The rovibrational kinetic energy for complexes of rigid molecules

Kevin A. Mitchell and Robert G. Littlejohn
Department of Physics, University of California,
Berkeley, California 94720

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Abstract

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 explicitly analysed 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]; as well as closely related systems of single molecules with internal rotation [8, 9]. In the present article 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 \cite{menou10} and by Gatti \textit{et al.} \cite{gatti11}. 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 for example Kaplan, Maitra, and Heller \cite{kaplan12}. 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 modeled on the derivation of Ref. \cite{ref13}, valid for clusters of point particles, but is augmented to include the rotational kinetic energy of the monomers; the current paper therefore generalises 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 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 \cite{gauge13, gauge14, gauge15, gauge16, gauge17, gauge18, gauge19}. In addition to rovibrational coupling, the geometric, or Berry’s, phase \cite{berry20} has important applications in Born-Oppenheimer theory \cite{bo21}, optics \cite{optics22, optics23}, and guiding centre motion \cite{guiding24}, to name but a few examples. The influence of gauge theory on our analysis here is most readily evident in the form of the kinetic energy Eq. (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 have also influenced our analysis of transformation properties presented in Sect. 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.

The article is structured as follows. Section 2 is devoted to the classical kinetic energy. The principal computation of the article, culminating in the rovibrational kinetic energy Eq. (27), is contained in Sect. 2.1. In Sect. 2.2 we show how the rovibrational kinetic energy of Eq. (27) can be placed in a different form, that of Eq. (33), which is more common in the rovibrational literature. Sect. 2.3 is a systematic discussion of how important quantities
transform under changes in the internal coordinates and body frame. Sect. 3 is an aside in which we discuss the form of quantum kinetic energy operators in general. In particular, Sect. 3.1 discusses an alternative to the usual Podolsky form of the quantum kinetic energy, and Sect. 3.2 illustrates how scaling the wave function introduces an extrapotential term into the kinetic energy. In Sect. 4 we apply the results of Sect. 3 to compute the quantum kinetic energy of a molecular complex. We work through a concrete example in Sect. 5 applying our formalism to the system of a single monomer and an atom. Sect. 6 contains conclusions.

2 The classical kinetic energy of a molecular complex

2.1 The principal derivation

In this paper, a molecular complex is modeled 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 noncollinear bodies. However, for mathematical simplicity, we initially assume that each monomer is noncollinear. Then, after deriving the rovibrational kinetic energy, we comment on the straightforward generalisation 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 $\alpha$, $\alpha = 1, \ldots, n$, is fixed to rigid body $\alpha$ 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 $v$, an $s$ superscript, that is $v^s$, indicates components in the SF; an $ia$ superscript indicates components in the IBF of body $\alpha$; 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 $v$ in the various frames are related by proper orthogonal $3 \times 3$ matrices, which we define by

$$v^s = Rv^c,$$  \hspace{1cm} (1)

$$v^s = S^s_{\alpha}v^{ia},$$  \hspace{1cm} (2)

$$v^c = S^c_{\alpha}v^{ia}.\hspace{1cm} (3)$$

The matrix $S^s_{\alpha}$ determines the orientation of body $\alpha$, that is, the IBF of body $\alpha$, in the SF; the matrix $R$ determines the orientation of the entire complex in the SF; and the matrix $S^c_{\alpha}$ determines the orientation of body $\alpha$ in the CBF.
The configuration of the complex of \( n \) rigid bodies is fully specified 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 \([27, 13]\) \( \mathbf{r}_\alpha^s, \alpha = 1, \ldots, n - 1 \). The orientations of the rigid bodies are specified by the \( n \) matrices \( \mathbf{S}_\alpha^s \in SO(3), \alpha = 1, \ldots, n \). Taken together, \( \mathbf{r}_\alpha^s, \alpha = 1, \ldots, n - 1 \) and \( \mathbf{S}_\alpha^s, \alpha = 1, \ldots, n \) 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 \( q^\mu, \mu = 1, \ldots, 6n - 6 \). The \( q^\mu \) may be separated into \( 3n - 6 \) coordinates parametrising the distances between the rigid bodies and \( 3n \) coordinates (Euler angles) parametrising the orientations of the bodies in the CBF. However, here we allow the \( q^\mu \) to be completely arbitrary, so long as they are invariant under rotations of the complex. The Jacobi vectors \( \mathbf{r}_\alpha^c \), referred to the collective body frame, and the matrices \( \mathbf{S}_\alpha^c \) are both functions of the internal coordinates \( q^\mu \). In practice, one may define the CBF by specifying the functions \( \mathbf{r}_\alpha^c(q) \) and \( \mathbf{S}_\alpha^c(q) \), where \( q \) without a superscript refers to the collection of all coordinates \( q^\mu \).

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

\[
T = \frac{1}{2} \sum_{\alpha=1}^{n-1} |\dot{\mathbf{r}}_\alpha^s|^2 + \frac{1}{2} \sum_{\alpha=1}^{n} \omega_\alpha^s \cdot \mathbf{M}_\alpha^s \omega_\alpha^s,
\]

where the dot is used for time derivatives, \( \mathbf{M}_\alpha^s \) is the moment of inertia of body \( \alpha \) in the SF, and \( \omega_\alpha^s \) is the angular velocity of body \( \alpha \).

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 \( \omega_\alpha^s \) measures the rotation rate of the IBF of body \( \alpha \) 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,

\[
\omega_\alpha^s \times = \dot{\mathbf{s}}_\alpha^s \mathbf{s}_\alpha^s T,
\]

\[
\omega_\alpha^{i\alpha} \times = \mathbf{s}_\alpha^s T \dot{\mathbf{s}}_\alpha^s.
\]
where the $T$ superscript denotes the matrix transpose. Note that these two formulas are consistent with the change of basis relation Eq. (2), that is
\[ \omega^s = S^c \omega^c, \]
as may be seen from the general relation
\[ Q(v \times)Q^T = (Qv) \times, \]
where the vector $v$ is arbitrary and $Q \in SO(3)$.

We proceed by expressing the kinetic energy Eq. (6) in terms of the internal velocities $\dot{q}^\mu$ and the total angular velocity $\omega^c$. 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
\[ \omega^s \times = \dot{R} R^T, \]
\[ \omega^c \times = R^T \dot{R}. \]

These equations are analogous to Eqs. (7) and (8). Equation (11) permits the time derivatives of Eqs. (4) and (5) to be expressed as
\[ \dot{r}^s_\alpha = \dot{R} r^c_\alpha + R r^c_{\alpha,\mu} \dot{q}^\mu = R (\omega^c \times r^c_\alpha + r^c_{\alpha,\mu} \dot{q}^\mu), \]
\[ \dot{S}^s_\alpha = \dot{R} S^c_\alpha + R S^c_{\alpha,\mu} \dot{q}^\mu = R \left( (\omega^c \times) S^c_\alpha + S^c_{\alpha,\mu} \dot{q}^\mu \right), \]
where the “$\mu$” subscript denotes the derivative with respect to the coordinate $q^\mu$. In the above equations, we have used the convention, which we adopt for the remainder of the paper, that the Greek indices $\mu, \nu, \ldots$ are implicitly summed from 1 to $6n-6$ when repeated. However, the Greek indices $\alpha, \beta, \ldots$ which label either the Jacobi vectors or monomers are summed explicitly. Combining Eqs. (7) and (13) and using Eq. (5), we find
\[ \omega^s_\alpha \times = R [ (\omega^c \times) + S^c_{\alpha,\mu} S^c_\alpha T \dot{q}^\mu ] R^T. \]

Since $S^c_{\alpha,\mu} S^c_\alpha T$ is antisymmetric, we define a vector $\tau^{\alpha \mu}$ such that
\[ \tau^{\alpha \mu} \times = S^c_{\alpha,\mu} S^c_\alpha T, \]
\[ \tau^{\alpha \mu} \times = S^c_\alpha T S^c_{\alpha,\mu}. \]

By comparison with Eqs. (7) and (8), we see that $\dot{q}^\mu \tau^{\alpha \mu}$ is the angular velocity of the IBF of body $\alpha$ with respect to the CBF. By inserting Eq. (13) into Eq. (14) and using Eq. (8), we find
\[ \omega^s_\alpha = R (\omega^c + \dot{q}^\mu \tau^{\alpha \mu}) = \omega^s + \dot{q}^\mu \tau^{s \alpha}. \]

The above equation expresses the angular velocity of the IBF of body $\alpha$ 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 $\alpha$ 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 Eqs. (12) and (17) in Eq. (6), we write the kinetic energy as
\[ T = \frac{1}{2} \omega \cdot M \omega + a_\mu \cdot \omega \dot{q}^\mu + \frac{1}{2} h_{\mu \nu} \dot{q}^\mu \dot{q}^\nu, \]  

where

\[ M = \sum_{\alpha=1}^{n-1} (r^2_\alpha - r_\alpha r_\alpha^T) + \sum_{\alpha=1}^{n} M_\alpha = \sum_{\alpha=1}^{n-1} (r^2_\alpha - r_\alpha r_\alpha^T) + \sum_{\alpha=1}^{n} S_\alpha M_\alpha S_\alpha^T, \]  

\[ a_\mu = \sum_{\alpha=1}^{n-1} r_\alpha \times r_{\alpha,\mu} + \sum_{\alpha=1}^{n} \tau_{\alpha \mu} = \sum_{\alpha=1}^{n-1} r_\alpha \times r_{\alpha,\mu} + \sum_{\alpha=1}^{n} S_\alpha M_\alpha \tau_{\alpha \mu}, \]  

\[ h_{\mu \nu} = \sum_{\alpha=1}^{n-1} r_{\alpha,\mu} \cdot r_{\alpha,\nu} + \sum_{\alpha=1}^{n} \tau_{\alpha \mu} \cdot M_\alpha \tau_{\alpha \nu} = \sum_{\alpha=1}^{n-1} r_{\alpha,\mu} \cdot r_{\alpha,\nu} + \sum_{\alpha=1}^{n} \tau_{\alpha \mu} \cdot M_\alpha \tau_{\alpha \nu}, \]

and where we henceforth suppress the \( c \) superscript on vectors and tensors referred to the CBF. We have also used \( I \) for the identity matrix and \( M_\alpha = R^T M_\alpha^s R \) and \( M_\alpha^{\text{IBF}} = S_\alpha^T M_\alpha S_\alpha^s \) for the moment of inertia of body \( \alpha \) in the CBF and IBF \( \alpha \) respectively. In the above equations, we present two expressions for each of the quantities \( M_\alpha, a_\mu, \) 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 \( S_\alpha(q) \) and \( r_\alpha(q) \) is shown explicitly by \( S_\alpha, r_\alpha, r_{\alpha,\mu}, \) and \( \tau_{\alpha \mu} \). Note that \( M_\alpha^{\text{IBF}} \) is the moment of inertia of body \( \alpha \) in its own IBF and as such is a constant matrix independent of both the shape and orientation.

By rearranging the terms in Eq. \( (18) \), we put the kinetic energy in the form

\[ T = \frac{1}{2} (\omega + A_\mu \dot{q}^\mu) \cdot M (\omega + A_\nu \dot{q}^\nu) + \frac{1}{2} g_{\mu \nu} \dot{q}^\mu \dot{q}^\nu, \]  

where

\[ A_\mu = M^{-1} a_\mu, \]  

\[ g_{\mu \nu} = h_{\mu \nu} - a_\mu \cdot M^{-1} a_\nu. \]

Converting the velocities to momenta, we find

\[ J = \frac{\partial T}{\partial \omega} = M (\omega + A_\mu \dot{q}^\mu), \]  

\[ p_\mu = \frac{\partial T}{\partial \dot{q}^\mu} = g_{\mu \nu} \dot{q}^\nu + A_\mu \cdot J. \]

The vector \( J \) is the total angular momentum of the complex. It satisfies the usual body-referred “anomalous” commutation relations \( \{ J_i, J_j \} = -\epsilon_{ijk} J_k \), where \( \epsilon_{ijk} \) is the usual Levi-Civita symbol. The classical kinetic energy is now expressible in terms of momenta as

\[ T = \frac{1}{2} J \cdot M^{-1} J + \frac{1}{2} (p_\mu - A_\mu \cdot J) g^{\mu \nu} (p_\nu - A_\nu \cdot J), \]  

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, notice that the appearance of \( A_\mu \) in the internal kinetic energy couples the internal degrees of freedom to the angular momentum. For this reason, we call \( A_\mu \) the Coriolis potential. Furthermore, we call \( g_{\mu \nu} \) the internal metric because it acts to square \( p_\mu - A_\mu \cdot J \). Note that the internal kinetic energy has the same \( \| p - eA \|^2 \) 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 Ref. [13] for a collection of point particles has exactly the same form as Eq. (27). However, for collections of point particles, the quantities defined in Eqs. (19) – (21) do not contain the terms with \( M_{i\alpha} \). 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; Eq. (27) is in fact a general result, valid for any \( SO(3) \) invariant metric. We will discuss this matter further in a future publication.

We comment now on how the preceding results are generalised to include collinear monomers and point particles. First, the number of coordinates changes. A noncollinear body requires three Euler angles to fully specify its orientation, 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 parametrising 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 Eq. (6) to Eq. (27) is essentially unchanged by the inclusion of collinear bodies and point particles, so long as one takes the moment of inertia tensor \( M_\alpha \) of a point particle to be 0. The moment of inertia tensor of a collinear body is explicitly \( M_\alpha = \kappa_\alpha (I - n_\alpha n_\alpha^T) \), where \( n_\alpha \) is a unit vector pointing along the collinear axis and \( \kappa_\alpha \) is the single nonzero principal moment. The quantity \( n_\alpha \) is a more natural measure of the orientation of a collinear body than \( S_\alpha \), since \( S_\alpha \) overparametrises the orientations. We therefore rewrite Eqs. (19) – (21) in the following form, more appropriate for a general complex,

\[
M = \sum_{\alpha=1}^{n-1} (r_\alpha^2 I - r_\alpha r_\alpha^T) + \sum_{\alpha=1}^{n_n} S_\alpha M_\alpha^{\alpha\alpha} S_\alpha^T + \sum_{\alpha=n_n+1}^{n_n+n_c} \kappa_\alpha (I - n_\alpha n_\alpha^T),
\] (28)
\[ a_\mu = \sum_{\alpha=1}^{n-1} \mathbf{r}_\alpha \times \mathbf{r}_{\alpha,\mu} + \sum_{\alpha=1}^{n_n} S_\alpha \mathbf{M}_\alpha^{i\alpha} \mathbf{T}_{\alpha,\mu}^{i\alpha} + \sum_{\alpha=n_n+1}^{n_n+n_c} \kappa_\alpha \mathbf{n}_\alpha \times \mathbf{n}_{\alpha,\mu}, \]  
\[ (29) \]

\[ h_{\mu\nu} = \sum_{\alpha=1}^{n-1} \mathbf{r}_{\alpha,\mu} \cdot \mathbf{r}_{\alpha,\nu} + \sum_{\alpha=1}^{n_n} \mathbf{T}_{\alpha,\mu}^{i\alpha} \cdot \mathbf{M}_\alpha^{i\alpha} \mathbf{T}_{\alpha,\nu}^{i\alpha} + \sum_{\alpha=n_n+1}^{n_n+n_c} \kappa_\alpha \mathbf{n}_{\alpha,\mu} \cdot \mathbf{n}_{\alpha,\nu}, \]
\[ (30) \]

where we have ordered the monomers with the noncollinear 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 \( \mathbf{M}_\alpha \) 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 modeling a collinear body as two point particles connected by a Jacobi vector. The above equations may be combined with Eqs. (23) and (24) to obtain the kinetic energy Eq. (27) of a general molecular complex. The only note of caution occurs if the entire complex should become collinear, in which case \( \mathbf{M} \) is not invertible and singularities may arise.

### 2.2 An alternative form of the kinetic energy

We rearrange the kinetic energy Eq. (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 \( \tilde{\mathbf{M}} \) by

\[ \tilde{\mathbf{M}} = \mathbf{M} - h_{\mu\nu} a_\mu a_\nu^T, \]
\[ (31) \]

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

\[ \mathbf{K} = h_{\mu\nu} a_\mu p_\nu. \]
\[ (32) \]

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

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

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

\[ g^{\mu\nu} \mathbf{M}^{-1} a_\nu = h^{\mu\nu} \tilde{\mathbf{M}}^{-1} a_\nu, \]
\[ (34) \]

\[ g^{\mu\nu} = h^{\mu\nu} + h^{\mu\rho} (a_\sigma \cdot \tilde{\mathbf{M}}^{-1} a_\rho) h^{\tau\nu}, \]
\[ (35) \]

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

which follow from Eqs. (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 utilise 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 specialised for systems of point particles. Since these results are essentially unchanged by the generalisation to include rigid bodies, we simply summarise here the key results from Ref. [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 \( q'^\mu \) which are functions of the old coordinates \( q^\mu \). A \( q \)-tensor transforms under such a change in coordinates by contracting each lower Greek index \( \mu \) with \( \partial q^\mu / \partial q'^\nu \) and each upper Greek index \( \mu \) 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

\[
\tau'_{\alpha \mu} = \frac{\partial q^\nu}{\partial q'^\mu} \tau_{\alpha \nu},
\]

where \( \tau'_{\alpha \mu} \) is computed from Eq. (37) using the new coordinates \( q'^\mu \) and \( \tau_{\alpha \mu} \) is computed using the old coordinates \( q^\mu \). Other rank one \( q \)-tensors are \( \tau'_{\alpha} \), \( a_{\mu} \), \( A_{\mu} \), \( p_{\mu} \), and \( \dot{q}_{\mu} \). Rank zero \( q \)-tensors, also called \( q \)-scalars, are invariant under coordinate transformations. They include \( S_{\alpha}^s \), \( S_{\alpha} \), \( R \), \( r_{\alpha} \), \( n_{\alpha} \), \( \omega_{\alpha} \), \( \omega^s \), \( M_{\alpha}^s \), \( M_{\alpha} \), \( M^s \), \( T \), \( J_{\alpha}^s \), and \( K_{\alpha}^s \), as well as these same quantities referred (where appropriate) to the CBF or IBF \( \alpha \). 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 \( R' \) with respect to the new frame is related to the old orientation \( R \) by

\[
R' = RU(q),
\]

where \( U(q) \in SO(3) \) is a smooth function of \( q \). The coordinates \( q^\mu \) are held fixed. The quantities \( r_{\alpha} \) and \( S_{\alpha} \) transform via

\[
\begin{align*}
\nonumber r'_{\alpha} &= U^T r_{\alpha}, \\
S'_{\alpha} &= U^T S_{\alpha},
\end{align*}
\]

where we have omitted the \( q \) dependence. We call \( r_{\alpha} \) 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 Eq. (39). The rank of the $R$-tensor is the number of Latin indices it possesses. Other rank one $R$-tensors include $n_\alpha$, $\omega_\alpha$, and $J$. Rank zero $R$-tensors, also called $R$-scalars, do not depend on the choice of CBF and include $T$ and $\dot{q}^\mu$. Rank two $R$-tensors include $M$ and $M_\alpha$.

The quantity $A_\mu$ is not an $R$-tensor. Instead, it has a more complicated transformation property

$$A'_\mu = U^T A_\mu - \gamma_\mu,$$

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 Ref. [13]. We simply note that such an analysis motivates the introduction of the Coriolis field strength,

$$B_{\mu\nu} = A_{\nu,\mu} - A_{\mu,\nu} - A_\mu \times A_\nu.$$

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

One should be aware that other quantities which have been introduced are also not $R$-tensors. These include $h_{\mu\nu}$ and $M$. However, it should be noted that both of these quantities have counterparts, $g_{\mu\nu}$ and $M$ respectively, which are $R$-tensors. For further insight into the relationship between these two pairs of quantities, see Ref. [13]. Various other quantities which are not $R$-tensors include $\tau_{\alpha\mu}$, $a_\mu$, $K$, $\omega$, and $p_\mu$.

An important observation is that the two decompositions of the kinetic energy, Eqs. (27) and (33), differ in their transformation properties. Specifically, Eq. (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 Eq. (27) as the fundamental rovibrational decomposition of the kinetic energy. However, depending on the CBF convention, the decomposition of Eq. (33) may very well be easier to compute. (See Sect. 4.) We refer to Ref. [13] for further discussion of these decompositions.

### 3 General expressions for the quantum kinetic energy

#### 3.1 The unscaled kinetic energy

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

We denote the classical kinetic energy by
\[ T = \frac{1}{2} \pi_a G^{ab}(x) \pi_b, \]  
(43)

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

\[ \pi_a = C^b_a(x)p_b, \]  
(44)

where \( p_a \) is the momentum canonically conjugate to \( x_a \) and the \( C^b_a \) are components of the change of basis matrix. Nauts and Chapuisat [30] call the more general momenta \( \pi_a \) quasi-momenta and reserve the term momenta for what we call the canonical momenta \( p_a \). The kinetic energy Eq. (43) is expressed in terms of the canonical momenta \( p_a \) by

\[ T = \frac{1}{2} p_c C^c_a G^{ab} C^d_b p_d = \frac{1}{2} p_a \tilde{G}^{ab} p_b, \]  
(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]

\[ \hat{T} = \frac{1}{2} \hat{p}_a \sqrt{\hat{G}} \hat{G}^{ab} \hat{p}_b, \]  
(46)

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

\[ \hat{p}_a = -i \frac{\partial}{\partial x^a}. \]  
(47)

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

\[ \hat{T} = \frac{1}{2} \hat{p}_a \tilde{G}^{ab} \hat{p}_b, \]  
(48)

or more generally,

\[ \hat{T} = \frac{1}{2} \hat{\pi}_a \tilde{G}^{ab} \hat{\pi}_b, \]  
(49)

where \( \hat{\pi}_a \) is the operator corresponding to the classical momentum \( \pi_a \),

\[ \hat{\pi}_a = C^b_a \hat{p}_b. \]  
(50)

As observed by van der Avoird et al. [4], even though the adjoint form of the kinetic energy represents the same differential operator as the Podolsky form, Eqs. (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 wave functions $\Phi$ and $\Phi'$ is

$$\langle \Phi | \hat{A}^\dagger | \Phi' \rangle = \langle \hat{A}\Phi | \Phi' \rangle,$$

(51)

where the inner product is defined via

$$\langle \Phi | \Phi' \rangle = \int \, dv \, \Phi^* \Phi',$$

(52)

and the volume element is

$$dv = \sqrt{G} \, dx^1 \ldots dx^d = \frac{\sqrt{G}}{|\det C|} \, dx^1 \ldots dx^d,$$

(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 following relation

$$\hat{p}_a^\dagger = \frac{1}{\sqrt{G}} \hat{p}_a \sqrt{G}.$$

(54)

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

$$\hat{\pi}_a^\dagger = \hat{\pi}_a + \frac{1}{\sqrt{G}} \left[ \hat{p}_b \sqrt{G} C_{a\,b} \right],$$

(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 Eqs. (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 noncanonical momenta related to the canonical momenta $[p_1, p_2, p_3] = [p_\alpha, p_\beta, p_\gamma]$ via

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

(56)

where

$$C = \begin{bmatrix}
-\cos \gamma & \sin \gamma & \cos \gamma \cot \beta \\
-\sin \beta & \cos \gamma & \sin \gamma \cot \beta \\
\sin \gamma & \cos \gamma & 0
\end{bmatrix}.$$

(57)

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

12
\[ dv = \sqrt{\det M} \sin \beta \, d\alpha \, d\beta \, d\gamma = 8\pi^2 \sqrt{\det M} \, dR, \quad \text{(58)} \]

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

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

Using the volume element \( dv \), 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 Eq. (49) acquires the familiar form

\[
\hat{T} = \frac{1}{2} \hat{J} \cdot M^{-1} \hat{J}. \quad \text{(60)}
\]

### 3.2 The scaled kinetic energy

Often it is useful to multiply the original wave function \( \Phi \) by some real positive function \( S(x) \) to form a new wave function \( \Psi \),

\[
\Psi = S \Phi. \quad \text{(61)}
\]

Such a scaling produces a new kinetic energy operator acting on the new wave function \( \Psi \). 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 Eq. (64). This adjoint allows for a different form for the scaled kinetic energy operator shown in Eq. (67) and the associated extrapotential term in Eq. (68).

We note that Eq. (61) induces a new inner product on the scaled wave functions. We denote this new inner product with an \( S \) subscript and define it via,

\[
\langle \Psi | \Psi' \rangle_S = \left\langle \frac{1}{S} \Psi \bigg| \frac{1}{S} \Psi' \right\rangle = \left\langle \Psi \bigg| \frac{1}{S^2} \Psi' \right\rangle = \int \frac{\sqrt{G}}{S^2} dx^1 \ldots dx^d \, \Psi^* \Psi'. \quad \text{(62)}
\]

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

\[
\left\langle \Psi \bigg| \hat{A}^{(S)} \Psi' \right\rangle_S = \left\langle \hat{A} \Psi \bigg| \Psi' \right\rangle_S = \left\langle \hat{A} \Psi \bigg| \frac{1}{S^2} \Psi' \right\rangle = \left\langle \Psi \bigg| \frac{1}{S^2} \hat{A}^{(S)} \Psi' \right\rangle = \left\langle \Psi \bigg| S^2 \hat{A}^{(S)} \frac{1}{S^2} \Psi' \right\rangle_S, \quad \text{(63)}
\]

which summarises as

\[
\hat{A}^{(S)} = S^2 \hat{A} \frac{1}{S^2}. \quad \text{(64)}
\]
Equation (64) combines with Eq. (55) to yield
\[
\hat{n}_a^{\dagger(S)} = \hat{n}_a^{\dagger} - 2[\hat{n}_a \ln S].
\] (65)

The scaling of the wave function transforms the kinetic energy operator into \(\hat{T}_S = \hat{S} \hat{T}(1/\hat{S})\). Combining Eqs. (49) and (64), we find
\[
\hat{T}_S = \frac{1}{2} \left( \frac{1}{\hat{S}} \hat{n}_a^{\dagger(S)} \right) G^{ab} \left( \hat{S} \hat{n}_b \frac{1}{\hat{S}} \right).
\] (66)

By more or less straightforward commutation of operators in the above equation and using Eqs. (55) and (65), we arrive at the main result of this section
\[
\hat{T}_S = \frac{1}{2} \hat{n}_a^{\dagger(S)} G^{ab} \hat{n}_b + V_S,
\] (67)

where
\[
V_S = -\frac{1}{2} \left( G^{ab} [\hat{n}_a \ln S] [\hat{n}_b \ln S] + [\hat{n}_a^{\dagger(S)} G^{ab} [\hat{n}_b \ln S]] \right)
= \frac{1}{2} \left( G^{ab} [\hat{n}_a \ln S] [\hat{n}_b \ln S] - [\hat{n}_a^{\dagger} G^{ab} [\hat{n}_b \ln S]] \right).
\] (68)

Comparing Eq. (67) to the unscaled expression Eq. (49), we note that the two operators differ by the additional scalar term in Eq. (67) and the different adjoints which are used. Thus, scaling the wave function 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 quantise the classical kinetic energy Eq. (27) using Eq. (49) derived in the previous section. This approach requires the operators \(\hat{p}_\mu, \hat{J}_i\), and their adjoints. Since the classical momentum \(p_\mu\) is canonically conjugate to \(q^\mu\), the quantised operator \(\hat{p}_\mu\) has the usual form of Eq. (47)
\[
\hat{p}_\mu = -i \frac{\partial}{\partial q^\mu}.
\] (69)

The quantised 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,
\[
[\hat{J}_i, M] = [\hat{J}_i] = [\hat{J}_i, A_\mu] = [\hat{J}_i, a_\mu] = [\hat{J}_i, g_{\mu\nu}] = [\hat{J}_i, h_{\mu\nu}] = [\hat{J}_i, \hat{p}_\mu] = 0.
\] (70)

To compute the volume element of Eq. (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 \(R\), which complement the \(d-3\) internal coordinates \(q^\mu\).
Here, $d = 3n + 3n_c + 2n_c - 3$ is the dimension of the centre of mass system. We adopt the Euler angle conventions used in Section 3. The noncanonical momenta $\hat{\pi}_i = \hat{J}_i$ and $\hat{\pi}_\mu = \hat{p}_\mu - \hat{J} \cdot \mathbf{A}_\mu$ are expressed in terms of the canonical momenta $\hat{p}_i = -i\partial / \partial \theta^i$ and $\hat{p}_\mu$ by

$$\left[ \begin{array}{c} \hat{J}_i \\ \hat{p}_\mu - \hat{J} \cdot \mathbf{A}_\mu \end{array} \right] = \left[ \begin{array}{cc} C_i^j & 0 \\ -\sum_k A^k C_k^j & \delta^\mu_\nu \end{array} \right] \left[ \begin{array}{c} \hat{p}_j \\ \hat{p}_\nu \end{array} \right],$$

(71)

where $C_i^j$ are the components of the matrix in Eq. (57) and the sum over $j$ is implicit. The full $d \times d$ matrix in Eq. (71) corresponds to the matrix $C^b_a$ in Eq. (50). Its determinant is equal to the determinant of the upper left block alone, that is $\det C = -1 / \sin \beta$. The metric $G_{ab}$ with respect to the momenta $\pi_i = J_i$ and $\pi_\mu = p_\mu - J \cdot \mathbf{A}_\mu$ is seen from Eq. (27) to have determinant

$$G = g \det \mathbf{M},$$

(72)

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

$$dv = \frac{\sqrt{G}}{|\det C|} d\alpha d\beta d\gamma dq^1 \ldots dq^{d-3} = \sqrt{g \det \mathbf{M}} \sin \beta d\alpha d\beta d\gamma dq^1 \ldots dq^{d-3} = 8\pi^2 \sqrt{g \det \mathbf{M}} dR dq^1 \ldots dq^{d-3}.$$  

(73)

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

$$G = h \det \tilde{\mathbf{M}},$$

(74)

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

Since $\det \mathbf{M}$ and $g$ are rotationally invariant, their presence in $dv$ 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 Eqs. (27) and (49), we find

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

(75)

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

$$\hat{p}_\mu^\dagger = \frac{1}{\sqrt{G}} \hat{p}_\mu \sqrt{G} = \frac{1}{\sqrt{g \det \mathbf{M}}} \hat{p}_\mu \sqrt{g \det \mathbf{M}},$$

(76)

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

We now scale the wave function by a factor

$$S = \sqrt{8\pi^2 G^{1/4}} = \sqrt{8\pi^2 (\det \mathbf{M})^{1/4} g^{1/4}}$$

(77)

to obtain a new form of the kinetic energy. First, we note that the transformed volume element is
\[ \frac{dv}{S^{2}} = dR dq^{1} \ldots dq^{d-3}. \] (78)

The angular momenta \( \hat{J}_i \) are still Hermitian with respect to this new volume element, that is \( \hat{J}_i^{(S)} = \hat{J}_i \), as may be noted from Eq. (77) and the fact that \( S \) is rotationally invariant. However, since the new volume element contains no \( q^\mu \) dependence in the Jacobian prefactor, we have the added benefit that \( \hat{p}_\mu \) is now Hermitian, that is \( \hat{p}_\mu^{(S)} = \hat{p}_\mu \). (79)

Therefore, the transformed kinetic energy of Eq. (61) takes the simple form

\[ \hat{T}_S = \frac{1}{2} \hat{J} \cdot \hat{M}^{-1} \hat{J} + \frac{1}{2} (\hat{p}_\mu - A_\mu \cdot \hat{J}) g^{\mu\nu}(\hat{p}_\nu - A_\nu \cdot \hat{J}) + V_S, \] (80)

where the extrapolation term may be reduced to

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

We observe that \( V_S \) is an \( R \)-scalar, but not a \( q \)-scalar. Therefore, \( V_S \) depends on the choice of internal coordinates, but not on the choice of CBF. Further discussion of this matter is given in Ref. [13].

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

\[ \hat{T} = \frac{1}{2} (\hat{J} - \hat{K}^I) \cdot \hat{M}^{-1} (\hat{J} - \hat{K}) + \frac{1}{2} \hat{p}_\mu h^{\mu\nu} \hat{p}_\nu, \] (82)

where

\[ \hat{K} = h^{\mu\nu} a_\mu \hat{p}_\nu. \] (83)

Similarly, the scaled kinetic energy becomes

\[ \hat{T}_S = \frac{1}{2} (\hat{J} - \hat{K}^{(S)}) \cdot \hat{M}^{-1} (\hat{J} - \hat{K}) + \frac{1}{2} \hat{p}_\mu h^{\mu\nu} \hat{p}_\nu + V_S. \] (84)

5 Example: a monomer-atom complex

We compute the rovibrational kinetic energy explicitly for a system containing a single noncollinear rigid monomer with moment of inertia \( M_1 \) and a single atom, for example, Ar-NH\(_3\). The kinetic energy of such systems has already 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 \( A_i^\mu \), Coriolis field strength \( B_i^{\mu\nu} \), and internal metric \( g_{\mu\nu} \) is new.

We define the CBF by fixing it to the rigid monomer. This implies that the matrix \( S \), defining the orientation of the monomer’s IBF in the CBF, is constant. We take this constant to be the identity,
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 $r$ locates the atom with respect to the monomer and its components may therefore be chosen as the internal coordinates, that is

$$[q^1, q^2, q^3] = [r_1, r_2, r_3].$$  \hspace{1cm} (86)

Thus,

$$r_{i,\mu} = \delta_{i\mu}.$$  \hspace{1cm} (87)

Furthermore, from Eqs. (85) and (88), we have

$$\tau_{\mu} = 0.$$  \hspace{1cm} (88)

Inserting Eqs. (85), (87), and (88) into Eqs. (28) – (30), we readily obtain

$$M = r^2I - rr^T + M^i_1,$$  \hspace{1cm} (89)

$$a_{i\mu} = (r \times r_{,\mu})_i = \sum_j \epsilon_{ij\mu} r_j,$$  \hspace{1cm} (90)

$$h_{\mu\nu} = r_{,\mu} \cdot r_{,\nu} = \delta_{\mu\nu},$$  \hspace{1cm} (91)

where the $i$ superscript on $M^i_1$ indicates that it is referred to the monomer’s IBF (which agrees here with the CBF) and is hence a constant matrix.

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

$$\tilde{M} = M^i_1,$$  \hspace{1cm} (92)

$$K = r \times p,$$  \hspace{1cm} (93)

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

$$T = \frac{1}{2}(J - r \times p) \cdot (M^i_1)^{-1}(J - r \times p) + \frac{1}{2}p \cdot p.$$  \hspace{1cm} (94)

The quantum kinetic energy requires the further result

$$G = h \det \tilde{M} = \det M^i_1,$$  \hspace{1cm} (95)

which follows from Eq. (74) and shows that $G$ is constant. Hence, from Eq. (76) it is clear that $\hat{p}_\mu$ is Hermitian with respect to the original inner product. Since $\hat{K} = r \times \hat{p}$ we find that $\hat{K}$ is also Hermitian with respect to both the original and the scaled inner products. Furthermore, the extrapolential term of Eq. (31) arising in the scaled kinetic energy vanishes.
Thus, both the original and the scaled quantum kinetic energies are identical and each is formed by simply replacing $\mathbf{p}$ and $\mathbf{J}$ in Eq. (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 Eq. (27), we assume the rigid body is a spherical top with $M_i = \kappa I_i$. The total moment of inertia tensor given in Eq. (89) may be explicitly inverted, with the form

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

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

$$A^i_{\mu} = \sum_j \frac{1}{r^2 + \kappa} \epsilon_{ij\mu} r_j,$$  

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

The inverse of the internal metric is

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

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

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

$$B^i_{\mu\nu} = \epsilon_{\mu\nu\sigma} \frac{1}{(r^2 + \kappa)^2} (r_{i} r_{\sigma} + 2 \kappa \delta_{i\sigma}).$$

As the separation $r$ of the atom from the monomer goes to infinity, the Coriolis field strength tends toward $B^i_{\mu\nu} \rightarrow \epsilon_{\mu\nu\sigma} r_{i} r_{\sigma} / r^4$. We change the CBF, as in Eq. (58), via a matrix $U(r)$ which rotates $\hat{\mathbf{z}}$ into $\mathbf{r} / r$. Then, since $B_{\mu\nu}$ is a rank one $\mathbf{R}$-tensor, as $r$ goes to infinity, the new field strength tensor approaches

$$B'_{\mu\nu} = U^T B_{\mu\nu} \rightarrow \epsilon_{\mu\nu\sigma} \frac{r_{\sigma}}{r^3} \hat{\mathbf{z}}.$$  

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 [14, 16, 19, 35]. We remark that the above asymptotic form is valid even if the monomer is an asymmetric top.

### 6 Conclusions

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 readily computed for specific choices of
coordinates and frames. We have provided a discussion of transformation properties to facil-
itate 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 theoretic reasoning we have managed to generalise 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 can then be readily ported over
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 will be the subject of future publica-
tions.

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