wave function obtainable by appropriate coupling of the wave-function parts into a whole.

Before we proceed to further details, let us list the types of operations that commute with the total Hamiltonian and leave it invariant. For this we restrict ourselves to the field-free case; external electric or magnetic fields can always be considered as perturbations. The invariants are:

1. Translation of the origin of the coordinate system.
2. Rotation of the coordinate frame about a space fixed axis.
3. Time reversal.
4. Inversion of all spatial coordinates.
5. Permutation of the coordinates, including spin, of identical nuclei.
6. Permutation of the coordinates, including spin, of the electrons.
The first three follow from the isotropy of space and time, where (1) leads to the infinite-order translation group, permitting a classification of the overall translation along some space fixed axis, not affecting internal molecular states. Invariant (2) leads to the infinite-order external rotation group. It effects a classification of all molecular states according to the quantum numbers \( J(F) \) and \( M_r(M,F) \), which designate the value of the total angular momentum (including nuclear spin for \( F \)) and its projection on some space fixed axis. In the field-free case we obtain a \( 2J+1 \) \((2F+1)\)-fold degeneracy. An external electric field will split such a state into \( J+1 \) components according to \(|M|\). Time reversal (3) is of little importance here; because of it, some separately degenerate representations can be considered to be degenerate. With an external magnetic field present, the time-reversal symmetry is broken, which leads to a splitting of the remaining double degeneracy for states with \( M \neq 0 \). The final invariant (6) need not be considered here in detail; it is taken care of by requiring the electronic wave function in (III.7) to be antisymmetric with respect to electron permutation (Pauli principle). The antisymmetry requirement, together with the specific electron spin coupling generally used when constructing an electronic wave function, leads to functions whose spatial and spin parts separately transform as conjugate pairs of irreducible representations of the permutation group, such that their product yields the antisymmetric irreducible representation. There is a subtle connection between the spin coupling and the permutation group, and the spin quantum number signifies the particular pair of conjugate irreducible representation chosen for spin and spatial part in (III.7).

The invariants (4) and (5) need to be explicated considerably. They are the basis for the conventional symmetry classification of electronic and vibrational states according to the molecular point group and of rotational states according to the four-group \( D_2 \) or \( D_\infty \) group for asymmetric- or symmetric-top rotors, respectively. However, the molecular point group and the internal rotation group are near-symmetry groups only, correct for rigid rotor molecules with small vibrational amplitudes, where rotational and rotation–vibration and electronic coupling can be neglected. Since we aim to deal just with these couplings, it is more appropriate to use the molecular symmetry (MS)\(^{16}\) or extended molecular symmetry (EMS)\(^{17}\) groups, based on the nuclear permutations (5) and coordinate inversion (4), which are fundamental invariants and permit a unifying classification of rotational, vibrational, and electronic (rovibronic) states. The nuclear permutation and inversion group has been introduced by Longuet-Higgins\(^{18}\) to deal with nonrigid molecules, and Bunker has detailed the MS and EMS groups derived from it in an excellent review.\(^{16}\)

The use of the MS or EMS group is complicated by the fact that nuclear permutations affect in general a rotation of the molecular fixed reference
frame. The MS group, however, is frequently isomorphic with the molecular point group, so that the point group with its more accustomed and more easily visualized operations may be used in place of the MS group. For more details and the connection between MS and point group, we refer the reader to the review by Bunker and confine our discussion to the essentials needed here.

To deal explicitly with the internal motion and the symmetry of a molecule, it is necessary to define a molecular fixed reference frame in terms of which the internal coordinates are described. We follow the standard procedure to define a nuclear (not molecular) fixed frame by first choosing some reference conformation $r_a^0$ for the position of nuclei measured relative to the center of mass, 0, of the reference; that is,

$$\sum_a M_a r_a^0 = 0$$  \hspace{1cm} (IV.3)

This reference conformation is arbitrary and will in general (but not always) be chosen to correspond to an equilibrium conformation of the molecule. Defining now the instantaneous position vectors of the nuclei with respect to 0 as $r_a$, an optimal separation of external (translation and rotation) and internal motion is obtained by requiring the Eckart conditions

$$\sum_a M_a (r_a - r_a^0) = 0$$  \hspace{1cm} (IV.4)

and

$$\sum_a M_a (r_a - r_a^0) \times r_a^0 = 0$$  \hspace{1cm} (IV.5)

to be satisfied. If internal torsion is to be considered, it is appropriate to impose in addition Sayvetz conditions for the definition of torsional angles.

Condition (IV.4) ensures that for internal motions the center of nuclear mass remains 0, while (IV.5) keeps the reference frame fixed. This reference frame $x, y, z$ with origin 0 is obtained by transforming the inertial tensor of the reference conformation

$$I = \sum_a M_a (r_a^0 r_a^0 \mathbf{1} - r_a^0 \otimes r_a^0)$$  \hspace{1cm} (IV.6)

into normal (diagonal) form.
We have used here the dyadic product

\[ r \otimes r = \begin{pmatrix} xx & xy & xz \\ yy & yz & yz \\ zz & zy & zz \end{pmatrix} \]  

(IV.7)

The translational motion is now the motion of 0 with respect to the origin of the laboratory fixed frame, and the external rotation is described in terms of the Euler angles that rotate the laboratory fixed frame \((X, Y, Z)\) into the molecular fixed frame \((x, y, z)\). Since (IV.5) implies

\[ \sum_{\alpha} M_{\alpha} r_{\alpha}^{0} \times r_{\alpha} = 0 \]  

(IV.8)

the Eckart conditions minimize the vibrational angular momentum and thus the coupling between rotation and vibration.

With the reference frame defined, we are in a position to specify the customarily used mass-scaled internal coordinates

\[ S_{k} = \sum_{\alpha} d_{k}(\alpha) \sqrt{M_{\alpha}} \left( r_{\alpha} - r_{\alpha}^{0} \right) \]  

(IV.9)

for \(k = 1, 2, \ldots, 3N - 6,\) or \(3N - 5\) in case of linear molecules. The requirement to satisfy the Eckart conditions, (IV.4) and (IV.5), results in the following relations among the coefficients \(d_{k}(\alpha)\):

\[ \sum_{\alpha} d_{k\mu}(\alpha) d_{\mu}(\alpha) = \delta_{kl} \quad \mu = x, y, z \]  

(IV.10)

\[ \sum_{\alpha} \sqrt{M_{\alpha}} d_{k}(\alpha) = 0 \]  

(IV.11)

and

\[ \sum_{\alpha} \sqrt{M_{\alpha}} r_{\alpha}^{0} \times d_{k}(\alpha) = 0 \]  

(IV.12)

as well as the inverse relation

\[ r_{\alpha} = r_{\alpha}^{0} + \sqrt{M_{\alpha}}^{-1} \sum_{k} d_{k}(\alpha) S_{k} \]  

(IV.13)

and the orthogonality relation

\[ \sum_{k} d_{k\mu}(\alpha) d_{k\mu}(\beta) = \delta_{\mu\nu} \left( \delta_{\alpha\beta} - \sqrt{M_{\alpha} M_{\beta}} / M \right) \]

\[ - \sum_{\kappa\rho\lambda} \sqrt{M_{\lambda} M_{\beta}} e_{\mu\kappa} e_{\rho\lambda} r_{\alpha}^{0} (I^{-1})_{\rho\alpha\beta} r_{\alpha}^{0} \]  

(IV.14)
where $e_{\mu\kappa\rho}$ is the three-dimensional Levi-Civita antisymmetric pseudotensor, which has nonzero elements

$$e_{xyz} = e_{yzx} = e_{zyx} = 1$$  \hspace{1cm} (IV.15)

and

$$e_{yxz} = e_{xzy} = e_{zyx} = -1$$

By introducing linearly independent mass-scaled internal coordinates via a linear transformation in accordance with (IV.9) through (IV.14), the translational and rotational moments of inertia have been separated off. The next step is the transformation of the internal coordinates to symmetry coordinates, which imposes additional constraints on the coefficients $d_k(\alpha)$ such that the $S_k$'s will transform as irreducible representations of the symmetry group of the system. This symmetry is determined through the topology of the potential surface $V(\mathfrak{R})$, resulting as a solution of (II.3). Its origin lies in the invariance of $\mathfrak{R}$ and $\mathfrak{R}_e$ with respect to (4) inversion of all spatial coordinates and (5) permutation of the coordinates, including spin, of identical nuclei. Thus we could classify the electronic wavefunction, the internal coordinates, and the rovibronic states according to the irreducible representations of the complete nuclear permutation and inversion (CNPI) group. The potential surface, corresponding to all electronic states, will always be totally symmetric in this group. With $A$ an element of this group, $A \in G$, and $P_A$ the corresponding operator, we have

$$P_A V(\mathfrak{R}) = V(A^{-1}\mathfrak{R}) = V(\mathfrak{R})$$  \hspace{1cm} (IV.16)

The number of elements in the CNPI group increases extremely rapidly with the number of identical nuclei; in ethane we would obtain, for example, a group with $6! \cdot 2! \cdot 2 = 2880$ elements, and using such a large group becomes laborious and unmanageable. Fortunately, we are most often not interested in all possible kinds of excursions of the nuclei, only in those which are feasible within a given, generally low energy. These “feasible” elements of the CNPI group introduced by Longuet-Higgins\textsuperscript{18} form a subgroup of the CNPI group, the MS group.\textsuperscript{16} The latter is a true symmetry group of the system, not a near-symmetry group like the point group. Hence it can be used for the classification of electronic, vibrational, and rotational states. For linear molecules, however, the MS needs to be extended to the EMS group,\textsuperscript{17} where the infinite-order rotation around the internuclear axis is included appropriately.
For rigid molecules the MS group is isomorphic with the molecular point group, a situation obtained in most cases; thus the point group classification can be used. Even for some "nonrigid" cases, a higher-order point group can frequently be used. However, using the MS group, or the isomorphic point group in its place, has the advantage of permitting a symmetry classification, even though the nuclear conformation is not in or near its equilibrium. When classifying rotational states (rovibration or rovibronic states), though, care must be taken, since the nuclear permutations and the inversion affect the nuclear fixed reference frame. This is so because the reference frame is not completely determined by requesting the inertia tensor, (IV.6), to be diagonal, a phase (direction) must still be specified, and this specification fixes the axes as described by Bunker.16 Confining ourselves to the classification of electronic and vibrational states and internal coordinates we need not concern ourselves here with the above-mentioned rotations or inversions of the reference frame.

We will give a few examples to get accustomed to the concepts stated above. For H$_2$O the elements of the CNPI and MS group are (all operations are feasible) $E$, the identity; (12), the exchange of H$_1$ with H$_2$; $E^*$, the coordinate inversion, and $(12)^* = E^* \cdot (12)$. The point group of the water molecule, $C_{2h}$, consists of the elements $E$, $C_2$, $\sigma_{ab}$, $\sigma_{cb}$, while the conventional rotation group for an asymmetric rotor is the four-group with the elements $R_0$, $R_{2a}$, $R_{2b}$, and $R_{2c}$, where $a$, $b$, and $c$ are the principal axis forming a right-handed system with $a$ and $b$ in the molecular plane and $b$ along the $C_2$ axis. To see the relations between these operations, consider $C_2$, which rotates the electronic wave function and the nuclear displacements by $\pi$ around the $b$-axis, leaving the nuclear reference sites and thus the reference frame unaffected. On the other hand, (12) of the MS group permutes nuclei 1 and 2, leaving the nuclear displacements and the electronic wavefunction unaffected; however, the nuclear reference frame is rotated by $\pi$ around $b$. Finally, $R_{2b}$ rotates the entire molecule, nuclei, reference frame, nuclear displacements, and electronic wave function by $\pi$ around the $b$-axis. Thus we have the relation $(12) = R_{2b}C_2$ and similarly for all the operations:

\[
E = R_0E \\
(12) = R_{2b}C_2 \\
E^* = R_{2c}\sigma_{ab} \\
(12)^* = R_{2a}\sigma_{cb}
\]  

(IV.17)

The advantage of using the MS group over the isomorphic $C_{2h}$ point group here is twofold: (1) the vibrational angular momentum, relative to the total
angular momentum, and thus the Coriolis coupling, is unchanged by the
operations of the MS group; and (2) the electronic wavefunctions, which
depend parametrically on the internal coordinates, can be classified
according to the irreducible representations of the MS group even for
asymmetric nuclear conformations. The latter point permits the derivation
of general selection rules; it allows a general symmetry classification of
matrix elements integrated over the electronic coordinates but dependent
on the internal nuclear coordinates, a classification we shall find extremely
useful.

To illustrate the latter point, take an electronic wave function
\( \psi (S_1, S_2, S_3; r) \), which depends parametrically on the internal symmetry co-
ordinates (i.e., \( S_1 \)—symmetric stretch, \( S_2 \)—symmetric bend, and \( S_3 \)—asymmetric stretch). Consider, for example, the operation (12) and we have

\[
(12) \psi (S_1, S_2, S_3; \xi \eta \delta) = \psi (S_1 S_2 - S_3; \xi \eta \delta) = \pm \psi (S_1 S_2 S_3; \xi \eta \delta)
\]

(IV.18)

with the sign determined by the symmetry or antisymmetry of \( \psi \) with re-
spect to (12), which is most easily seen when \( S_3 = 0 \), although (IV.17) holds
for all values of \( \Theta \). To be sure, we could have used just as well the opera-
tions of the point group of the symmetric reference conformation here.

Generally, the action of an operator \( P_A \) corresponding to the operation
\( A \) of the group of the system upon an electronic wavefunction gives for
nondegenerate states

\[
P_A \psi (\mathcal{R}, r) = \psi (A^{-1} \mathcal{R}, A^{-1} r) = x_\Gamma (A) \psi (\mathcal{R}, r)
\]

(IV.19)

where \( x_\Gamma (A) \) is the character corresponding to \( A \) in the irreducible repre-
sentation \( \Gamma \). A point group and its classification can be used, which is just
as well in most cases, provided that the group of the symmetric reference
conformation isomorphic with the MS group is employed. Equation
(IV.19) is general and relates the electronic wave functions of one nuclear
conformation to those of another conformation. The characters are most
easily ascertained in the symmetric reference conformation (i.e., when all
displacements are zero), since now the relation is one of the electronic
wave function to another with the same nuclear conformation used con-
ventionally. To be sure, at a fixed displaced nuclear conformation, the rep-
resentation of the electronic wave function will correspond to those of a
lower (point) group. However, the representation \( \Gamma \) displayed in (IV.19)
corresponding to the higher symmetry is still useful, and we propose the
terminology "the state is of lineage \( \Gamma \)".