

Separation of the Molecular Motions of a Diatomic Molecule

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Summary: An attempt is made to show in a straightforward way how a body-fixed (BF) frame of reference may be constructed for a diatomic molecule such that rotational and translational motions could be described as motions of the BF frame and internal (vibrational and electronic) motions could be described with respect to the BF frame. A diatomic molecule is a special case which we do not need to impose any condition, such as the Eckart's conditions, on the BF frame. The correct form of the total angular momentum operators is derived quantum mechanically. The Hougen-Watson isomorphic Hamiltonian is rederived. For conformity, the method is developed in strict analogy to the first author's previous works, with the necessary variations for the diatomic molecule.

Introduction

From the spectrum of a molecule we can obtain, in general, experimental information on the relations between the structure and physical properties of molecules. Investigation of the rotation-vibration spectra of polyatomic molecules, for instance, is of basic importance for determining precise molecular geometry in different vibrational states, for obtaining information on molecular force fields, vibration-rotation interaction parameters, dipole moments, and calculation of thermodynamics function [1].

The spectra of atoms are only due to electronic transitions, whereas the molecule's spectrum depends on the characteristics of the nuclear motions as well as on the electronic motions. The motions of the nuclei are three kinds: the translational motion of the molecule as a whole, which is discarded because of no spectroscopic interest; the rotation of the molecule; and the vibrations of the nuclei within the molecule.

The molecular motions are not independent of each other, and interactions between them are responsible for the complexity of their spectra. Furthermore, the existence of several sources of angular momenta, and consequently a variety of ways of coupling them together make such a complexity even worse. It is clear that if such a complex spectrum can be analyzed the information obtained should be correspondingly great.

A molecule containing N nuclei and n electrons has $3(N+n)$ independent cartesian coordinates with respect to a laboratory fixed frame (LF frame). In order to separate translational, rotational, vibrational, and electronic modes of molecular motions, we may transform the set of $3(N+n)$ LF cartesian coordinates $\{R_{\lambda}^f \text{ } f=X,Y,Z; \lambda=1,2,\dots, (N+n)\}$ to a set of generalized coordinates $\{q_{\tau}; \tau=1,2,\dots,3(N+n)\}$, called molecular coordinates, defined by subsets $\{3 \text{ translational}\}$, $\{3 \text{ (or } 2) \text{ rotational}\}$, $\{3N-6 \text{ (or } 5) \text{ vibrational}\}$, and $\{3n \text{ electronic}\}$ variables. The corresponding transformation in the hamiltonian operator for the energy of the molecule gives an expression in which the energy of each separate motion and the interactions between each two motions are very revealing. Furthermore, the Born-Oppenheimer approximation [2-4] which approximates the nuclear and electronic motions independent, becomes more clear in the transformed hamiltonian operator.

The present account is written as an attempt at a modern presentation of the separation of the molecular motions of a diatomic molecule which is necessary for understanding the fine structure of their spectra and the spectroscopic aspects of the applications already mentioned. A diatomic molecule may be regarded as the prototype of all other molecules and therefore, the present calculation could be a guide for the corresponding treatment of a polyatomic molecule in general [5,6,14].

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*In this article, the Index λ refers to a general particle, and the indices f,g,h refer to a general direction of the LF frame axes.

As a result of the absence of a third rotational variable in a diatomic molecule (and a linear configuration in general), the BF frame* components of total angular momentum do not obey the usual commutation relations for angular momenta (the LF frame components, of course, behave normally). It can nevertheless be shown that if the hamiltonian is subjected to a unitary transformation in such a way to introduce the third rotational variable as an independent variable, then the BF frame components of total angular momentum would behave normally and the awkward angular terms in hamiltonian would be dropped out.

Section 2 is devoted to the general theory, and rest of the paper illustrates the theory.

2. Hamiltonian and total angular momentum

If a collection of coulomb interacting particles have cartesian coordinates $R = \{R_{f\lambda}\}$ with respect to a lab-fixed coordinate system, with the conjugate momenta $\{P_{f\lambda}\}$, then the classical hamiltonian of the whole system is:

$$H = \sum_{f\lambda} \frac{P_{f\lambda}^2}{2m_\lambda} + V(R) \quad (1)$$

where $V(R)$ is the potential energy of the entire system and consists of all the coulomb interactions between all pairs of particles.

Since the rule of correspondence in quantum mechanics is valid for cartesian coordinate systems [13], the operator form of (1) is simply:

$$H = \sum_{f\lambda} \left[-\frac{\hbar^2}{2m_\lambda} \frac{\partial^2}{\partial R_{f\lambda}^2} + V(R) \right] \quad (2)$$

and the Schrodinger equation is:

$$\left[\sum_{f\lambda} \left[-\frac{\hbar^2}{2m_\lambda} \frac{\partial^2}{\partial R_{f\lambda}^2} + V(R) \right] \right] \psi_R = E \psi_R \quad (3)$$

The hamiltonian (2) as a function of cartesian coordinates $R_{f\lambda}$ and derivatives with respect to them $\partial/\partial R_{f\lambda}$, can be transformed to a new set of real generalized coordinates $q = \{ \}$ if the transformation laws for the coordinates:

$$R_{f\lambda} = R_{f\lambda}(q) \quad (4)$$

and the derivatives

$$\frac{\partial}{\partial R_{f\lambda}} = \sum_{\tau} \left(\frac{\partial q_{\tau}}{\partial R_{f\lambda}} \right) \frac{\partial}{\partial q_{\tau}} \quad (5)$$

are known. As it can be guessed, the wavefunction in q -space is different from that in R -space. In fact, if ψ_q is the wavefunction in q -space, then the normalization condition for the two spaces is:

$$\int \psi_q^* \psi_q \prod_{\tau} dq_{\tau} = \int \psi_R^* \psi_R \prod_{f\lambda} dR_{f\lambda} \quad (6)$$

where $g^{-1/2}$ is the jacobian of the transformation $J(R_{f\lambda}/q)$ which is the determinant of the matrix formed by values $\partial R_{f\lambda}/\partial q_{\tau}$. Therefore, we may define

$$\psi_R = (p_q^2/g)^{1/4} \psi_q \quad (7)$$

In some coordinate system a volume element of the form dq is conveniently used, where the weight factor q is some function of the coordinates q . In this case we may define:

$$\psi_R = (p_q^2/g)^{1/4} \psi_q \quad (8)$$

By substituting for $\partial/\partial R_{f\lambda}$ and ψ_R from (5) and (8) in (3), the hamiltonian operator in terms of generalized coordinates can be derived.

For a system of particles the operators for the components of total angular momentum with respect to the origin of a lab-fixed cartesian coordinate system are defined by

$$J_f = -i\hbar \sum_{g,h\lambda} \epsilon_{fgh} R_{g\lambda} \frac{\partial}{\partial R_{h\lambda}} \quad (9)$$

in which ϵ_{fgh} is the permutation symbol defined in the appendix. When expressed in terms of the generalized coordinates q , then eq. (9) becomes

$$J_f = \sum_{\tau} (-i\hbar \sum_{g,h\lambda} \epsilon_{fgh} R_{g\lambda} \frac{\partial q_{\tau}}{\partial R_{h\lambda}}) \frac{\partial}{\partial q_{\tau}} \quad (10)$$

*See section 3 for the definition of the BF frame

$$= \sum_{\tau} [J_{f\tau}, \quad] \partial / \partial q_{\tau} \quad (11)$$

where $[J_{f\tau}, \quad]$ is the commutator between J_f and

Transformation equations to generalized coordinate

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

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

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

(iii) Without shifting the origin, changing to the BF frame in order to separate the nuclear framework rotational variables from the nuclear framework vibrational variables.

If the position of a particle (an electron or a nucleus) is R_{λ} in the LF frame and r_{λ} in BF frame, then the general transformation equation may be formulated as (Fig.1).

$$r_{\lambda} = R_{\lambda} - R - d \quad (12)$$

where R is the position of the molecular center of mass with respect to the LF frame:

$$R = \sum_{\lambda} m_{\lambda} R_{\lambda} / M \quad (13)$$

with $M = \sum_{\lambda} m_{\lambda}$ the total mass of the molecule. Here \underline{d} is a vector from the molecular center of mass to the nuclear center of mass. Since the origin of the BF frame is at the nuclear center of mass* (Two nuclei of the diatomic molecule are taken along the z axis of the BF frame)

$$\sum_j m_j r_{jz} = 0 \quad (14)$$

therefore,

$$d = -R + \sum_i m_i R_i / m_N \quad (15)$$

$$= - (m/M) \sum_s r_s \quad (16)$$

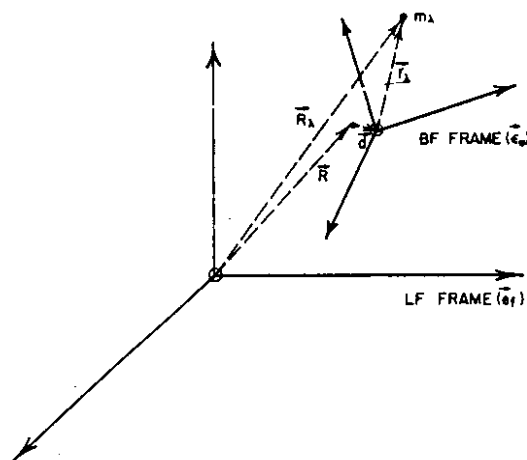


Fig.1: Transformation to the β F frame system. ϵ_{α} ($\alpha = x, y, z$) are the unit vectors along the BF frame axes, and e_f ($f = X, Y, Z$) are the unit vectors along the LF frame axes.

where m_N is the total mass of the nuclei and the second identity comes from the molecular center of mass condition. Introducing (15) into (12) we may write

$$r_s = R_s - \sum_i m_i R_i / m_N \quad (17)$$

for electrons, and

$$r_{zj} = R_j - \sum_i m_i R_i / m_N \quad (18)$$

for the nuclei.

If the instantaneous distance between the two nuclei R is taken as a vibrational variable, then

$$R = [\sum_f (R_{f2} - R_{f1})^2]^{1/2} \quad (19)$$

Before closing this section, we may summarize the transformation equations to the molecular coordinates as:

*In this article the indices i, j refer to the nuclei; s, t to the electrons and u is a general rotational variable.

$$R = \sum_{\lambda} m_{\lambda} R_{\lambda} / M \quad (20)$$

$$R = [\sum_f (R_{f2} - R_{f1})^2]^{\frac{1}{2}} \quad (21)$$

$$r_s = R_s - \sum_i m_i R_i / m_n \quad (22)$$

and the rotational variables which are implicitly contained in (17) and (22) will be discussed in next section.

4. The calculation of $\partial q_i / \partial R_{fi}$

In Section 3 we derived the transformation equations from the old coordinate (LF frame coordinates) to the new coordinate (molecular coordinates). To be able to obtain the molecular hamiltonian we need to calculate, as the first step, the derivative of the molecular coordinates with respect to the LF frame coordinates and upon insertion into (5). It should be noted that equation (5) in terms of molecular coordinates can be written as

$$\begin{aligned} \partial / \partial R_{f\lambda} &= \sum_g (\partial R_g / \partial R_{f\lambda}) \partial / R_g + \\ &\sum_u (\partial u / \partial R_{f\lambda}) \partial / \partial u + \\ &(\partial R / \partial R_{f\lambda}) \partial / \partial R \\ &+ \sum_{\gamma s} (\partial r_{\gamma s} / \partial R_{f\lambda}) \partial / \partial r_{\gamma s} \quad (23) \end{aligned}$$

From (20)

$$\partial R_g / \partial R_{f\lambda} = m_{\lambda} M^{-1} \delta_{fg} \quad (24)$$

and from (12)

$$\partial R_{f\lambda} / \partial R_g = \delta_{fg} \quad (25)$$

Here δ_{fg} is the Kronecker delta symbol.

The evaluation of u / R_{fi} (the BF frame is attached to the nuclear framework of the molecule) requires a mathematical trick as follows. Since the

vectors e_{α} along the BF frame axes are orthogonal $e_{\alpha} \cdot e_{\beta} = \delta_{\alpha\beta}$, it follows that the derivative of these unit vectors with respect to the nuclear coordinates R_{fi} , in the most general form can be written as

$$\partial e_{\alpha} / \partial R_{fi} = \epsilon_{\alpha} \chi_{\omega_f}^i \quad (26)$$

where ω_f^i are some vectors to be determined. If e_g are the unit vectors along the LF frame axes, then (26) can be written as

$$\begin{aligned} e_g \cdot (\partial e_{\gamma} / \partial R_{fi}) &= e_g \cdot (\epsilon_{\gamma} \chi_{\omega_f}^i) \\ &= \sum_u (C_{g\gamma} / \partial u) (\partial u / \partial R_{fi}) \quad (27) \end{aligned}$$

where $C_{g\gamma} = e_g \cdot e_{\gamma}$ equals the cosine of the angle between the axes e_g of the BF system and the e_{γ} of the LF system. The matrix constructed from $C_{g\lambda}$ ($g = X, Y, Z; \lambda = x, y, z$) is designated by C. Since L is orthogonal, then $C^T (C / U)$ is a skew-symmetric matrix and can be written in terms of skew-symmetric matrices $\epsilon_{\alpha\beta\gamma} = (\epsilon_{\alpha})_{\beta\gamma}$ as follows

$$(C^T \partial C / \partial u)_{\beta\gamma} = \sum_{\alpha} X_{u\alpha} (\epsilon_{\alpha})_{\beta\gamma} \quad (28)$$

$$\partial C_{g\gamma} / \partial u = \sum_{\alpha\beta} X_{u\alpha} C_{g\beta} (\epsilon_{\alpha})_{\beta\gamma} \quad (29)$$

where $X_{u\alpha}$ are some coefficients. Introducing (29) into (27) we obtain easily

$$\partial u / \partial R_{fi} = \sum_{\alpha} \omega_f^i (X^{-1})_{\alpha u} \quad (30)$$

where X^{-1} is reciprocal to X. The form of matrices $(\epsilon_{\alpha})_{\beta\gamma}$ and $(X^{-1})_{\alpha\mu}$ are given in the appendix.

The matrix C contains three independent rotational variables of which two are sufficient to specify the orientation of a linear configuration in space. Therefore, we may let the third variable enter into the calculation as an arbitrary parameter, let this arbitrary parameter be called χ , then from (30)

$$\partial \chi / \partial R_{fi} = 0 = \sum_{\alpha} \omega_f^i (\chi^{-1})_{\alpha\chi}$$

* α, β, γ go over x, y, z unless otherwise explicitly indicated.

Thus

$$\frac{\partial}{\partial R_{f\lambda}} = -\sum_{\alpha} A_{\alpha} \omega_{\alpha}^i \quad (\alpha = x, y), \quad (31)$$

where

$$A_{\alpha} = (\chi^{-1})_{\alpha\lambda} / (\chi^{-1})_{z\lambda} \quad (32)$$

From (30) and (31) we may write

$$\partial u / \partial R_{fi} = \sum_{\alpha} \omega_{\alpha}^i (\gamma^{-1})_{\alpha u} \quad (\alpha = x, y) \quad (33)$$

For the two rotational variables u , where the 3x3 matrix Y^{-1} is defined by

$$(\gamma^{-1})_{\alpha u} = (\chi^{-1})_{\alpha u} - A_{\alpha} (\chi^{-1})_{zu} \quad (33')$$

The form of matrix Y^{-1} is given in the appendix.

Note that the inverse derivative R / R_{fi} , from (21) (12) and (16) as

$$\partial R_{fi} / \partial u = \sum_{\gamma} (C_{f\gamma} / \partial u) (r_{\gamma i} \delta_{\gamma z} + d_{\gamma}) \quad (34)$$

The derivative of the vibrational variable R with respect to the nuclear coordinates R_{fi} , from (21) is as follows.

$$\partial R / \partial R_{f1} = -C_{fz}, \quad \partial R / \partial R_{f2} = C_{fz} \quad (35)$$

Note that the nuclear number 2 is taken on the positive side of the z axis.

Finally, from (22) and (26), the derivative of the electronic variables with respect to the LF frame coordinates are

$$\partial r_{\gamma s} / \partial R_{ft} = \delta_{st} C_{f\gamma} \quad (36)$$

and

$$\partial r_{\gamma s} / \partial R_{fi} = -m_i m_N^{-1} C_{f\gamma} + \omega_f^i (r_s \chi_{\gamma}^i) \quad (37)$$

We devote the rest of this section to the derivative of some very useful identities which we shall use them in the following sections.

By chain rule of differentiation, we can write

$$\sum_{\lambda} (\partial q_{\tau} / \partial R_{f\lambda}) (\partial R_{f\lambda} / \partial q_{\sigma}) = \delta_{\tau\sigma} \quad (38)$$

therefore, if we take $\{u, R, \text{ or } r_{ys}\}$ and $= R_g$, then from (25) and (38) we arrive at the conclusion that

$$\sum_{\lambda} (\partial q_{\tau} / \partial R_{f\lambda}) = 0 \quad (39)$$

and in particular

$$\sum_i \omega_{fi}^i = 0 \quad (40)$$

Now, in (38), let both τ and $\sigma = u$, then from (30), (34), (29), and the above results, we obtain

$$\sum_i \omega_{fi}^i \sum_{\alpha} e_{\alpha\beta z} C_{f\beta} r_{zi} = 1$$

which implies

$$\omega_{f\alpha}^2 = [e_f (\epsilon_z \chi_{\alpha}^i)] / R \quad (\alpha = a, y) \quad (41)$$

Hence

$$\sum_{fi} m_i^{-1} \omega_{fi}^i \omega_{f\alpha}^i = I^{-1} \delta_{\alpha\beta} \quad (\alpha = x, y) \quad (42)$$

with

$$I = \mu R^2 \quad (43)$$

as the instantaneous moment of inertia of the diatomic molecule.

For polyatomic molecules a rigorous method of calculating $\omega_{f\alpha}^i$ is provided by the conditions which are imposed on the BF frame. The conditions actually employed are known as the Eckart's conditions [7]. For the details of the method, the reader is referred to references cited [5,6,14].

5. Total angular momentum in terms of the molecular coordinates

In next section we shall show that the molecular hamiltonian can be very nicely formu-

lated in terms of the BF components of the electronic and the total angular momentum of the diatomic molecule. Therefore, it is reasonable to continue our discussion with the derivation of the angular momenta in terms of the molecular coordinates.

To obtain the angular momentum (10) in terms of molecular coordinates, we need to calculate the commutator between J_f and those coordinates as follows. Using equations (24), (26), (33), (35), (36), and (37) with the extensive help of (31), (40), and (41), it is easy to verify that

$$[J_f, R_g] = ih \sum_h e_{fgh} R_h \quad (44)$$

$$[J_f, u] = ih \sum_\alpha C_{f\alpha} (\gamma^{-1})_{\alpha u} \quad (45)$$

$$[J_f, R] = 0 \quad (46)$$

and

$$[J_f, r_{\gamma s}] = -ih \sum_\alpha C_{f\alpha} A_\alpha \sum_\beta e_{z\beta\gamma} r_{\beta s} \quad (47)$$

The commutator between J_f and ϵ_β by using (26), (31), and (41) can be also calculated as

$$[J_f, \epsilon_\beta] = ih \epsilon_\beta x_{\epsilon_f} - ih \sum_\alpha C_{f\alpha} A_\alpha (\epsilon_\beta x_{\epsilon_2}) \quad (48)$$

Introducing (44)-(47) into (10) gives

$$J_f = ih \sum_{ah} e_{fgh} R_g \frac{\partial}{\partial R_h} + \sum_\alpha C_{f\alpha} [ih \sum_u (\gamma^{-1})_{\alpha u} \frac{\partial}{\partial u} + A_\alpha L_z] \quad (49)$$

where the electronic angular momentum L_α is defined by

$$L_\alpha = -ih \sum_{\beta\gamma s} e_{\alpha\beta\gamma} r_{\beta s} \frac{\partial}{\partial r_{\gamma s}} \quad (50)$$

The first term in (49) is the angular momentum of the center of mass of the molecule with respect to the origin of the LF frame, and the second term is the total angular momentum of the molecule about the center of mass. We shall continue to use the same notation J_f for the angular momentum operators about the center of mass:

$$J_f = \sum_\alpha C_{f\alpha} [ih \sum_u (\gamma^{-1})_{\alpha u} \frac{\partial}{\partial u} + A_\alpha L_z] \quad (51)$$

If J_f is projected along the BF frame axes, the components J_α are then

$$J_\alpha = \frac{1}{2} \sum_f (C_{f\alpha} J_f + J_f C_{f\alpha}) \quad (52)$$

or

$$J_\alpha = ih \sum_u (\gamma^{-1})_{\alpha u} \frac{\partial}{\partial u} + A_\alpha L_z + \frac{1}{2} ih \sum_\beta e_{z\alpha\beta} A_\beta \quad (53)$$

where (48) has been used. Here (52) comes from the fact that J_α does not commute with $C_{f\alpha}$ as seen from (48). We see that the only source of angular momentum along the z axis of the BF frame is the z component of the electronic angular momentum (as it ought to be).

6. Molecular translational-rovibronic hamiltonian

Having obtained all the required relations, let us turn to derive the molecular hamiltonian in terms of the molecular coordinates. To do this, we substitute from (24), (33), (35), (36) and (37) for the derivatives in (23), and inserting resultant expression into (2). To simplify the result, we take advantage of the identities (39)-(43) and the expressions (48), (50), and (53). We obtain the molecular hamiltonian as

$$H = T_{\text{trans.}} + T_{\text{rot-int.}} + T_{\text{vib.}} + T_{\text{elec.}} + V \quad (54)$$

with

$$T_{\text{trans.}} = -\frac{\hbar^2 \nabla_R^2}{2M} \quad (55)$$

$$T_{\text{rot-int.}} = 2I^{-1} \sum_\alpha (J_\alpha - L_\alpha + \frac{1}{2} i h e_{z\alpha\beta} A_\beta) (J_\alpha - L_\alpha - \frac{1}{2} i h e_{z\alpha\beta} A_\beta) \quad (56)$$

$$T_{\text{vib}} = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) \quad (57)$$

$$T_{\text{elec.}} = (-\frac{\hbar^2}{2m} \sum_s \nabla_s^2 + \frac{-\hbar^2}{2m_N} \sum_{st} \nabla_s \nabla_t) \quad (58)$$

where, T_{trans} , T_{vib} , and T_{elec} represent the translational, vibrational, and electronic contributions to the total kinetic energy of the molecule, respectively. The second term is the contribution of rotational kinetic energy and the energy of interactions (between vibrations and rotations plus electronic motions) to the total kinetic energy of the molecule. Finally, the last term is the potential energy of the entire system of electrons and nuclei.

7. Transformation to an isomorphic hamiltonian

As pointed out in introduction, the hamiltonian (54) has the disadvantage that the components of the total angular momentum J_α (with respect to the BF frame) do not satisfy the usual commutation relations. In fact, it is rather easy to show that

$$[J_\alpha, J_\beta] = -\frac{1}{2} i h e_{\alpha\beta\gamma} \sum_\gamma (A_\gamma J_\gamma + J_\gamma A_\gamma), \quad (59)$$

which is quite different from the simple relation

$$[J_\alpha, J_\beta] = -i h \sum_\gamma e_{\alpha\beta\gamma} J_\gamma \quad (60)$$

applicable to non-linear molecules [5]. This anomalous behaviour comes from the fact that the third rotational variable χ is an arbitrary parameter. If we let this parameter be an independent variable, we may remove this difficulty. Let us write the explicit expressions of J_α for both a linear (eqs. (53) and 44) and a non-linear (see ref.5) molecule. These are as follows, respectively:

$$\begin{aligned} J_x - \frac{1}{2} i h A_y &= -i h (\sin \chi \partial / \partial \theta - \csc \theta \cos \chi \partial / \partial \phi) + \\ &\cot \theta \cos \chi J_z \\ J_y - \frac{1}{2} i h A_x &= -i h (\cos \chi \partial / \partial \theta + \csc \theta \sin \chi \partial / \partial \phi) - \\ &\cot \theta \sin \chi J_z \quad J_z = L_z \quad (61) \end{aligned}$$

and

$$\begin{aligned} J'_x &= -i h (\sin \chi \partial / \partial \theta - \csc \theta \cos \chi \partial / \partial \phi) + \\ &\cot \theta \cos \chi J'_z \\ J'_y &= -i h (\cos \chi \partial / \partial \theta + \csc \theta \sin \chi \partial / \partial \phi) - \\ &\cot \theta \sin \chi J'_z \\ J'_z &= -i h \partial / \partial \chi \quad (62) \end{aligned}$$

It should be emphasized that χ in (61) is an arbitrary parameter. Comparing (61) and (62), we see that we need to do the following changes in order to bring (61) in normal forms (that is, the forms which obey the usual commutation relations)

-taking the parameter χ as an independent variable;

-calling the right hand sides of the first two equations J'_x, J'_y , respectively;

-defining a new z component of angular momentum as $J'_z = i h / \chi$

Inserting the above changes into the hamiltonian (54), we obtain a synthetic hamiltonian [9] whose eigenfunctions have one more variable and therefore one more quantum number than the eigenfunctions of the true hamiltonian. However, a simple restriction on the synthetic hamiltonian singles out that portion of the full hamiltonian which is *isomorphic* with the true hamiltonian: only eigenvalues of the synthetic hamiltonian that are eigenvalues of the true hamiltonian are those corresponding to the eigenvalue zero of $J'_z - L_z$.

It can nevertheless be shown, as presented below, that the above treatment is formally equivalent to a *unitary transformation* of the true hamiltonian [10,8].

$$H_{iso} = U H U^\dagger \quad (63)$$

and the true eigenkets:

$$[E \rangle_{iso} = U |E \rangle \quad (64)$$

It is not hard to show that the operators H and H_{iso} have the set of eigenvalues E . Let us fix χ in (61) to a value ϵ and define

$$U = \exp[i(\chi - \epsilon)L_z / h] \quad (65)$$

This choice of U corresponds to a rotation of the BF frame through $\chi - \epsilon$ about the z axis. All terms in (54), except the second, are invariant under this unitary transformation (because of the cylindrical symmetry, the potential energy V commute with L_z and therefore with U). Thus we may concentrate on the transformation of the summation in the second term which can be written as

$$\begin{aligned} & \Sigma_{\alpha} U(J_{\alpha} - L_{\alpha} + \frac{1}{2} i h e_{\alpha\beta} A_{\beta}) U^{\dagger} U(J_{\alpha} - L_{\alpha} - \frac{1}{2} i h e_{\alpha\beta} A_{\beta}) U^{\dagger} = \\ & \Sigma_{\alpha} \{ U(J_{\alpha} + \frac{1}{2} i h e_{\alpha\beta} A_{\beta}) U^{\dagger} - U L_{\alpha} U^{\dagger} \} \\ & [U(J_{\alpha} - \frac{1}{2} i h e_{\alpha\beta} A_{\beta}) U - U L_{\alpha} U^{\dagger}] \quad (66). \end{aligned}$$

We can write

$$\begin{aligned} U(J_{\chi} - \frac{1}{2} i h A_{\chi}) U &= -i h [\sin(\epsilon - \chi + \chi) \partial / \partial \theta - \csc \theta \cos(\epsilon - \chi + \chi) \partial / \partial \phi] \\ &+ \cot \theta \cos(\epsilon - \chi + \chi) L_z \\ &= \cos(\chi - \epsilon) [J'_{\chi} - A_{\chi} (J'_z - L_z)] - \\ &\sin(\chi - \epsilon) [J'_y + A_y (J'_z - L_z)], \quad (67) \end{aligned}$$

similarly

$$\begin{aligned} & U(J_y + \frac{1}{2} i h A_y) U^{\dagger} \\ &= \sin(\chi - \epsilon) [J'_{\chi} - A_{\chi} (J'_z - L_z)] \\ &+ \cos(\chi - \epsilon) [J'_y + A_y (J'_z - L_z)] \quad (68) \end{aligned}$$

where J'_{χ} , J'_y , and J'_z have the same forms as those in (62).

In the transformation of L_{α} ($\alpha = x, y$) we use the following operator identity which is valid for any two operators A and B:

we obtain

$$U L_y U^{\dagger} = \sin(\chi - \epsilon) L_{\chi} - \cos(\chi - \epsilon) L_y \quad (69)$$

Now we impose the restriction mentioned in the second paragraph of the present section and introduce (67)-(69) in the second term of (54). The isomorphic hamiltonian becomes

$$H_{iso} = T_{trans.} + T_{rot.-int.} +$$

$$T_{vib.} + T_{elect.} + V \quad (70)$$

Where $T_{trans.}$, $T_{vib.}$ and $T_{elec.}$ are given by (55), (57), and (58), respectively and

$$T_{rot. int.} = 2I^{-1} \Sigma_{\alpha} (J'_{\alpha} - L_{\alpha})^2 \quad (\alpha = x, y) \quad (71)$$

Finally, it should be emphasized that the expressions (54) and (70) are valid provided that $(/g)^{1/2}$ in (18) does not depend on the molecular coordinates. Taking $= Y'R^2$ (see A5 for the definition of Y'), then $(/g)^{1/4}$ becomes a constant and the forms (54) and (70) remain unchanged [5,6].

Appendix: The matrices $(e_{\alpha})_{\beta\delta}$, χ^{-1} , and Y^{-1}

The definition of the permutation symbol:

$$\begin{aligned} e_{\alpha\beta\gamma} &= +1 \quad ; \alpha, \beta, \gamma \quad \text{in cyclic order,} \\ &= -1 \quad ; \alpha, \beta, \gamma \quad \text{not in cyclic order,} \\ &= 0 \quad ; \quad \text{two indices alike} \quad (A1) \end{aligned}$$

implies that

$$\begin{aligned} e_x &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, e_y = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ e_z &= \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (A2) \end{aligned}$$

This matrices are also introduced in ref. (11)

Taking the Eulerian angles θ , Φ , χ as the rotational variables and using the convention of Wilson et al. (12) for these angles, then from (28) and the above matrices, it is straightforward to show that

$$\chi^{-1} = \begin{pmatrix} \sin \chi & -\cos \theta \cos \chi & \cot \theta \cos \chi \\ \cos \chi & \csc \theta \sin \chi & -\cot \theta \sin \chi \\ 0 & 0 & 1 \end{pmatrix} \quad (A3)$$

Then (33') gives

$$Y^{-1} = \begin{pmatrix} \sin \chi & -\csc \theta \cos \chi & 0 \\ \cos \chi & \csc \theta \sin \chi & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (A4)$$

The determinant of the first block of Y^{-1} equals $\csc \theta$, so that

$$Y' = \sin \theta \quad (A5)$$

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