

The rovibrational kinetic energy for complexes of rigid molecules

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The rovibrational kinetic energy for an arbitrary number of rigid molecules is computed. The result has the same general form as the kinetic energy in the molecular rovibrational Hamiltonian, although certain quantities are augmented to account for the rotational energy of the monomers. No specific choices of internal coordinates or body frame are made in order to accommodate the large variety of such conventions. However, special attention is paid to how key quantities transform when these conventions are changed. An example system is analysed explicitly as an illustration of the formalism.

1. Introduction

The rovibrational kinetic energy of a molecular (rigid body) complex has previously been computed explicitly for a number of specific cases. Examples include calculations for the atom–monomer system, consisting of a point particle and a rigid body, by Brocks and van Koeven [1], van der Avoird [2], and Makarewicz and Bauder [3]; the molecular dimer, consisting of two rigid bodies, by Brocks *et al.* [4] and van der Avoird [5]; the molecular trimer by Xantheas and Sutcliffe [6] and van der Avoird, Olthof and Wormer [7]; and closely related systems of single molecules with internal rotation [8, 9]. In the present paper we derive the rovibrational kinetic energy of an arbitrary molecular complex containing an arbitrary number of rigid bodies. That is, we express the kinetic energy in terms of the total angular momentum of the complex and the momenta associated with the internal degrees of freedom. The term ‘rovibrational’ is perhaps misleading since it implies small amplitude vibrations of the complex, an assumption we do not make. A rovibrational kinetic energy for a general molecular complex has been proposed earlier by Makarewicz and Bauder [3]; their analysis differs markedly from ours in that they do not impose rigidity conditions on the monomers nor do they distinguish the relative rotational motion of the monomers from the internal vibrations of the monomers.

One method for deriving the rovibrational kinetic energy of a system of rigid bodies would be to begin with the rovibrational kinetic energy of a system of point particles and then impose rigidity constraints within certain subsets of these particles. A general analysis of internal constraints on n -body systems has been

given by Menou and Chapuisat [10] and by Gatti *et al.* [11]. These authors observe that such a formalism may be applied to find the rovibrational kinetic energy of a rigid body complex, though they do not derive such a kinetic energy. The constrained systems approach has the advantage of naturally allowing the relaxation of the rigidity constraints to include small internal vibrations of the monomers. However, within a strictly rigid body, the positions, masses, and velocities of the constituent particles are irrelevant. Rather, only the overall orientation, moment of inertia, and angular velocity are of interest. Therefore, in our derivation of the rovibrational kinetic energy, we assume from the outset that the bodies are rigid and use a kinetic energy consisting of only the translational and rotational energies of the rigid bodies. It should be mentioned that whichever approach is followed there exists an ambiguous extrapotential term in the quantum kinetic energy. The origin of this ambiguity rests in the lack of knowledge about the potential which confines the system to the manifold of rigid shapes (see, e.g. Kaplan *et al.* [12]). For simplicity, we neglect any extrapotential terms arising from the constraint process and adopt the standard form (translational plus rotational energies) for the quantum kinetic energy of a rigid body.

Our approach is modelled on the derivation of [13], valid for clusters of point particles, but is augmented to include the rotational kinetic energy of the monomers; the current paper therefore generalizes many results valid for point particles to systems of extended rigid bodies.

Also, in deriving the rovibrational kinetic energy, we make no specific choice of internal coordinates or body frame. This allows our results to be applicable to the wide range of coordinate and frame conventions suitable to different molecular complexes. We discuss how

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the various quantities appearing in the kinetic energy transform under changes of internal coordinates and body frame. We also present two distinct decompositions of the kinetic energy into rotational and vibrational (internal) contributions. The first decomposition is independent of the conventions for internal coordinates and body frame. The second decomposition has a form more common to rovibrational Hamiltonians in the literature, though it is not independent of coordinate and frame conventions.

The current paper has been influenced by recent work exhibiting the importance of gauge theory and geometric phase in the study of rovibrational coupling [13–19]. In addition to rovibrational coupling, the geometric, or Berry's, phase [20] has important applications in Born–Oppenheimer theory [21], optics [22, 23], and guiding centre motion [24], to name a few examples. The influence of gauge theory on our analysis here is most readily evident in the form of the kinetic energy equation (27) which, owing to the appearance of a gauge potential, is reminiscent of the kinetic energy of a charged particle in a magnetic field. Notions of gauge invariance and covariance also have influenced our analysis of transformation properties presented in section 2.3. Although our development is influenced by the techniques and concepts of gauge theory and geometric phase, this paper requires no specific background in either field.

2. The classical kinetic energy of a molecular complex

2.1. The principal derivation

In this paper, a molecular complex is modelled by a collection of n rigid bodies or monomers. No constraints are placed on the positions or orientations of the monomers or on the symmetry of the moment of inertia tensors. In particular, we allow the monomers to be point particles (atoms), collinear bodies, or non-collinear bodies. However, for mathematical simplicity, initially we assume that each monomer is non-collinear. Then, after deriving the rovibrational kinetic energy, we comment on the straightforward generalization of allowing complexes containing collinear monomers and point particles.

We begin by introducing three classes of frames which are important in our derivation. The space frame (SF) is the inertial, laboratory-fixed frame. There are n individual body frames (IBF), one for each body. IBF $_{\alpha}$, $\alpha = 1, \dots, n$, is fixed to rigid body α and rotates with the body. Finally, there is a single collective body frame (CBF), which is fixed to the complex as a whole. The CBF differs from the other frames in that it must be specified for each shape or internal configuration of the complex. In general, this specification produces singularities in the CBF, a fact which has been studied

in three- and four-atom systems [25, 26]. There is no canonical way of choosing the CBF, though there are several methods commonly used in such Hamiltonians, such as fixing the CBF to the principal axes of the complex or to one of the IBFs. In this paper we will make no specific choice of CBF.

We employ the following notation to denote the frame to which the components of a vector are referred. For an arbitrary vector \mathbf{v} , an s superscript, that is \mathbf{v}^s , indicates components in the SF; an $i\alpha$ superscript indicates components in the IBF of body α ; and a c superscript indicates components in the CBF. (For notational simplicity, at a certain point we will drop the c superscript, leaving it understood thereafter that a vector without a superscript is implicitly in the CBF.) The components of \mathbf{v} in the various frames are related by proper orthogonal 3×3 matrices, which we define by

$$\mathbf{v}^s = R\mathbf{v}^c, \quad (1)$$

$$\mathbf{v}^s = S_{\alpha}^s \mathbf{v}^{i\alpha}, \quad (2)$$

$$\mathbf{v}^c = S_{\alpha}^c \mathbf{v}^{i\alpha}. \quad (3)$$

The matrix S_{α}^s determines the orientation of body α , in the SF; the matrix R determines the orientation of the entire complex in the SF; and the matrix S_{α}^c determines the orientation of body α in the CBF.

The configuration of the complex of n rigid bodies is specified fully by the centre of mass position of each body and the orientation of each body. To eliminate the overall translational degrees of freedom, we fix the centre of mass of the entire complex at the origin. The centre of mass positions of the n bodies are then determined by $n - 1$ Jacobi vectors [27, 13] \mathbf{r}_{α}^s , $\alpha = 1, \dots, n - 1$. The orientations of the rigid bodies are specified by the n matrices $S_{\alpha}^s \in \text{SO}(3)$, $\alpha = 1, \dots, n$. Taken together, \mathbf{r}_{α}^s , $\alpha = 1, \dots, n - 1$ and S_{α}^s , $\alpha = 1, \dots, n$ specify a lab description of the configuration. To shift to an internal–external, or shape–orientation, description of the configuration, we introduce $6n - 6$ internal, or shape, coordinates q^{μ} , $\mu = 1, \dots, 6n - 6$. The q^{μ} may be separated into $3n - 6$ coordinates parametrizing the distances between the rigid bodies and $3n$ coordinates (Euler angles) parametrizing the orientations of the bodies in the CBF. However, here we allow the q^{μ} to be completely arbitrary, so long as they are invariant under rotations of the complex. The Jacobi vectors \mathbf{r}_{α}^c , referred to the collective body frame, and the matrices S_{α}^c are both functions of the internal coordinates q^{μ} . In practice, one may define the CBF by specifying the functions $\mathbf{r}_{\alpha}^c(q)$ and $S_{\alpha}^c(q)$, where q without a superscript refers to the collection of all coordinates q^{μ} . The orientation $R \in \text{SO}(3)$ (defined in equation (1)) of the complex and

the shape q^μ fully determine the configuration in the SF, as may be seen by the following equations:

$$\mathbf{r}_\alpha^s = R\mathbf{r}_\alpha^c(q), \quad (4)$$

$$\mathbf{S}_\alpha^s = R\mathbf{S}_\alpha^c(q). \quad (5)$$

Equation (4) is an application of equation (1), and equation (5) is implied by equations (1)–(3). The above equations relate the internal–external description of a configuration (in terms of R and q) to the original description (in terms of \mathbf{r}_α^s and \mathbf{S}_α^s).

We assume that the masses of the n bodies have been absorbed into our definition of the Jacobi vectors. Thus, the kinetic energy of the complex, without the overall translational contribution, is

$$T = \frac{1}{2} \sum_{\alpha=1}^{n-1} |\dot{\mathbf{r}}_\alpha^s|^2 + \frac{1}{2} \sum_{\alpha=1}^n \omega_\alpha^s \cdot M_\alpha^s \omega_\alpha^s, \quad (6)$$

where the dot is used for time derivatives, M_α^s is the moment of inertia of body α in the SF, and ω_α^s is the angular velocity of body α .

In general, an angular velocity is a vector which measures the rotation rate of one frame with respect to another frame. The components of this vector may be referred to either of these two frames (or to an arbitrary third frame for that matter). For example, the angular velocity ω_α^s measures the rotation rate of the IBF of body α with respect to the SF; its components are referred to the SF.

We introduce the notation $\mathbf{v} \times$ for the antisymmetric matrix which maps a vector \mathbf{u} into the vector $\mathbf{v} \times \mathbf{u}$. Then,

$$\omega_\alpha^s \times = \dot{\mathbf{S}}_\alpha^s \mathbf{S}_\alpha^{sT}, \quad (7)$$

$$\omega_\alpha^{ja} \times = \mathbf{S}_\alpha^{sT} \dot{\mathbf{S}}_\alpha^s, \quad (8)$$

where the T superscript denotes the matrix transpose. Note that these two formulas are consistent with the change of basis relation equation (2), that is $\omega_\alpha^s = \mathbf{S}_\alpha^s \omega_\alpha^{ja}$, as may be seen from the general relation

$$\mathbf{Q}(\mathbf{v} \times) \mathbf{Q}^T = (\mathbf{Q}\mathbf{v}) \times, \quad (9)$$

where the vector \mathbf{v} is arbitrary and $\mathbf{Q} \in SO(3)$.

We proceed by expressing the kinetic energy equation (6) in terms of the internal velocities \dot{q}^μ and the total angular velocity ω^f . The total angular velocity measures the rotation rate of the CBF with respect to the SF. It has components in both the SF and the CBF which are

$$\omega^s \times = \dot{R}R^T, \quad (10)$$

$$\omega^f \times = R^T \dot{R}. \quad (11)$$

These equations are analogous to equations (7) and (8). Equation (11) permits the time derivatives of equations (4) and (5) to be expressed as

$$\dot{\mathbf{r}}_\alpha^s = \dot{R}\mathbf{r}_\alpha^c + R\mathbf{r}_{\alpha,\mu}^c \dot{q}^\mu = R(\omega^f \times \mathbf{r}_\alpha^c + \mathbf{r}_{\alpha,\mu}^c \dot{q}^\mu), \quad (12)$$

$$\dot{\mathbf{S}}_\alpha^s = \dot{R}\mathbf{S}_\alpha^c + R\mathbf{S}_{\alpha,\mu}^c \dot{q}^\mu = R[(\omega^f \times) \mathbf{S}_\alpha^c + \mathbf{S}_{\alpha,\mu}^c \dot{q}^\mu], \quad (13)$$

where the ‘ μ ’ subscript denotes the derivative with respect to the coordinate q^μ . In the above equations we have used the convention, which we adopt for the remainder of the paper, that the Greek indices μ, ν, \dots are implicitly summed from 1 to $6n - 6$ when repeated. However, the Greek indices α, β, \dots which label either the Jacobi vectors or monomers are summed explicitly. Combining equations (7) and (13) and using equation (5), we find

$$\omega_\alpha^s \times = R[(\omega^f \times) + \mathbf{S}_{\alpha,\mu}^c \mathbf{S}_\alpha^{cT} \dot{q}^\mu] R^T. \quad (14)$$

Since $\mathbf{S}_{\alpha,\mu}^c \mathbf{S}_\alpha^{cT}$ is antisymmetric, we define a vector $\tau_{\alpha\mu}$ such that

$$\tau_{\alpha\mu}^c \times = \mathbf{S}_{\alpha,\mu}^c \mathbf{S}_\alpha^{cT}, \quad (15)$$

$$\tau_{\alpha\mu}^{ia} \times = \mathbf{S}_\alpha^{cT} \mathbf{S}_{\alpha,\mu}^c. \quad (16)$$

By comparison with equations (7) and (8), we see that $\dot{q}^\mu \tau_{\alpha\mu}^c$ is the angular velocity of the IBF α with respect to the CBF. By inserting equation (15) into (14) and using equation (9), we find

$$\omega_\alpha^s = R(\omega^f + \dot{q}^\mu \tau_{\alpha\mu}^c) = \omega^s + \dot{q}^\mu \tau_{\alpha\mu}^s. \quad (17)$$

The above equation expresses the angular velocity of the IBF of body α with respect to the SF as the sum of the angular velocity of the CBF with respect to the SF plus the angular velocity of the IBF of body α with respect to the CBF. However, this decomposition has no inherent physical meaning since it depends on the convention used to define the CBF. By appropriately changing this convention, either of these two terms could be made to vanish.

Using equations (12) and (17) in equation (6), we write the kinetic energy as

$$T = \frac{1}{2} \omega^f M \omega^f + \mathbf{a}_\mu \cdot \omega_\mu^j + \frac{1}{2} h_{\mu\nu} \dot{q}^\mu \dot{q}^\nu, \quad (18)$$

where

$$M = \sum_{\alpha=1}^{n-1} (r_\alpha^2 I - \mathbf{r}_\alpha \mathbf{r}_\alpha^T) + \sum_{\alpha=1}^n M_\alpha = \sum_{\alpha=1}^{n-1} (r_\alpha^2 I - \mathbf{r}_\alpha \mathbf{r}_\alpha^T) + \sum_{\alpha=1}^n \mathbf{S}_\alpha M_\alpha^{ia} \mathbf{S}_\alpha^T, \quad (19)$$

$$\mathbf{a}_\mu = \sum_{\alpha=1}^{n-1} \mathbf{r}_\alpha \times \mathbf{r}_{\alpha,\mu} + \sum_{\alpha=1}^n M_\alpha \tau_{\alpha\mu} = \sum_{\alpha=1}^{n-1} \mathbf{r}_\alpha \times \mathbf{r}_{\alpha,\mu} + \sum_{\alpha=1}^n \mathbf{S}_\alpha M_\alpha^{ia} \tau_{\alpha\mu}^{ia}, \quad (20)$$

$$h_{\mu\nu} = \sum_{\alpha=1}^{n-1} \mathbf{r}_{\alpha,\mu} \cdot \mathbf{r}_{\alpha,\nu} + \sum_{\alpha=1}^n \tau_{\alpha\mu} \cdot \mathbf{M}_{\alpha} \tau_{\alpha\nu} = \sum_{\alpha=1}^{n-1} \mathbf{r}_{\alpha,\mu} \cdot \mathbf{r}_{\alpha,\nu} + \sum_{\alpha=1}^n \tau_{\alpha\mu}^{i\alpha} \cdot \mathbf{M}_{\alpha}^{i\alpha} \tau_{\alpha\nu}^{i\alpha}, \quad (21)$$

and where henceforth we suppress the c superscript on vectors and tensors referred to the CBF. We have also used I for the identity matrix and $\mathbf{M}_{\alpha} = \mathbf{R}^T \mathbf{M}_{\alpha}^s \mathbf{R}$ and $\mathbf{M}_{\alpha}^{i\alpha} = \mathbf{S}_{\alpha}^{sT} \mathbf{M}_{\alpha}^s \mathbf{S}_{\alpha}^s$ for the moment of inertia of body α in the CBF and IBF α respectively. In the above equations, we present two expressions for each of the quantities M , \mathbf{a}_{μ} , and $h_{\mu\nu}$. The first expression involves quantities referred entirely to the CBF. The second expression is slightly more complex but has the advantage that all of the dependence on $\mathbf{S}_{\alpha}(q)$ and $\mathbf{r}_{\alpha}(q)$ is shown explicitly by \mathbf{S}_{α} , \mathbf{r}_{α} , $\mathbf{r}_{\alpha,\mu}$, and $\tau_{\alpha\mu}^{i\alpha}$. Note that $\mathbf{M}_{\alpha}^{i\alpha}$ is the moment of inertia of body α in its own IBF and as such is a constant matrix independent of both the shape and orientation.

By rearranging the terms in equation (18), we put the kinetic energy in the form

$$T = \frac{1}{2}(\omega + \mathbf{A}_{\mu} \dot{q}^{\mu}) \cdot \mathbf{M}(\omega + \mathbf{A}_v \dot{q}^v) + \frac{1}{2} g_{\mu\nu} \dot{q}^{\mu} \dot{q}^v, \quad (22)$$

where

$$\mathbf{A}_{\mu} = \mathbf{M}^{-1} \mathbf{a}_{\mu}, \quad (23)$$

$$g_{\mu\nu} = h_{\mu\nu} - \mathbf{a}_{\mu} \cdot \mathbf{M}^{-1} \mathbf{a}_{\nu}. \quad (24)$$

Converting the velocities to momenta, we find

$$\mathbf{J} = \frac{\partial T}{\partial \omega} = \mathbf{M}(\omega + \mathbf{A}_{\mu} \dot{q}^{\mu}), \quad (25)$$

$$p_{\mu} = \frac{\partial T}{\partial \dot{q}^{\mu}} = g_{\mu\nu} \dot{q}^v + \mathbf{A}_{\mu} \cdot \mathbf{J}. \quad (26)$$

The vector \mathbf{J} is the total angular momentum of the complex. It satisfies the usual body-referred ‘anomalous’ commutation relations $\{J_i, J_j\} = -\sum_k \varepsilon_{ijk} J_k$, where ε_{ijk} is the usual Levi-Civita symbol. The classical kinetic energy is now expressible in terms of momenta as

$$T = \frac{1}{2} \mathbf{J} \cdot \mathbf{M}^{-1} \mathbf{J} + \frac{1}{2} (p_{\mu} - \mathbf{A}_{\mu} \cdot \mathbf{J}) g^{\mu\nu} (p_{\nu} - \mathbf{A}_{\nu} \cdot \mathbf{J}), \quad (27)$$

where $g^{\mu\nu}$ is the inverse of $g_{\mu\nu}$.

Equation (27) decomposes the kinetic energy into two terms. The first term is the kinetic energy the complex would have if it were a rigid body of fixed shape. We regard this term as the rotational kinetic energy of the complex. The second term we regard as the internal, or vibrational, kinetic energy. Often in such rotation–vibration decompositions a different rotational term appears which contains a modified moment of inertia tensor and a modified angular momentum vector. We will relate the above decomposition to such alternative

decompositions in the next section. For now, however, note that the appearance of \mathbf{A}_{μ} in the internal kinetic energy couples the internal degrees of freedom to the angular momentum. For this reason, we call \mathbf{A}_{μ} the Coriolis potential. Furthermore, we call $g_{\mu\nu}$ the internal metric because it acts to square $p_{\mu} - \mathbf{A}_{\mu} \cdot \mathbf{J}$. Note that the internal kinetic energy has the same ‘ $|\mathbf{p} - e\mathbf{A}|^2$ ’ form as the kinetic energy of a particle in a magnetic field, where the role of the vector, or gauge, potential is played by the Coriolis potential and the role of the electric charge is played by the angular momentum.

The kinetic energy given in [13] for a collection of point particles has exactly the same form as equation (27). However, for collections of point particles, the quantities defined in equations (19)–(21) do not contain the terms with $\mathbf{M}_{\alpha}^{i\alpha}$. The appearance of these terms, and of course the introduction of an extra $3n$ internal coordinates, are the sole modifications necessary to augment the kinetic energy of a system of point particles to include the rotational kinetic energy of the monomers. The fundamental reason why the form of the kinetic energy is the same for these two cases is the rotational symmetry of the kinetic energy operator; equation (27) is in fact a general result, valid for any $\text{SO}(3)$ invariant metric. We will discuss this matter further in a future publication.

We comment now on how the preceding results are generalized to include collinear monomers and point particles. First, the number of coordinates changes. A non-collinear body requires three Euler angles to specify its orientation fully, whereas a collinear body requires only two spherical coordinates to specify its orientation (the direction of its collinear axis). A point particle, of course, requires no orientational coordinates. Therefore, instead of $6n - 3$ coordinates as before, there are $3n + 3n_n + 2n_c - 3$ coordinates parametrizing the centre of mass system. Here, $n = n_n + n_c + n_p$ is the total number of monomers, where n_n is the number of noncollinear monomers, n_c is the number of collinear monomers, and n_p is the number of point particles.

We next describe the form of the rovibrational kinetic energy when incorporating collinear bodies and point particles. First, the computation leading from equation (6) to equation (27) is essentially unchanged by the inclusion of collinear bodies and point particles, so long as one takes the moment of inertia tensor \mathbf{M}_{α} of a point particle to be 0. The moment of inertia tensor of a collinear body is explicitly $\mathbf{M}_{\alpha} = \kappa_{\alpha} (I - \mathbf{n}_{\alpha} \mathbf{n}_{\alpha}^T)$, where \mathbf{n}_{α} is a unit vector pointing along the collinear axis and κ_{α} is the single nonzero principal moment. The quantity \mathbf{n}_{α} is a more natural measure of the orientation of a collinear body than \mathbf{S}_{α} , since \mathbf{S}_{α} overparametrizes the orientations. Therefore we rewrite equations (19)–(21)

in the following form, more appropriate for a general complex:

$$M = \sum_{\alpha=1}^{n-1} (r_{\alpha}^2 I - \mathbf{r}_{\alpha} \mathbf{r}_{\alpha}^T) + \sum_{\alpha=1}^{n_n} S_{\alpha} M_{\alpha}^{i\alpha} S_{\alpha}^T + \sum_{\alpha=n_n+1}^{n_n+n_c} \kappa_{\alpha} (I - \mathbf{n}_{\alpha} \mathbf{n}_{\alpha}^T), \quad (28)$$

$$\mathbf{a}_{\mu} = \sum_{\alpha=1}^{n-1} \mathbf{r}_{\alpha} \times \mathbf{r}_{\alpha,\mu} + \sum_{\alpha=1}^{n_n} S_{\alpha} M_{\alpha}^{i\alpha} \tau_{\alpha\mu}^{i\alpha} + \sum_{\alpha=n_n+1}^{n_n+n_c} \kappa_{\alpha} \mathbf{n}_{\alpha} \times \mathbf{n}_{\alpha,\mu}, \quad (29)$$

$$h_{\mu\nu} = \sum_{\alpha=1}^{n-1} \mathbf{r}_{\alpha,\mu} \cdot \mathbf{r}_{\alpha,\nu} + \sum_{\alpha=1}^{n_n} \tau_{\alpha\mu}^{i\alpha} \cdot M_{\alpha}^{i\alpha} \tau_{\alpha\nu}^{i\alpha} + \sum_{\alpha=n_n+1}^{n_n+n_c} \kappa_{\alpha} \mathbf{n}_{\alpha,\mu} \cdot \mathbf{n}_{\alpha,\nu}, \quad (30)$$

where we have ordered the monomers with the non-collinear bodies first, the collinear bodies second, and the point particles last. We omit the straightforward proof of these equations relying instead on the following two observations. First, the orientational contribution from the point particles has dropped out since M_{α} is 0 for such particles. Next, the orientational contribution from a collinear body is identical to the contribution of a single Jacobi vector. This fact is easily understood by modelling a collinear body as two point particles connected by a Jacobi vector. The above equations may be combined with equations (23) and (24) to obtain the kinetic energy equation (27) of a general molecular complex. The only note of caution occurs if the entire complex should become collinear, in which case M is not invertible and singularities may arise.

2.2. An alternative form of the kinetic energy

We rearrange the kinetic energy equation (27) to place it in a form which is more common in the literature on rovibrational Hamiltonians. We define the modified moment of inertia tensor \tilde{M} by

$$\tilde{M} = M - h^{\mu\nu} \mathbf{a}_{\mu} \mathbf{a}_{\nu}^T, \quad (31)$$

where $h^{\mu\nu}$ is the inverse matrix of $h_{\mu\nu}$, and the vector \mathbf{K} , often called the angular momentum of vibration, by

$$\mathbf{K} = h^{\mu\nu} \mathbf{a}_{\mu} p_{\nu}. \quad (32)$$

We use these definitions to place the kinetic energy in the form

$$T = \frac{1}{2} (\mathbf{J} - \mathbf{K}) \cdot \tilde{M}^{-1} (\mathbf{J} - \mathbf{K}) + \frac{1}{2} p_{\mu} h^{\mu\nu} p_{\nu}. \quad (33)$$

The above equation may be verified by comparing the terms of order J^2 , J^1 , and J^0 in equations (33) and (27). The equality of the respective terms is apparent from the following identities:

$$g^{\mu\nu} M^{-1} \mathbf{a}_{\nu} = h^{\mu\nu} \tilde{M}^{-1} \mathbf{a}_{\nu}, \quad (34)$$

$$g^{\mu\nu} = h^{\mu\nu} + h^{\mu\sigma} (\mathbf{a}_{\sigma} \cdot \tilde{M}^{-1} \mathbf{a}_{\tau}) h^{\tau\nu}, \quad (35)$$

$$\tilde{M}^{-1} = M^{-1} + g^{\mu\nu} \mathbf{A}_{\mu} \mathbf{A}_{\nu}^T, \quad (36)$$

which follow from equations (31) and (24).

Equation (33) provides an alternative rovibrational decomposition of the kinetic energy, in a form common in the literature for rovibrational Hamiltonians. For example, the Wilson–Howard–Watson molecular Hamiltonian [28, 29] is expressed in this manner using the Eckart conventions, for which various simplifications occur.

2.3. Changing the internal coordinates and the collective body frame

When the conventions for the internal coordinates or the CBF are changed, the quantities defined in this paper do not, in general, remain invariant. Instead, they transform via a precise set of rules. Although the analysis of these rules is not critical to the logical flow of this paper, we include an account of them for the following two reasons. An understanding of transformation rules facilitates conversion between different sets of conventions. This is important in actual problems, where it is not uncommon to utilize more than one coordinate or frame convention, especially for large amplitude motions. Also, knowledge of transformation properties leads to the definition and consideration of quantities which transform in a simple manner (that is invariantly or covariantly). Such quantities often have special geometric or physical significance. The review of Littlejohn and Reinsch [13] contains an in depth discussion of transformation properties specialized for systems of point particles. Since essentially these results are unchanged by the generalization to include rigid bodies, we simply summarize here the key results from [13] and comment on how they are to be extended.

We first introduce the important concept of q tensors. We consider a new set of coordinates q'^{μ} which are functions of the old coordinates q^{μ} . A q tensor transforms under such a change in coordinates by contracting each lower Greek index μ with $\partial q'^{\mu} / \partial q^{\nu}$ and each upper Greek index μ with $\partial q^{\nu} / \partial q'^{\mu}$. The rank of the tensor is the total number of such indices, whether upper or lower. For example, $\tau_{\alpha\mu}$ is a rank one q tensor because it transforms via

$$\tau'_{\alpha\mu} = \frac{\partial q^\nu}{\partial q'^\mu} \tau_{\alpha\nu}, \quad (37)$$

where $\tau'_{\alpha\mu}$ is computed from equation (15) using the new coordinates q'^μ and $\tau_{\alpha\mu}$ is computed using the old coordinates q^μ . Other rank one q tensors are $\tau_{\alpha\mu}^{\text{la}}$, \mathbf{a}_μ , \mathbf{A}_μ , p_μ , and \dot{q}^μ . Rank zero q tensors, also called q scalars, are invariant under coordinate transformations. They include \mathbf{S}_α^s , \mathbf{S}_α , \mathbf{R} , \mathbf{r}_α^s , \mathbf{n}_α^s , ω_α^s , ω^s , \mathbf{M}_α^s , \mathbf{M}^s , $\tilde{\mathbf{M}}^s$, T , \mathbf{J}^s , and \mathbf{K}^s , as well as these same quantities referred (where appropriate) to the CBF or IBF α . Rank two q tensors include $h_{\mu\nu}$, $h^{\mu\nu}$, $g_{\mu\nu}$, and $g^{\mu\nu}$.

Next, we define the concept of an R tensor, which is important when changing the CBF. We consider a new CBF such that the orientation matrix \mathbf{R}' with respect to the new frame is related to the old orientation \mathbf{R} by

$$\mathbf{R}' = \mathbf{R}U(q), \quad (38)$$

where $U(q) \in \text{SO}(3)$ is a smooth function of q . The coordinates q^μ are held fixed. The quantities \mathbf{r}_α and \mathbf{S}_α transform via

$$\mathbf{r}'_\alpha = U^T \mathbf{r}_\alpha, \quad (39)$$

$$\mathbf{S}'_\alpha = U^T \mathbf{S}_\alpha, \quad (40)$$

where we have omitted the q dependence. We call \mathbf{r}_α a rank one R tensor because it has one Latin index which transforms with one copy of U^T . In general, an R tensor transforms by contracting each Latin index with U^T as in equation (39). The rank of the R tensor is the number of Latin indices it possesses. Other rank one R tensors include \mathbf{n}_α , ω_α , and \mathbf{J} . Rank zero R tensors, also called R scalars, do not depend on the choice of CBF and include T and \dot{q}^μ . Rank two R tensors include \mathbf{M} and \mathbf{M}_α .

The quantity \mathbf{A}_μ is not an R tensor. Instead, it has a more complicated transformation property

$$\mathbf{A}'_\mu = U^T \mathbf{A}_\mu - \gamma_\mu, \quad (41)$$

where $\gamma_\mu \times = U^T U_{,\mu}$. An interpretation of this transformation property as the gauge transformation law of a non-Abelian gauge potential is given in [13]. We simply note that such an analysis motivates the introduction of the Coriolis field strength,

$$\mathbf{B}_{\mu\nu} = \mathbf{A}_{\nu,\mu} - \mathbf{A}_{\mu,\nu} - \mathbf{A}_\mu \times \mathbf{A}_\nu. \quad (42)$$

The Coriolis field strength is a rank two q tensor and a rank one R tensor. We will use the Coriolis field strength only briefly in section 5. However, it plays a central role in the gauge theoretical approach to rovibrational coupling.

One should be aware that other quantities which have been introduced also are not R tensors. These include $h_{\mu\nu}$ and $\tilde{\mathbf{M}}$. However, it should be noted that both of

these quantities have counterparts, $g_{\mu\nu}$ and \mathbf{M} , respectively, which are R tensors. For further insight into the relationship between these two pairs of quantities, see [13]. Various other quantities which are not R tensors include $\tau_{\alpha\mu}$, \mathbf{a}_μ , \mathbf{K} , ω , and p_μ .

An important observation is that the two decompositions of the kinetic energy, equations (27) and (33), differ in their transformation properties. Specifically, equation (27) decomposes the kinetic energy into two terms which are q and R scalars. Equation (33), on the other hand, decomposes the kinetic energy into two terms which are q scalars but not R scalars. Thus, the latter decomposition is dependent on the choice of CBF, whereas the former is not. For this reason, we view equation (27) as the fundamental rovibrational decomposition of the kinetic energy. However, depending on the CBF convention, the decomposition of equation (33) very well may be easier to compute (see section 5). Reference [13] provides further discussion of these decompositions.

3. General expressions for the quantum kinetic energy

3.1. The unscaled kinetic energy

Temporarily we abandon the specific system of a molecular complex in order to present expressions for the quantum kinetic energy of a general system. Largely the results of this section are similar to previous work of Nauts and Chapuisat [30] which, in turn, relies on several earlier references. We note also that van der Avoird *et al.* [7] have employed a similar formalism for the water trimer. Here we will summarize relevant aspects of these results to fix notation and to lay the foundation for section 4. Also, we apply the formalism to the simple example of a single rigid body, which will be of future use. In section 3.2 we present a new approach to scaling the wavefunction.

We denote the classical kinetic energy by

$$T = \frac{1}{2} \pi_a G^{ab}(x) \pi_b, \quad (43)$$

where x stands for a collection of generalized position variables x^a , $a = 1, \dots, d$ (d is the number of degrees of freedom), π_a , $a = 1, \dots, d$, are generalized momenta, and G^{ab} are the components of the inverse metric tensor G^{-1} . When repeated, the indices a, b, c, \dots are assumed to be summed from 1 to d , both in equation (43) and the subsequent development. The momenta π_a are linear combinations of the canonical momenta,

$$\pi_a = C_a^b(x) p_b, \quad (44)$$

where p_a is the momentum canonically conjugate to x_a and the C_a^b are components of the change of basis matrix. Nauts and Chapuisat [30] call the more general momenta π_a quasi-momenta and reserve the term

momenta for what we call the canonical momenta p_a . The kinetic energy equation (43) is expressed in terms of the canonical momenta p_a by

$$T = \frac{1}{2} p_c C_a^c G^{ab} C_b^d p_d = \frac{1}{2} p_a \tilde{G}^{ab} p_b, \quad (45)$$

where \tilde{G}^{ab} are the components of the inverse metric $\tilde{G}^{-1} = C^T G^{-1} C$ with respect to the canonical momenta. From now on, we omit the explicit x dependence.

The quantum kinetic energy \hat{T} is often expressed in the Podolsky form [31]

$$\hat{T} = \frac{1}{2} \frac{1}{\tilde{G}^{1/2}} \hat{p}_a \tilde{G}^{1/2} \tilde{G}^{ab} \hat{p}_b, \quad (46)$$

where $\tilde{G} = \det \tilde{G}$ and where \hat{p}_a is the momentum operator conjugate to x^a ,

$$\hat{p}_a = -i \frac{\partial}{\partial x^a}, \quad (47)$$

setting $\hbar = 1$. The operator \hat{T} may be expressed also using the adjoints of the momentum operators:

$$\hat{T} = \frac{1}{2} \hat{p}_a^\dagger \tilde{G}^{ab} \hat{p}_b \quad (48)$$

or, more generally,

$$\hat{T} = \frac{1}{2} \hat{\pi}_a^\dagger G^{ab} \hat{\pi}_b, \quad (49)$$

where $\hat{\pi}_a$ is the operator corresponding to the classical momentum π_a ,

$$\hat{\pi}_a = C_a^b \hat{p}_b. \quad (50)$$

As observed by van der Avoird *et al.* [7], even though the adjoint form of the kinetic energy represents the same differential operator as the Podolsky form, equations (48) and (49) are convenient for evaluating matrix elements since the adjoint of the momentum operator effectively acts on the bra to the left.

Equations (48) and (49) are straightforward consequences of the definition of the adjoint. For an arbitrary operator \hat{A} , the matrix element of \hat{A}^\dagger with respect to wavefunctions Φ and Φ' is

$$\langle \Phi | \hat{A}^\dagger | \Phi' \rangle = \langle \hat{A} | \Phi | \Phi' \rangle, \quad (51)$$

where the inner product is defined via

$$\langle \Phi | \Phi' \rangle = \int d\nu \Phi^* \Phi', \quad (52)$$

and the volume element is

$$d\nu = \tilde{G}^{1/2} dx^1 \dots dx^d = \frac{G^{1/2}}{|\det C|} dx^1 \dots dx^d, \quad (53)$$

where $G = \det G$. From this definition, one finds that the momenta \hat{p}_a are not in general Hermitian but rather satisfy the relation

$$\hat{p}_a^\dagger = \frac{1}{\tilde{G}^{1/2}} \hat{p}_a \tilde{G}^{1/2}. \quad (54)$$

More generally, the momenta $\hat{\pi}_a$ satisfy

$$\hat{\pi}_a^\dagger = \hat{\pi}_a + \frac{1}{\tilde{G}^{1/2}} [\hat{p}_b \tilde{G}^{1/2} C_a^b], \quad (55)$$

where the square bracket notation indicates that \hat{p}_b acts only on the terms inside the brackets. Equations (46), (54), and (50) combine to prove equations (48) and (49).

An important illustration of the preceding formalism and one which we shall need later is that of a single rigid body. We define Euler angles $[x^1, x^2, x^3] = [\alpha, \beta, \gamma]$ in the usual way by $R(\alpha, \beta, \gamma) = R_z(\alpha) R_y(\beta) R_z(\gamma)$, where R rotates the space frame into the body frame and R_i is a rotation about the i th space axis. The body-referred angular momenta $[\pi_1, \pi_2, \pi_3] = [J_1, J_2, J_3]$ are non-canonical momenta related to the canonical momenta $[p_1, p_2, p_3] = [p_\alpha, p_\beta, p_\gamma]$ via [32]

$$\begin{bmatrix} J_1 \\ J_2 \\ J_3 \end{bmatrix} = C \begin{bmatrix} p_\alpha \\ p_\beta \\ p_\gamma \end{bmatrix}, \quad (56)$$

where

$$C = \begin{bmatrix} -\frac{\cos \gamma}{\sin \beta} & \sin \gamma & \cos \gamma \cot \beta \\ \frac{\sin \gamma}{\sin \beta} & \cos \gamma & -\sin \gamma \cot \beta \\ 0 & 0 & 1 \end{bmatrix}. \quad (57)$$

The classical kinetic energy in terms of the angular momenta is $T = \mathbf{J} \cdot \mathbf{M}^{-1} \mathbf{J} / 2$ where $\mathbf{M} = \mathbf{G}$ is the body-referred moment of inertia tensor, which is independent of the Euler angles. The volume element is computed from equation (53) to be

$$d\nu = (\det \mathbf{M})^{1/2} \sin \beta d\alpha d\beta d\gamma = 8\pi^2 (\det \mathbf{M})^{1/2} d\mathbf{R}, \quad (58)$$

where $d\mathbf{R} = \sin \beta d\alpha d\beta d\gamma / (8\pi^2)$ is the normalized Haar measure on $\text{SO}(3)$. The quantum kinetic energy is expressed in terms of the operators \hat{J}_i

$$\begin{bmatrix} \hat{J}_1 \\ \hat{J}_2 \\ \hat{J}_3 \end{bmatrix} = C \begin{bmatrix} -i\partial/\partial\alpha \\ -i\partial/\partial\beta \\ -i\partial/\partial\gamma \end{bmatrix}. \quad (59)$$

Using the volume element $d\nu$, one may verify that \hat{J}_i is Hermitian. (On a deeper level, \hat{J}_i is Hermitian because it is a symmetry of the kinetic energy.) Thus, the quantum kinetic energy equation (49) acquires the familiar form

$$\hat{T} = \frac{1}{2} \hat{\mathbf{J}} \cdot \mathbf{M}^{-1} \hat{\mathbf{J}}. \quad (60)$$

3.2. The scaled kinetic energy

Often it is useful to multiply the original wavefunction Φ by some real positive function $s(x)$ to form a new wavefunction Ψ ,

$$\Psi = s \Phi. \quad (61)$$

Such a scaling produces a new kinetic energy operator acting on the new wavefunction Ψ . In this section, we derive the form of this new kinetic energy operator. Similar discussions are given by Nauts and Chapuisat [30] and Chapuisat, Belafhal and Nauts [33]. The most notable distinction between our approach and these earlier accounts is our introduction of a new adjoint, shown in equation (64). This adjoint allows for a different form for the scaled kinetic energy operator shown in equation (67) and the associated extrapotential term in equation (68).

We note that equation (61) induces a new inner product on the scaled wavefunctions. We denote this new inner product with an s subscript and define it via,

$$\begin{aligned} \langle \Psi | \Psi' \rangle_s &= \left\langle \frac{1}{s} \Psi \left| \frac{1}{s} \Psi' \right. \right\rangle = \left\langle \Psi \left| \frac{1}{s^2} \Psi' \right. \right\rangle \\ &= \int \frac{\tilde{G}^{1/2}}{s^2} dx^1 \dots dx^d \Psi^* \Psi'. \end{aligned} \quad (62)$$

Thus, $\tilde{G}^{1/2}/s^2 dx^1 \dots dx^d$ is the volume element associated with the scaled wavefunctions. The operator adjoint taken with respect to this new inner product will be different in general from the adjoint taken with respect to the old inner product. To avoid confusion we will denote the new adjoint by $\hat{A}^{\dagger(s)}$. These two adjoints are related by the following computation

$$\begin{aligned} \langle \Psi | \hat{A}^{\dagger(s)} \Psi' \rangle_s &= \langle \hat{A} \Psi | \Psi' \rangle_s = \left\langle \hat{A} \Psi \left| \frac{1}{s^2} \Psi' \right. \right\rangle \\ &= \left\langle \Psi \left| \hat{A}^\dagger \frac{1}{s^2} \Psi' \right. \right\rangle = \left\langle \Psi \left| s^2 \hat{A}^\dagger \frac{1}{s^2} \Psi' \right. \right\rangle_s, \end{aligned} \quad (63)$$

which summarizes as

$$\hat{A}^{\dagger(s)} = s^2 \hat{A}^\dagger \frac{1}{s^2}. \quad (64)$$

Equation (64) combines with equation (55) to yield

$$\hat{\kappa}_a^{\dagger(s)} = \hat{\kappa}_a^\dagger - 2[\hat{\kappa}_a \ln s]. \quad (65)$$

The scaling of the wavefunction transforms the kinetic energy operator into $\hat{T}_s = s \hat{T} (1/s)$. Combining equations (49) and (64), we find

$$\hat{T}_s = \frac{1}{2} \left(\frac{1}{s} \hat{\kappa}_a^{\dagger(s)} s \right) G^{ab} \left(s \hat{\kappa}_b \frac{1}{s} \right). \quad (66)$$

By more or less straightforward commutation of operators in the above equation and using equations (55) and (65), we arrive at the main result of this section

$$\hat{T}_s = \frac{1}{2} \hat{\kappa}_a^{\dagger(s)} G^{ab} \hat{\kappa}_b + V_s, \quad (67)$$

where

$$\begin{aligned} V_s &= -\frac{1}{2} (G^{ab} [\hat{\kappa}_a \ln s] [\hat{\kappa}_b \ln s] + [\hat{\kappa}_a^{\dagger(s)} G^{ab} [\hat{\kappa}_b \ln s]]) \\ &= \frac{1}{2} (G^{ab} [\hat{\kappa}_a \ln s] [\hat{\kappa}_b \ln s] - [\hat{\kappa}_a^\dagger G^{ab} [\hat{\kappa}_b \ln s]]). \end{aligned} \quad (68)$$

Comparing equation (67) with the unscaled expression (49), we note that the two operators differ by the additional scalar term in equation (67) and the different adjoints which are used. Thus, scaling the wavefunction may be used to place the adjoint of the momenta in an alternative, perhaps more attractive, form, but only at the expense of introducing an extrapotential term into the kinetic energy.

4. The quantum kinetic energy of a molecular complex

We quantize the classical kinetic energy equation (27) using equation (49) derived in the previous section. This approach requires the operators \hat{p}_μ , \hat{J}_i , and their adjoints. Since the classical momentum p_μ is canonically conjugate to q^μ , the quantized operator \hat{p}_μ has the usual form of equation (47)

$$\hat{p}_\mu = -i \frac{\partial}{\partial q^\mu}. \quad (69)$$

The quantized angular momenta \hat{J}_i satisfy the standard ‘anomalous’ commutation relations $[\hat{J}_i, \hat{J}_j] = -i \sum_k \epsilon_{ijk} \hat{J}_k$ and of course commute with all rotationally invariant operators, for example,

$$\begin{aligned} [\hat{J}_i, \mathbf{M}] &= [\hat{J}_i, \tilde{\mathbf{M}}] = [\hat{J}_i, \mathbf{A}_\mu] = [\hat{J}_i, \mathbf{a}_\mu] = [\hat{J}_i, \mathbf{g}_{\mu\nu}] \\ &= [\hat{J}_i, h_{\mu\nu}] = [\hat{J}_i, \hat{p}_\mu] = 0. \end{aligned} \quad (70)$$

To compute the volume element of equation (53) we require explicit coordinates covering all directions of configuration space. This means defining three Euler angles $[\theta^1, \theta^2, \theta^3] = [\alpha, \beta, \gamma]$, describing the collective orientation \mathbf{R} , which complement the $d-3$ internal coordinates q^μ . Here, $d = 3n + 3n_n + 2n_c - 3$ is the dimension of the centre of mass system. We adopt the Euler angle conventions used in section 3. The non-canonical momenta $\hat{\kappa}_i = \hat{J}_i$ and $\hat{\kappa}_\mu = \hat{p}_\mu - \hat{\mathbf{J}} \cdot \mathbf{A}_\mu$ are expressed in terms of the canonical momenta $\hat{p}_i = -i\partial/\partial\theta$ and \hat{p}_μ by

$$\begin{bmatrix} \hat{J}_i \\ \hat{p}_\mu - \hat{\mathbf{J}} \cdot \mathbf{A}_\mu \end{bmatrix} = \begin{bmatrix} C_i^j & 0 \\ -\sum_k A_\mu^k C_k^j & \delta_\mu^\nu \end{bmatrix} \begin{bmatrix} \hat{p}_j \\ \hat{p}_\nu \end{bmatrix}, \quad (71)$$

where C_i^j are the components of the matrix in equation (57) and the sum over j is implicit. The full $d \times d$ matrix

in equation (71) corresponds to the matrix c_a^b in equation (50). Its determinant is equal to the determinant of the upper left block alone, that is $\det \mathbf{C} = -1/\sin \beta$. The metric G_{ab} with respect to the momenta $\pi_i = J_i$ and $\pi_\mu = p_\mu - \mathbf{J} \cdot \mathbf{A}_\mu$ is seen from equation (27) to have determinant

$$G = g \det \mathbf{M}, \quad (72)$$

where $g = \det g_{\mu\nu}$. The volume element is therefore

$$\begin{aligned} d\nu &= \frac{G^{1/2}}{|\det \mathbf{C}|} d\alpha d\beta d\gamma dq^1 \dots dq^{d-3} \\ &= (g \det \mathbf{M})^{1/2} \sin \beta d\alpha d\beta d\gamma dq^1 \dots dq^{d-3} \\ &= 8\pi^2 (g \det \mathbf{M})^{1/2} d\mathbf{R} dq^1 \dots dq^{d-3}. \end{aligned} \quad (73)$$

An identity we will use later is the following alternative expression for G :

$$G = h \det \tilde{\mathbf{M}}, \quad (74)$$

where h is the determinant of $h_{\mu\nu}$. This identity follows from the fact that the change of basis connecting equation (27) with equation (33) is orthogonal.

Since $\det \mathbf{M}$ and g are rotationally invariant, their presence in $d\nu$ is irrelevant for the computation of \hat{J}_i^\dagger . Therefore, the computation of \hat{J}_i^\dagger reduces to the case of a single rigid rotor examined in section 3, from which we recall that $\hat{J}_i^\dagger = \hat{J}_i$. Therefore, from equations (27) and (49), we find

$$\hat{T} = \frac{1}{2} \hat{\mathbf{J}} \cdot \mathbf{M}^{-1} \hat{\mathbf{J}} + \frac{1}{2} (\hat{p}_\mu^\dagger - \mathbf{A}_\mu \cdot \hat{\mathbf{J}}) g^{\mu\nu} (\hat{p}_\nu - \mathbf{A}_\nu \cdot \hat{\mathbf{J}}). \quad (75)$$

The ordering of the operators \hat{J}_i with respect to the other factors is irrelevant, on account of equation (70). The ordering of the \hat{p}_μ with respect to $g^{\mu\nu}$ and \mathbf{A}_μ , however, is essential. Note that the \hat{p}_μ are not in general Hermitian but rather satisfy

$$\hat{p}_\mu^\dagger = \frac{1}{G^{1/2}} \hat{p}_\mu G^{1/2} = \frac{1}{(g \det \mathbf{M})^{1/2}} \hat{p}_\mu (g \det \mathbf{M})^{1/2}, \quad (76)$$

as seen from equation (54) and the fact that $\tilde{G} = G/(\det \mathbf{C})^2 = G(\sin \beta)^2$.

We now scale the wavefunction by a factor

$$s = (8\pi^2)^{1/2} G^{1/4} = (8\pi^2)^{1/2} (\det \mathbf{M})^{1/4} g^{1/4} \quad (77)$$

to obtain a new form of the kinetic energy. First, we note that the transformed volume element is

$$\frac{d\nu}{s} = d\mathbf{R} dq^1 \dots dq^{d-3}. \quad (78)$$

The angular momenta \hat{J}_i are still Hermitian with respect to this new volume element, that is $\hat{J}_i^{(s)\dagger} = \hat{J}_i$, as may be noted from equation (65) and the fact that s is rotationally invariant. However, since the new volume element

contains no q^μ dependence in the Jacobian prefactor, we have the added benefit that \hat{p}_μ is now Hermitian, that is

$$\hat{p}_\mu^{(s)\dagger} = \hat{p}_\mu. \quad (79)$$

Therefore, the transformed kinetic energy of equation (67) takes the simple form

$$\hat{T}_s = \frac{1}{2} \hat{\mathbf{J}} \cdot \mathbf{M}^{-1} \hat{\mathbf{J}} + \frac{1}{2} (\hat{p}_\mu - \mathbf{A}_\mu \cdot \hat{\mathbf{J}}) g^{\mu\nu} (\hat{p}_\nu - \mathbf{A}_\nu \cdot \hat{\mathbf{J}}) + \nu_s, \quad (80)$$

where the extrapotential term may be reduced to

$$\nu_s = \frac{1}{2} G^{-1/4} \left[\frac{\partial}{\partial q^\mu} g^{\mu\nu} \frac{\partial}{\partial q^\nu} G^{1/4} \right]. \quad (81)$$

We observe that ν_s is an \mathbf{R} scalar, but not a q scalar. Therefore, ν_s depends on the choice of internal coordinates, but not on the choice of CBF. Further discussion of this matter is given in [13].

The quantum kinetic energy also may be placed in a form analogous to equation (33). The unscaled kinetic energy equation (75) becomes

$$\hat{T} = \frac{1}{2} (\hat{\mathbf{J}} - \hat{\mathbf{K}}^\dagger) \cdot \tilde{\mathbf{M}}^{-1} (\hat{\mathbf{J}} - \hat{\mathbf{K}}) + \frac{1}{2} \hat{p}_\mu^\dagger h^{\mu\nu} \hat{p}_\nu, \quad (82)$$

where

$$\hat{\mathbf{K}} = h^{\mu\nu} \mathbf{a}_\mu \hat{p}_\nu. \quad (83)$$

Similarly, the scaled kinetic energy becomes

$$\hat{T}_s = \frac{1}{2} (\hat{\mathbf{J}} - \hat{\mathbf{K}}^{(s)\dagger}) \cdot \tilde{\mathbf{M}}^{-1} (\hat{\mathbf{J}} - \hat{\mathbf{K}}) + \frac{1}{2} \hat{p}_\mu h^{\mu\nu} \hat{p}_\nu + \nu_s. \quad (84)$$

5. Example: a monomer-atom complex

We compute the rovibrational kinetic energy explicitly for a system containing a single non-collinear rigid monomer with moment of inertia M_1 and a single atom, for example, ArNH_3 . The kinetic energy of such systems has been studied by Brocks and van Koeven [1], van der Avoird [2], and Makarewicz and Bauder [3]. Our presentation is mainly designed to illustrate the formalism of the preceding sections, although we believe that the derivation of the Coriolis potential A_μ^i , Coriolis field strength $B_{\mu\nu}^i$, and internal metric $g_{\mu\nu}$ is new.

We define the CBF by fixing it to the rigid monomer. This implies that the matrix \mathbf{S} , defining the orientation of the monomer's IBF in the CBF, is constant. We take this constant to be the identity,

$$\mathbf{S}(q) = \mathbf{I}. \quad (85)$$

Since there is only one rigid body and one Jacobi vector, we drop all ' α ' subscripts, except on M_1 , where the '1' serves to distinguish the moment of inertia of the monomer from the total moment of inertia M of the complex. The Jacobi vector \mathbf{r} locates the atom with

respect to the monomer, and therefore its components may be chosen as the internal coordinates, that is

$$[q^1, q^2, q^3] = [r_1, r_2, r_3]. \quad (86)$$

Thus,

$$r_{i,\mu} = \delta_{i\mu}. \quad (87)$$

Furthermore, from equations (15) and (85), we have

$$\tau_\mu = 0. \quad (88)$$

Inserting equations (85), (87), and (88) into (28)–(30), we obtain

$$M = r^2 I - \mathbf{r}\mathbf{r}^T + M_1^i, \quad (89)$$

$$a_{i\mu} = (\mathbf{r} \times \mathbf{r}_{,\mu})_i = \sum_j \varepsilon_{ij\mu} r_j, \quad (90)$$

$$h_{\mu\nu} = \mathbf{r}_{,\mu} \cdot \mathbf{r}_{,\nu} = \delta_{\mu\nu}, \quad (91)$$

where the i superscript on M_1^i indicates that it is referred to the monomer's IBF (which agrees here with the CBF) and hence is a constant matrix.

We proceed first to construct the kinetic energy equation (33), which results here in a simpler form than equation (27). Using equations (31) and (32) we compute

$$\tilde{M} = M_1^i, \quad (92)$$

$$\mathbf{K} = \mathbf{r} \times \mathbf{p}, \quad (93)$$

where $\mathbf{p} = [p_1, p_2, p_3]$. These are particularly simple results and, together with equation (91), yield the classical kinetic energy

$$T = \frac{1}{2}(\mathbf{J} - \mathbf{r} \times \mathbf{p}) \cdot (M_1^i)^{-1}(\mathbf{J} - \mathbf{r} \times \mathbf{p}) + \frac{1}{2}\mathbf{p} \cdot \mathbf{p}. \quad (94)$$

The quantum kinetic energy requires the further result

$$G = \hbar \det \tilde{M} = \det M_1^i, \quad (95)$$

which follows from equation (74) and shows that G is constant. Hence, from equation (76) it is clear that \hat{p}_μ is Hermitian with respect to the original inner product. Since $\hat{\mathbf{K}} = \mathbf{r} \times \hat{\mathbf{p}}$ we find that $\hat{\mathbf{K}}$ also is Hermitian with respect to both the original and the scaled inner products. Furthermore, the extrapotential term of equation (81) arising in the scaled kinetic energy vanishes. Thus, both the original and the scaled quantum kinetic energies are identical and each is formed simply by replacing \mathbf{p} and \mathbf{J} in equation (94) with $\hat{\mathbf{p}}$ and $\hat{\mathbf{J}}$, respectively. Our results agree with earlier derivations by Brocks and van Koeven [1] and van der Avoird [2].

To simplify the algebra in constructing the kinetic energy equation (27), we assume the rigid body is a spherical top with $M_1^i = \kappa I$. The total moment of inertia

tensor given in equation (89) may be inverted explicitly, with the form

$$M^{-1} = \frac{1}{r^2 + \kappa} I + \frac{1}{\kappa(r^2 + \kappa)} \mathbf{r}\mathbf{r}^T, \quad (96)$$

and combined with equations (23) and (24) to yield explicit forms for the Coriolis potential and the internal metric,

$$A_{\mu}^i = \sum_j \frac{1}{r^2 + \kappa} \varepsilon_{ij\mu} r_j, \quad (97)$$

$$g_{\mu\nu} = \frac{1}{r^2 + \kappa} (\kappa \delta_{\mu\nu} + r_\mu r_\nu). \quad (98)$$

The inverse of the internal metric is

$$g^{\mu\nu} = \frac{1}{\kappa} [(r^2 + \kappa) \delta_{\mu\nu} - r_\mu r_\nu]. \quad (99)$$

Equations (96), (97), and (99) combine with (27) to yield an explicit form for the classical kinetic energy. As earlier, the quantum kinetic energy, both original and scaled, is obtained simply by replacing \mathbf{p} and \mathbf{J} by their operator counterparts, without the need for Hermitian conjugates or an extrapotential term.

It is interesting to compute the Coriolis field strength defined by equation (42),

$$B_{\mu\nu}^i = \varepsilon_{\mu\nu\sigma} \frac{1}{(r^2 + \kappa)^2} (r_i r_\sigma + 2\kappa \delta_{i\sigma}). \quad (100)$$

As the separation r of the atom from the monomer goes to infinity, the Coriolis field strength $B_{\mu\nu}^i \rightarrow \varepsilon_{\mu\nu\sigma} r_i r_\sigma / r^4$. We change the CBF, as in equation (38), via a matrix $U(\mathbf{r})$ which rotates $\hat{\mathbf{z}}$ into \mathbf{r}/r . Then, since $\mathbf{B}_{\mu\nu}$ is a rank one \mathbf{R} tensor, as r goes to infinity, the new field strength tensor $\mathbf{B}'_{\mu\nu}$ changes as

$$\mathbf{B}'_{\mu\nu} = U^T \mathbf{B}_{\mu\nu} U - \varepsilon_{\mu\nu\sigma} \frac{r_\sigma \hat{\mathbf{z}}}{r^3}. \quad (101)$$

The above asymptotic form is that of a (non-Abelian) monopole field [34]. A similar monopole field is already known to exist in the three-body problem [15, 16], a fact which has led to several useful applications [15, 16, 19, 35]. We remark that the above asymptotic form is valid even if the monomer is an asymmetric top.

6. Conclusion

We have computed the kinetic energy of an arbitrary molecular complex for arbitrary coordinate and body frame conventions. In so doing, we have tried to provide an efficient framework in which explicit Hamiltonians may be computed for specific choices of coordinates and frames. We have provided a discussion of transformation properties to facilitate the changing of these conventions. Our formalism is illustrated with the example

of a monomer-atom system, and more complex systems may be handled with similar ease within our framework.

One of the more novel and intriguing aspects of our derivation is the appearance of the Coriolis potential and the various insights which are possible by adopting a gauge theoretical viewpoint. We briefly cite two areas of current research which are based on this perspective. First, using gauge theoretical reasoning we have managed to generalize the Eckart conditions, so often employed for small vibrations in molecules, to systems of rigid bodies. Much of the formalism for small vibrational analysis in molecules then can be ported over readily to study small amplitude vibrations in clusters of rigid molecules. Second, we have been able to understand rotational splittings in molecules with internal rotors as a sort of Coriolis Aharonov-Bohm effect. These applications and others are planned for future publications.

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References

- [1] BROCKS, G., and VAN KOEVEN, D., 1988, *Molec. Phys.*, **63**, 999.
- [2] VAN DER AVOIRD, A., 1993, *J. chem. Phys.*, **98**, 5327.
- [3] MAKAREWICZ, J., and BAUDER, A., 1995, *Molec. Phys.*, **84**, 853.
- [4] BROCKS, G., VAN DER AVOIRD, A., SUTCLIFFE, B. T., and TENNYSON, J., 1983, *Molec. Phys.*, **50**, 1025.
- [5] VAN DER AVOIRD, A., WORMER, P. E. S., and MOSZYNSKI, R., 1994, *Chem. Rev.*, **94**, 1931.
- [6] XANTHEAS, S. S., and SUTCLIFFE, B. T., 1995, *J. chem. Phys.*, **103**, 8022.
- [7] VAN DER AVOIRD, A., OLTHOF, E. H. T., and WORMER, P. E. S., 1996, *J. chem. Phys.*, **105**, 8034.
- [8] LISTER, D. G., MACDONALD, J. N., and OWEN, N. L., 1978, *Internal Rotation and Inversion* (New York: Academic Press).
- [9] GORDY, W., and COOK, R. L., 1984, *Microwave Molecular Spectra* (New York: Wiley).
- [10] MENOU, M., and CHAPUISAT, X., 1993, *J. molec. Spectrosc.*, **159**, 300.
- [11] GATTI, F., JUSTUM, Y., MENOU, M., NAUTS, A., and CHAPUISAT, X., 1997, *J. molec. Spectrosc.*, **181**, 403.
- [12] KAPLAN, L., MAITRA, N. T., and HELLER, E. J., 1997, *Phys. Rev. A*, **56**, 2592.
- [13] LITTLEJOHN, R. G., and REINSCH, M., 1997, *Rev. mod. Phys.*, **69**, 213.
- [14] GUICHARDET, A., 1984, *Ann. Inst. Henri Poincaré*, **40**, 329.
- [15] IWAI, T., 1987, *J. math. Phys.*, **28**, 964.
- [16] IWAI, T., 1987, *J. math. Phys.*, **28**, 1315.
- [17] IWAI, T., 1988, *J. math. Phys.*, **29**, 1325.
- [18] SHAPER, A., and WILCZEK, F., 1989, *Amer. J. Phys.*, **57**, 514.
- [19] MONTGOMERY, R., 1996, *Nonlinearity*, **9**, 1341.
- [20] SHAPER, A., and WILCZEK, F., 1989, *Geometric Phases in Physics* (Singapore: World Scientific).
- [21] MEAD, C. A., 1992, *Rev. mod. Phys.*, **64**, 51.
- [22] CHIAO, R. Y., and WU, Y.-S., 1986, *Phys. Rev. Lett.*, **57**, 933.
- [23] TOMITA, A., and CHIAO, R. Y., 1986, *Phys. Rev. Lett.*, **57**, 937.
- [24] LITTLEJOHN, R. G., 1988, *Phys. Rev. A*, **38**, 6034.
- [25] LITTLEJOHN, R. G., MITCHELL, K. A., AQUILANTI, V., and CAVALLI, S., 1998, *Phys. Rev. A*, **58**, 3705.
- [26] LITTLEJOHN, R. G., MITCHELL, K. A., REINSCH, M., AQUILANTI, V., and CAVALLI, S., 1998, *Phys. Rev. A*, **58**, 3718.
- [27] AQUILANTI, V., and CAVALLI, S., 1986, *J. chem. Phys.*, **85**, 1355.
- [28] KROTO, H. W., 1975, *Molecular Rotation Spectra* (Chichester: Wiley).
- [29] PAPOUSEK, D., and ALIEV, M. R., 1982, *Molecular Vibrational-Rotational Spectra* (Amsterdam: Elsevier).
- [30] NAUTS, A., and CHAPUISAT, X., 1985, *Molec. Phys.*, **55**, 1287.
- [31] PODOLSKY, B., 1928, *Phys. Rev.*, **32**, 812.
- [32] BIEDENHARN, L. C., and LOUCK, J. D., 1981, *Angular Momentum in Quantum Physics* (Reading, MA: Addison-Wesley) p. 64.
- [33] CHAPUISAT, X., BELAFHAL, A., and NAUTS, A., 1991, *J. molec. Spectrosc.*, **149**, 274.
- [34] GODDARD, P., NUYS, J., and OLIVE, D., 1977, *Nucl. Phys. B*, **125**, 1.
- [35] MITCHELL, K. A., and LITTLEJOHN, R. G., 1997, *Phys. Rev. A*, **56**, 83.