

Complete molecular Hamiltonian based on the Born-Oppenheimer adiabatic approximation

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For a study of the rotational and the vibrational motions of nonrigid molecular systems in terms of differential geometry, quantum molecular dynamics is set up without using the Eckart frame. The vibrational motions turn out to induce on the internal space a "gauge" field attached to the rotational motions. A method of obtaining the internal Hamiltonian for nonrigid molecules is presented. The space of internal wave functions on which the internal Hamiltonian acts is associated with the space of wave functions that are simultaneous eigenfunctions of \hat{P} and \hat{J}^2 , where \hat{P} and \hat{J} denote the total linear momentum operator and the total angular momentum operator, respectively. The internal Hamiltonian to be obtained shows that the internal motions are coupled with the gauge field.

I. INTRODUCTION

Recently, quantum-mechanical treatments of chemical reaction dynamics have received much attention, and the use of the Eckart frame for the separation of the collective motions from the internal motion of the reaction system has been one of the guiding principles in this direction of research.¹⁻¹⁰ Here, the collective motions of the system mean the translational and the rotational motions of the system. The theoretical developments on the separability of the collective motions from the internal motion have been found also in the nonrigid molecular-dynamics theory,¹¹⁻¹⁶ which calls attention to the concept of the "structure" of molecular system using the Born-Oppenheimer adiabatic approximation of the electronic motion.^{17,18}

If a chemical reaction proceeds via the formation of a series of reaction intermediates, then we can draw the picture of the reaction process as the successive formation of the "supermolecules." That is, the reaction intermediates are in one-to-one correspondence with the supermolecules. This suggests we treat the global dynamic processes of chemical reaction as the sequential array of the molecular dynamics of supermolecules.

The supermolecule as a reaction intermediate is usually a transient species. It may finally decay into the continuum of the scattering states after a finite period of its lifetime. Consequently, the quantum mechanic of the supermolecule is required to describe the large-amplitude vibrational motions of nonrigid molecules. The treatment of nonrigid molecules is based on the precise knowledge of the large-amplitude potential, which is nowadays available by virtue of the extensive developments in quantum chemistry. In keeping with the introduction of the large-amplitude potential, new notions such as a coordinate-dependent reduced mass or an angle-dependent reduced moment of inertia⁸ are introduced, which depend on the internal configuration of the nonrigid molecule.

In quantum chemistry of the reaction system isolated in the uniform and isotropic medium, the conservation of energy, momentum, and angular momentum is a fundamental property. In the usual treatments of reaction dynamics using the Born-Oppenheimer adiabatic approximation, the nuclear motion should obey these conservation laws, because the system is invariant under the translation and the rotation. As a consequence of the conservation laws, the degrees of freedom of the reaction system reduces from $3N$ to $n = 3N - 6$, N being the number of nuclei. The remaining n degrees of freedom serve to describe the internal motion.

Usually, the internal motion is treated by using the Eckart frame. By definition, the Eckart frame is a frame relative to which the molecular motion is vibrational. A differential geometry concerning the Eckart frame can be found in a recent work of Iwai,¹⁹ according to which the Eckart frame is determined for any configuration of the molecule, but not uniquely.

The internal motion of reaction system is described by the coordinate system which consists of the n -independent configurational parameters q^1, q^2, \dots, q^n such as bond lengths, valence angles, angles between a bond and a plane defined by three atoms, and angles between the two planes.⁴

The geometry of the internal space of variables q^1, q^2, \dots, q^n is concerned with the well-known Riemannian metric known as the Wilson's G matrix.^{10,20,21} This metric is considered as useful in the vicinity of the equilibrium configuration of molecular system, where small-amplitude molecular vibrations may take place.^{20,21} But it should be noted that the calculation of the G matrix is straightforward in the molecular configuration space with no recourse to the location of the equilibrium configuration itself. Hence, it is not surprising that the G matrix is used as the local metric separating the internal motion from the collective motions of the molecular system.⁴

In the present paper, the rotational and the vibrational

motions of the molecular system are described in terms of differential geometry. After setting up rotational and vibrational vectors in an exact way in Sec. II, quantum molecular dynamics is established in Sec. III without using the Eckart frame. The vibrational vectors prove to induce on the internal space a gauge field attached to the rotational vectors. The internal motions are shown to be coupled with the gauge field. Particularly, the internal Hamiltonian is obtained under the condition of zero-total linear and angular momentum in Sec. III, Eq. (3.7). An example of the triatomic molecular system is examined in Sec. IV.

It is to be noted that we do not treat the dynamic processes in which the configuration takes linear form, or the conversion of the handedness of the moving frame takes place.

II. A GEOMETRIC SETTING

A. Rotations and vibrations

According to Guichardet²² and Iwai,¹⁹ the first configuration space is the set X_0 of all n -ples $x = (x_1, x_2, \dots, x_N)$ with $x_\alpha \in \mathbb{R}^3$ and $x_\alpha \neq x_\beta$ if $\alpha \neq \beta$. We denote by $(|)$ the standard inner product in \mathbb{R}^3 . Since the translational motion can be separated out from molecular dynamics, we have the center-of-mass (c.m.) system X for molecular configurations as

$$X = \left\{ x \in X_0 \mid \sum_{\alpha} m_{\alpha} x_{\alpha} = 0 \right\}. \quad (2.1)$$

X is always arcwise connected.²² In this space X , we let act the group $G = \text{SO}(3)$ of rotations

$$gx = (gx_1, gx_2, \dots, gx_N), \quad g \in G, \quad x \in X. \quad (2.2)$$

If the molecular configurations are not linear, every orbit of G can be topologically identified with the group space. Then an individual molecular structure corresponds to a point in the orbit space

$$M = X/G. \quad (2.3)$$

This abstract manifold M is referred to as the internal space. Associated with the group action of $G = \text{SO}(3)$, a moving frame²³ $\{e_1, e_2, e_3\}$ in \mathbb{R}^3 is defined by

$$e_1 = ge_1^0, \quad e_2 = ge_2^0, \quad e_3 = ge_3^0, \quad (2.4)$$

where $\{e_1^0, e_2^0, e_3^0\}$ is a laboratory frame (LF), and $g \in G$. With respect to LF, the orientation of the moving frame is expressed in terms of the Eulerian angles²⁴ $\phi^1, \phi^2, \phi^3 = \phi, \theta, \psi$ as shown in Fig. 1. Any molecular configuration can then be assigned by internal coordinates q^i relative to the moving frame and the Eulerian angles ϕ^a .

The rotational motion is defined uniquely once the molecular structure gets "frozen." The configuration of the frozen molecule is represented by a point in M . But the real molecule is "hot" and draws a curve in M because of the vibrational motion.

Consider the angular velocity ω defined by

$$\omega = I^{-1} \sum_{\alpha} m_{\alpha} x_{\alpha} \times dx_{\alpha}, \quad (2.5a)$$

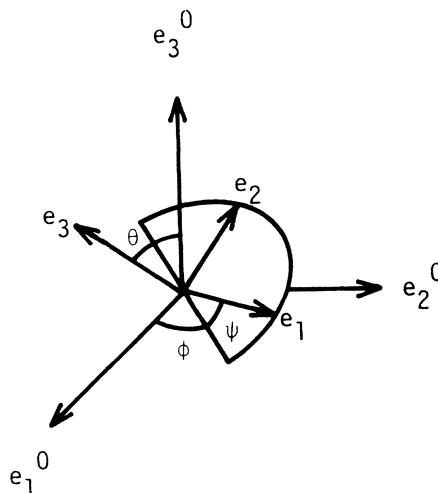


FIG. 1. Orientation of the moving frame $\{e_1, e_2, e_3\}$ with respect to the laboratory frame $\{e_1^0, e_2^0, e_3^0\}$ in terms of the Eulerian angles.

where I is the tensor of inertia with respect to the c.m. system,

$$I = \sum_{\alpha} m_{\alpha} [(x_{\alpha} | x_{\alpha}) - |x_{\alpha})(x_{\alpha} |)], \quad x \in X. \quad (2.5b)$$

We note here that the angular velocity ω is contributed by the total increment dx_{α} ,

$$dx_{\alpha} = \sum_i (\partial x_{\alpha} / \partial q^i) dq^i + \sum_a (\partial x_{\alpha} / \partial \phi^a) d\phi^a. \quad (2.6)$$

In differential geometry, the ω is interpreted as a connection form on X , where X is treated as a principal fiber bundle^{25,26} over the base manifold M with structure group $G = \text{SO}(3)$, and the Lie algebra of $\text{SO}(3)$ is naturally identified with \mathbb{R}^3 .

The connection form ω on X is then expanded with respect to the moving frame in the form

$$\omega = e_1 \omega^1 + e_2 \omega^2 + e_3 \omega^3, \quad (2.7a)$$

where each ω^a is expressed as

$$\omega^a = \sum_b \theta_b^a d\phi^b + \sum_i \beta_i^a dq^i, \quad (2.7b)$$

with

$$(I^{-1} \sum_{\alpha} (m_{\alpha} x_{\alpha} \times \partial x_{\alpha} / \partial \phi^a) | e_b) = \theta_a^b, \quad (2.8a)$$

and

$$(I^{-1} \sum_{\alpha} (m_{\alpha} x_{\alpha} \times \partial x_{\alpha} / \partial q^i) | e_a) = \beta_i^a. \quad (2.8b)$$

Thus the forms ω^a and dq^i constitute a local basis of the

space of one forms on X . We now define vector fields J_a and ξ_i dual to these forms under the conditions

$$\omega^a(J_b) = \delta^a_b, \quad \omega^a(\xi_i) = 0, \quad (2.9)$$

$$dq^i(J_a) = 0, \quad dq^i(\xi_j) = \delta^i_j. \quad (2.10)$$

Then we have

$$J_a = \sum_b (\theta^{-1})_a^b \partial / \partial \phi^b \quad (2.11a)$$

and

$$\xi_i = \partial / \partial q^i - \sum_a \beta_i^a J_a, \quad (2.11b)$$

where

$$\sum_c (\theta^{-1})_a^c \theta_c^b = \delta_a^b. \quad (2.11c)$$

In differential geometry, the ξ_i is called the horizontal lift of the vector of the internal motion $\partial / \partial q^i$. Since the angular velocity ω vanishes for all ξ_i , the ξ_i are called the vibrational vectors.²² Contrary to this, the vectors J_a are rotational. In fact, for each J_a , one has $\omega(J_a) = e_a$, which means that J_a is an infinitesimal rotation around e_a . Furthermore, we can prove

$$\begin{aligned} J &= \sum_\alpha x_\alpha \times \partial / \partial x_\alpha \\ &= e_1 J_1 + e_2 J_2 + e_3 J_3, \end{aligned} \quad (2.12)$$

and

$$J_1 = \csc \theta \sin \psi \partial / \partial \phi + \cos \psi \partial / \partial \theta - \cot \theta \sin \psi \partial / \partial \psi, \quad (2.13a)$$

$$J_2 = \csc \theta \cos \psi \partial / \partial \phi - \sin \psi \partial / \partial \theta - \cot \theta \cos \psi \partial / \partial \psi, \quad (2.13b)$$

$$J_3 = \partial / \partial \psi. \quad (2.13c)$$

The latter expression of the rotational vectors are familiar in the standard treatment of rotational motion of rigid rotator molecules.²⁷⁻²⁹

The vibration-rotation coupling appears in the commutator of the vibrational vectors

$$[\xi_i, \xi_j] = - \sum_a F_{ij}^a J_a, \quad (2.14a)$$

with

$$F_{ij}^a = \partial \beta_j^a / \partial q^i - \partial \beta_i^a / \partial q^j. \quad (2.14b)$$

This means that infinitesimal vibrations are coupled to give rise to an infinitesimal rotation. This is the reason for the nonseparability of the vibrational motion and the rotational motion. Thus we may call (2.14a) the Coriolis coupling. The F_{ij}^a can be interpreted as a gauge field on M and the β_j^a as the gauge potential.

B. The Eckart condition

In this section we relate the rather abstract geometric object J_a and ξ_i to the Eckart condition. The components

of x_α are denoted by $x_\alpha^a, a = 1, 2, 3$, below.

First, we expand the rotational vectors J_a in $\partial / \partial x_\alpha^b$,

$$\begin{aligned} J_a &= \sum_\alpha \sum_b B_a^{ab} \partial / \partial x_\alpha^b \\ &= \sum_\alpha (B_a^\alpha | \partial / \partial x_\alpha), \end{aligned} \quad (2.15a)$$

with

$$B_a^\alpha = \sum_b e_b^0 B_a^{ab}. \quad (2.15b)$$

Equation (2.12) is paired with e_a along with Eq. (2.15a) to give

$$B_a^{ab} = (e_a | x_\alpha \times e_b^0), \quad (2.16a)$$

so that

$$B_a^\alpha = e_a \times x_\alpha. \quad (2.16b)$$

Second, the vibrational vectors ξ_i are expanded in the form

$$\begin{aligned} \xi_i &= \sum_\alpha \sum_b B_i^{ab} \partial / \partial x_\alpha^b \\ &= \sum_\alpha (B_i^\alpha | \partial / \partial x_\alpha), \end{aligned} \quad (2.17a)$$

with

$$B_i^\alpha = \sum_b e_b^0 B_i^{ab}. \quad (2.17b)$$

Equations (2.8b), (2.11b), (2.16a), and (2.17a) are combined to yield

$$\begin{aligned} B_i^{ab} &= (\partial x_\alpha / \partial q^i | e_b^0) \\ &\quad - \left(\sum_\beta m_\beta x_\beta \times \partial x_\beta / \partial q^i | I^{-1} | x_\alpha \times e_b^0 \right), \end{aligned} \quad (2.18a)$$

so that

$$B_i^\alpha = \partial x_\alpha / \partial q^i - \left[I^{-1} \sum_\beta m_\beta x_\beta \times \partial x_\beta / \partial q^i \right] \times x_\alpha. \quad (2.18b)$$

The expansion coefficients have the following dynamic properties:

$$\sum_\alpha m_\alpha B_a^\alpha = 0, \quad (2.19a)$$

$$\sum_\alpha m_\alpha B_i^\alpha = 0, \quad (2.19b)$$

$$\sum_\alpha m_\alpha x_\alpha \times B_i^\alpha = 0. \quad (2.19c)$$

Equations (2.19a) and (2.19b) result from Eqs. (2.16b) and

(2.18b), respectively, together with $\sum_{\alpha} m_{\alpha} x_{\alpha} = 0$, and imply that B_a^{α} and B_i^{α} are tangent to X . Equation (2.19c) can be shown by pairing Eq. (2.18b) with e_b^0 and using the definition of the tensor of inertia. The latter Eqs. (2.19b) and (2.19c) mean that the B_i satisfy the Eckart condition.³

$$\sum_{\alpha} m_{\alpha} (B_a^{\alpha} | B_b^{\alpha}) = (e_a | I | e_b) = I_{ab} , \quad (2.21a)$$

$$\begin{aligned} \sum_{\alpha} m_{\alpha} (B_i^{\alpha} | B_j^{\alpha}) &= \sum_{\alpha} m_{\alpha} (\partial x_{\alpha} / \partial q^i | \partial x_{\alpha} / \partial q^j) - \left(\sum_{\alpha} m_{\alpha} x_{\alpha} \times \partial x_{\alpha} / \partial q^i | I^{-1} | \sum_{\beta} m_{\beta} x_{\beta} \times \partial x_{\beta} / \partial q^j \right) \\ &= a_{ij} , \end{aligned} \quad (2.21b)$$

and

$$\sum_{\alpha} m_{\alpha} (B_a^{\alpha} | B_i^{\alpha}) = 0 . \quad (2.21c)$$

The matrix $||a_{ij}||$ will be soon shown to be the inverse of the Wilson's G matrix.

In a converse way to the above, we can obtain dual vectors s_a^{α} and s_i^{α} to B_a^{α} and B_i^{α} . To do so, we decompose $\partial / \partial x_{\alpha}$ into the rotational and vibrational parts

$$\partial / \partial x_{\alpha} = (\partial / \partial x_{\alpha})_{\text{rot}} + (\partial / \partial x_{\alpha})_{\text{vib}} , \quad (2.22)$$

where, the rotational part is expanded in J_a ,

$$(\partial / \partial x_{\alpha})_{\text{rot}} = \sum_a s_a^{\alpha} J_a , \quad (2.23a)$$

with

$$s_a^{\alpha} = \sum_b e_b^0 s_{ab}^{\alpha} , \quad (2.23b)$$

and the vibrational part is expanded in ξ_i ,

$$(\partial / \partial x_{\alpha})_{\text{vib}} = \sum_i s_i^{\alpha} \xi_i , \quad (2.24a)$$

The c.m. system X is endowed with a metric through the kinetic energy of the molecule,

$$ds^2 = \sum_{\alpha} m_{\alpha} (dx_{\alpha} | dx_{\alpha}) . \quad (2.20)$$

With respect to this metric, the vectors B_a^{α} and B_i^{α} can be proved, after calculation, to satisfy

with

$$s_i^{\alpha} = \sum_b e_b^0 s_{ib}^{\alpha} . \quad (2.24b)$$

Inserting Eq. (2.22) with Eqs. (2.23a) and (2.24a) in Eq. (2.15a), we obtain

$$\sum_{\alpha} (B_a^{\alpha} | s_b^{\alpha}) = \delta_a^b , \quad \sum_{\alpha} (B_a^{\alpha} | s_i^{\alpha}) = 0 . \quad (2.25)$$

In the same way, from Eq. (2.17a) we have

$$\sum_{\alpha} (B_i^{\alpha} | s_b^{\alpha}) = 0 , \quad \sum_{\alpha} (B_i^{\alpha} | s_j^{\alpha}) = \delta_i^j . \quad (2.26)$$

It is now a matter of calculation to find out s_a^{α} and s_i^{α} from Eqs. (2.16a) and (2.18a) in the form

$$s_{ab}^{\alpha} = m_{\alpha} (x_{\alpha} \times e_b^0 | I^{-1} | e_a) , \quad (2.27a)$$

so that

$$s_a^{\alpha} = (I^{-1} e_a) \times m_{\alpha} x_{\alpha} , \quad (2.27b)$$

and

$$s_{ab}^i = \sum_k m_{\alpha} \left[(e_b^0 | \partial x_{\alpha} / \partial q^k) - (x_{\alpha} \times e_b^0 | I^{-1} | \sum_{\beta} m_{\beta} x_{\beta} \times \partial x_{\beta} / \partial q^k) \right] a^{ki} , \quad (2.28a)$$

so that

$$s_i^{\alpha} = \sum_k m_{\alpha} (\partial x_{\alpha} / \partial q^k) a^{ki} - \left[I^{-1} \sum_k \left(\sum_{\beta} m_{\beta} x_{\beta} \times \partial x_{\beta} / \partial q^k \right) a^{ki} \right] \times m_{\alpha} x_{\alpha} , \quad (2.28b)$$

where the matrix $||a^{ij}||$ is the inverse of $||a_{ij}||$ given by Eq. (2.21b), satisfying

$$\sum_k a_{ik} a^{kj} = \delta_i^j . \quad (2.28c)$$

It is easy to verify that the vectors s_a^{α} and s_i^{α} have the same properties as Eq. (2.19),

$$\sum_{\alpha} s_a^{\alpha} = 0 , \quad (2.29a)$$

and

$$\sum_{\alpha} s_i^{\alpha} = 0 , \quad (2.29b)$$

$$\sum_{\alpha} x_{\alpha} \times s_i^{\alpha} = 0 . \quad (2.29c)$$

The latter Eqs. (2.29b) and (2.29c) shows that the s_i^{α} satisfy the condition of the Wilson's s vector.²¹ In a dual manner to Eq. (2.21), the vectors s_a^{α} and s_i^{α} satisfy

$$\sum_{\alpha} (1/m_{\alpha}) (s_a^{\alpha} | s_b^{\alpha}) = (I^{-1})_{ab} , \quad (2.30a)$$

$$\sum_{\alpha} (1/m_{\alpha})(s_{\alpha}^i | s_{\alpha}^j) = a^{ij}, \quad (2.30b)$$

$$\sum_{\alpha} (1/m_{\alpha})(s_{\alpha}^a | s_{\alpha}^i) = 0. \quad (2.30c)$$

Since the s_{α}^i satisfy the condition of the Wilson's s vector, as shown in Eqs. (2.29b) and (2.29c), the matrix $||a^{ij}||$ satisfying Eq. (2.30b) is nothing but the Wilson's G matrix.²¹

We conclude this section by remarking that the vibrational components $(\partial/\partial x_{\alpha})_{\text{vib}}$ do not contribute to the angular momentum J ,

$$J = \sum_{\alpha} x_{\alpha} \times (\partial/\partial x_{\alpha})_{\text{rot}}$$

and

$$\sum_{\alpha} x_{\alpha} \times (\partial/\partial x_{\alpha})_{\text{vib}} = 0. \quad (2.31)$$

III. QUANTUM MECHANICS

This section deals with quantum mechanics of nonrigid molecules on the basis of the geometric setting in Sec. II.

Consider the matrix element of the kinetic energy operator \hat{T} with respect to an arbitrary pair of basis functions Ψ_{λ} , say Ψ_1 and Ψ_2 . Let X_C be the c.m. coordinates. Then we have

$$\langle \Psi_1 | \hat{T} | \Psi_2 \rangle = (\hbar^2/2) \int \left[(1/m)(\partial\Psi_1^*/\partial X_C | \partial\Psi_2/\partial X_C) + \sum_{\alpha} (1/m_{\alpha})(\partial\Psi_1^*/\partial x_{\alpha} | \partial\Psi_2/\partial x_{\alpha}) \right] dV / \int \Psi_1^* \Psi_2 dV, \quad (3.1a)$$

where m is the total mass,

$$m = \sum_{\alpha} m_{\alpha}, \quad (3.1b)$$

and the volume element dV is given by the standard $3N$ -form. Making full use of the results of Sec. II B, we have the integrand of Eq. (3.1a) in the form

$$\sum_{\alpha} (1/m_{\alpha})(\partial\Psi_1^*/\partial x_{\alpha} | \partial\Psi_2/\partial x_{\alpha}) = \sum_{a,b} (I^{-1})_{ab} (J_a \Psi_1^*) (J_b \Psi_2) + \sum_{i,j} a^{ij} (\xi_i \Psi_1^*) (\xi_j \Psi_2). \quad (3.2)$$

The volume element takes the form

$$\begin{aligned} dV &= J_{\text{int}} dX_C^1 \wedge dX_C^2 \wedge dX_C^3 \wedge \omega^1 \wedge \omega^2 \wedge \omega^3 \wedge dq^1 \wedge \cdots \wedge dq^n \\ &= \sin\theta J_{\text{int}} dX_C^1 \wedge dX_C^2 \wedge dX_C^3 \wedge d\phi \wedge d\theta \wedge d\psi \wedge dq^1 \wedge \cdots \wedge dq^n, \end{aligned} \quad (3.3a)$$

where

$$J_{\text{int}} = \left[\left(m / \prod_{\alpha} m_{\alpha} \right)^3 \det ||I_{ab}|| \det ||a_{ij}|| \right]^{1/2}, \quad (3.3b)$$

and

$$\det ||\theta_a^b|| = \sin\theta. \quad (3.3c)$$

We take the basis function of the form

$$\Psi_{\lambda} = \exp[i(k | X_C)] \sum_K \chi_{MK}^L \Phi_K^L. \quad (3.4)$$

Here $k = (k_1, k_2, k_3)$ is the wave vector of translational motion, and χ_{MK}^L are the coefficients of the L th irreducible unitary representation of $G = \text{SO}(3)$, and Φ_K^L are functions of n internal coordinates q^1, q^2, \dots, q^n . For the total linear momentum operator

$$\hat{P} = -i\hbar \partial/\partial X_C, \quad (3.5a)$$

we have

$$\hat{P} \exp[i(k | X_C)] = \hbar k \exp[i(k | X_C)], \quad (3.5b)$$

and for the total angular momentum operator

$$\hat{J} = -i\hbar \mathbf{J}, \quad (3.6a)$$

we have

$$\hat{J}^2 \chi_{MK}^L = \hbar^2 L(L+1) \chi_{MK}^L, \quad (3.6b)$$

$$\hat{J}_z \chi_{MK}^L = \hbar M \chi_{MK}^L, \quad (3.6c)$$

$$\hat{J}_3 \chi_{MK}^L = \hbar K \chi_{MK}^L, \quad (3.6d)$$

where M ($|M| \leq L$) denotes the Z component of the total angular momentum with respect to LF and K denotes the 3rd component of the total angular momentum with respect to the moving frame.

Now, we are in a position to separate collective motions from quantum-mechanical nonrigid molecular dynamics. Indeed, when labeled by L , the space of wave functions $(\Phi_K^L), K = L, L-1, \dots, -L$, on which the operator of internal motion acts is associated with the space of vector functions (3.4) with M ranging from L to $-L$.

Applying (3.2) to (3.4), and performing the integration on $\text{SO}(3)$, i.e., with respect to the Eulerian angles, we will find the matrix elements for the internal wave functions. The first term of (3.2) gives rise to the matrix-valued centrifugal potentials²⁹ and the rest to the matrix-valued second-order differential operator coupled with the gauge field (2.14b).

For simplicity, we set up quantum molecular dynamics under the condition of zero-total linear and angular

momentum,³⁰ $\hat{P}\Psi_\lambda = \hat{J}\Psi_\lambda = 0$. In this case, Eq. (3.1) is reduced to

$$\langle \Psi_1 | \hat{T} | \Psi_2 \rangle = \frac{\int \Psi_1^* (\hat{T}_{\text{int}} \Psi_2) J_{\text{int}} dq^1 dq^2 \cdots dq^n}{\int \Psi_1^* \Psi_2 J_{\text{int}} dq^1 dq^2 \cdots dq^n}, \quad (3.7a)$$

where

$$\hat{T}_{\text{int}} = \frac{1}{2} \sum_{j,k} J_{\text{int}}^{-1/2} \Pi_j J_{\text{int}} a^{jk} \Pi_k J_{\text{int}}^{-1/2}, \quad (3.7b)$$

with

$$\Pi_j = J_{\text{int}}^{-1/2} (-i\hbar \partial / \partial q^j) J_{\text{int}}^{1/2}. \quad (3.7c)$$

\hat{T}_{int} is a purely internal Hamiltonian which describes vibrational motion only. From Eq. (2.14a), we see that the Coriolis coupling is not observed in this case.

IV. TRIATOMIC MOLECULES

A. Hamiltonian operator on the c.m. system

This section deals with the quantum-mechanical operators of a three-body system.³¹⁻³³ Using Guichardet coordinates²² q^1, q^2, q^3 , we have the position vectors in the form

$$x_1 = X_C + q^1 e_1, \quad (4.1a)$$

$$x_2 = X_C + q^2 e_1 + q^3 e_2, \quad (4.1b)$$

$$x_3 = X_C - (1/m_3)(m_1 q^1 + m_2 q^2) e_1 - (m_2/m_3) q^3 e_2, \quad (4.1c)$$

where $q^1 > 0$ and $q^3 > 0$. In this coordinate system, both the internal coordinates q^i and the moving frame appear in an easily comprehensible form. The Guichardet coordinates q^1, q^2, q^3 are related to the usual configurational parameters as follows (also, see Fig. 2):

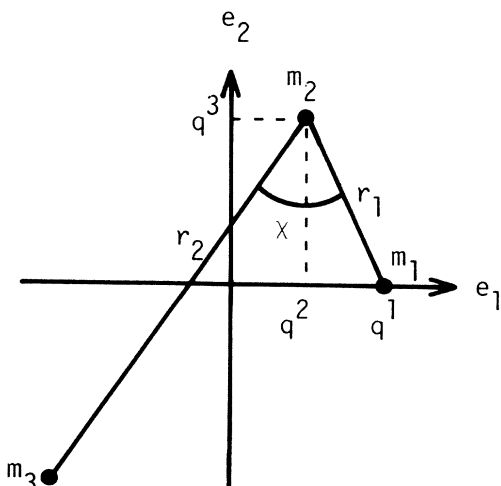


FIG. 2. Guichardet coordinates and the conventional configurational parameters.

$$r_1^2 = (q^2 - q^1)^2 + (q^3)^2, \quad (4.2a)$$

$$r_2^2 = (1/m_3)^2 [m_1 q^1 + (m_2 + m_3) q^2]^2 + (1/m_3)^2 (m_2 + m_3)^2 (q^3)^2, \quad (4.2b)$$

$$r_1 r_2 \cos \chi = (1/m_3) [-m_1 (q^1)^2 + (m_1 - m_2 - m_3) q^1 q^2 + (m_2 + m_3) (q^2)^2]. \quad (4.2c)$$

The matrix of the inertia tensor is given as

$$||I_{ab}|| = \begin{vmatrix} I_{11} & I_{12} & 0 \\ I_{12} & I_{22} & 0 \\ 0 & 0 & I_{33} \end{vmatrix}, \quad (4.3a)$$

where

$$I_{11} = (m_2/m_3)(m_2 + m_3)(q^3)^2, \quad (4.3b)$$

$$I_{22} = (1/m_3) [m_1(m_1 + m_3)(q^1)^2 + m_2(m_2 + m_3)(q^2)^2 + 2m_1 m_2 q^1 q^2], \quad (4.3c)$$

$$I_{33} = (1/m_3) \{ m_1(m_1 + m_3)(q^1)^2 + m_2(m_2 + m_3)[(q^2)^2 + (q^3)^2] + 2m_1 m_2 q^1 q^2 \}, \quad (4.3d)$$

$$I_{12} = -(m_2/m_3) [m_1 q^1 + (m_2 + m_3) q^2] q^3, \quad (4.3e)$$

and

$$\det ||I_{ab}|| = I_{33} (m_1 m_2 m / m_3) (q^1)^2 (q^3)^2. \quad (4.3f)$$

The metric tensor on the internal space M is computed from Eq. (2.21b) as

$$a_{11} = -(1/I_{33}) (m_1 m_2 q^3 / m_3)^2 + m_1 (m_1 + m_3) / m_3, \quad (4.4a)$$

$$a_{22} = -(1/I_{33}) [m_2 (m_2 + m_3) q^3 / m_3]^2 + m_2 (m_2 + m_3) / m_3, \quad (4.4b)$$

$$a_{33} = -(1/I_{33}) \{ (m_2 / m_3) [m_1 q^1 + (m_2 + m_3) q^2] \}^2 + m_2 (m_2 + m_3) / m_3, \quad (4.4c)$$

$$a_{12} = -(1/I_{33}) (m_1 m_2 / m_3) (m_2 / m_3) (m_2 + m_3) (q^3)^2 + m_1 m_2 / m_3, \quad (4.4d)$$

$$a_{23} = (1/I_{33}) (m_2 / m_3) (m_2 + m_3) q^3 (m_2 / m_3) \times [m_1 q^1 + (m_2 + m_3) q^2], \quad (4.4e)$$

$$a_{31} = (1/I_{33}) (m_1 m_2 / m_3) q^3 (m_2 / m_3) \times [m_1 q^1 + (m_2 + m_3) q^2], \quad (4.4f)$$

and

$$\det ||a_{ij}|| = (1/I_{33}) (m_1 m_2 m / m_3)^2 (q^1)^2. \quad (4.4g)$$

Therefore, the volume element is given by

$$dV = \sin\theta J_{\text{int}} dX_C^1 \wedge dX_C^2 \wedge dX_C^3 \wedge d\phi \wedge d\theta \wedge d\psi \wedge dq^1 \wedge dq^2 \wedge dq^3, \quad (4.5a)$$

where J_{int} is computed from Eqs. (3.3b), (4.3f), and (4.4g),

$$J_{\text{int}} = (m/m_3)^3 (q^1)^2 q^3. \quad (4.5b)$$

Moreover, the vibrational vectors ξ_i are given as follows:

$$\xi_1 = \partial/\partial q^1 + (1/I_{33})(m_1 m_2/m_3) q^3 J_3, \quad (4.6a)$$

$$\xi_2 = \partial/\partial q^2 + (1/I_{33})(m_2/m_3)(m_2 + m_3) q^3 J_3, \quad (4.6b)$$

$$\xi_3 = \partial/\partial q^3 - (1/I_{33})(m_2/m_3)[m_1 q^1 + (m_2 + m_3) q^2] J_3. \quad (4.6c)$$

We have at hand all materials with which we can write out the Hamiltonian operator on the c.m. system. In fact, integration of Eq. (3.2) by part together with Eqs. (2.13) and (4.3)–(4.6) gives the desired Hamiltonian operator. The potential term is added, depending on the situation.

The vibration-rotation coupling appears in the nonvanishing commutators

$$[\xi_i, \xi_j] = -F_{ij}^3 J_3, \quad (4.7a)$$

where

$$F_{12}^3 = (2m_1 m_2 m/m_3 I_{33}^2) q^1 q^3, \quad (4.7b)$$

$$dv_{\text{int}} = \sin\chi dr_1 \wedge dr_2 \wedge d\chi, \quad (4.8b)$$

$$\begin{aligned} \hat{t}_{\text{int}} = & -(\hbar^2/2\mu_1)\partial^2/\partial r_1^2 + (\hbar^2/2\mu_1)l^2/r_1^2 - (\hbar^2/2\mu_2)\partial^2/\partial r_2^2 + (\hbar^2/2\mu_2)l^2/r_2^2 \\ & - (\hbar^2/m_2)\cos\chi(\partial/\partial r_1 - 1/r_1)(\partial/\partial r_2 - 1/r_2) + (\hbar^2/m_2)\sin\chi(\partial/\partial\chi)[(1/r_2)\partial/\partial r_1 + (1/r_1)\partial/\partial r_2] \\ & - (\hbar^2/m_2)(1/r_1 r_2)(\cos\chi l^2 + \sin\chi \partial/\partial\chi), \end{aligned} \quad (4.8c)$$

where

$$1/\mu_1 = 1/m_1 + 1/m_2, \quad (4.8d)$$

$$1/\mu_2 = 1/m_2 + 1/m_3, \quad (4.8e)$$

and

$$l^2 = -\partial^2/\partial\chi^2 - \cot\chi \partial/\partial\chi. \quad (4.8f)$$

In this expression, $\hbar^2 l^2$ denotes the square of the angular momentum corresponding to the internal rotational motion. The above Hamiltonian has the well-known form of standard three-body Hamiltonian.³⁴ This has been used in the study of the vibrational predissociation of van der Waals molecules.³⁵

In conclusion, we make brief remarks on our geometric method. Application of the present theory to the problems of the reaction coordinates^{36–48} and the vibrational coordinates^{21,49} will be of practical importance in understanding the complex dynamic processes of chemical reactions in terms of the local character of the reaction sys-

$$F_{23}^3 = (2m_1 m_2 m/m_3 I_{33}^2) q^1 q^1, \quad (4.7c)$$

$$F_{31}^3 = (2m_1 m_2 m/m_3 I_{33}^2) q^1 q^2. \quad (4.7d)$$

If the total angular momentum vanishes, then vibration-rotation coupling is not observed. In this case the purely internal Hamiltonian is given by Eq. (3.7).

B. Reduction to the case of zero-total linear and angular momentum

This section deals with the case of zero-total linear and angular momentum using the usual configurational parameters as the internal coordinates. For the application of the present theory to chemical-reaction dynamics, the usual configurational parameters are more useful than Guichardet coordinates.

Since the internal coordinates q^i are chosen arbitrarily in Eq. (3.7), Eq. (3.7) becomes

$$\begin{aligned} \langle \Psi_1 | \hat{T} | \Psi_2 \rangle \\ = \int \Phi_1^{\text{int}*}(\hat{t}_{\text{int}} \Phi_2^{\text{int}}) dv_{\text{int}} / \int \Phi_1^{\text{int}*} \Phi_2^{\text{int}} dv_{\text{int}}, \end{aligned} \quad (4.8a)$$

with

tem. Recently, in this connection, topological properties of potential-energy hypersurfaces have been studied by Mezey,⁵⁰ where the equivalence classes of configurations are used to obtain the reduced configuration space which is equivalent to the quotient space M given in Eq. (2.3) of the present paper.

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