Vibration–rotation kinetic energy operators: A geometric algebra approach

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The elements of the reciprocal metric tensor \( g^{(q,q)} \), which appear in the exact internal kinetic energy operators of polyatomic molecules can, in principle, be written as the mass-weighted sum of the inner products of measuring vectors associated to the nuclei of the molecule. In the case of vibrational degrees of freedom, the measuring vectors are simply the gradients of the vibrational coordinates. It is more difficult to find these vectors for the rotational degrees of freedom, because the components of the total angular momentum operator are not conjugated to any rotational coordinates. However, by the methods of geometric algebra, the rotational measuring vectors are easily calculated for any geometrically defined body-frame, without any restrictions to the number of particles in the system. In order to show that the rotational measuring vectors produced by the present method agree with the known results, the general formulas are applied to the triatomic bond–z, and to the triatomic angle bisector frame. All the rotational measuring vectors are also explicitly derived for a new triatomic body frame defined in terms of two Jacobi vectors. As a final application, all the rotational measuring vectors are presented for a new \( N \)-atomic frame defined in terms of \( N-1 \) Jacobi vectors, and for a simple \( N \)-atomic frame defined in terms of \( N \) nuclear position vectors (\( N=3,4,5,6,\ldots \)). © 2001 American Institute of Physics.

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I. INTRODUCTION

In order to study the internal motions of the molecular system, one must somehow find the Hamiltonian operator

\[
\hat{H} = \hat{T} + \hat{V}
\]

(1)
of the molecule. In practice, both the kinetic and potential energy operators are expressed in some coordinates. If the Born–Oppenheimer approximation is valid, the potential energy operator can be formed straightforwardly. For example, one can use \textit{ab initio} data to fit the potential energy surface in any suitable vibrational coordinates of the nuclei. In the current literature, the use of the genuine curvilinear internal displacement coordinates has become popular. They offer several advantages over their rectilinear approximations, which the normal coordinates are based on. For example, the potential energy surfaces can usually be represented in a more compact form in curvilinear displacement coordinates than in their rectilinear approximations, to name only one of the advantages (see Ref. 1 and references therein). But the internal motion of the molecule includes rotation as well as vibration. It is the addition of the rotational degrees of freedom, which makes the theoretical description of the internal motions of molecular system difficult, even when the rectilinear coordinates are used.\textsuperscript{2} Furthermore, the kinetic energy operator is more complicated in curvilinear internal coordinates than in rectilinear internal coordinates. Thus, it is no surprise that the study of the vibration–rotation of polyatomic molecules is still an active part of current molecular spectroscopy and theoretical chemistry.

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The elements of the reciprocal metric tensor \( g^{(q,q)} \), which appear in the exact internal kinetic energy operator of the polyatomic molecule can, in principle, be written as the mass-weighted sum of the inner products of the measuring vectors \( \mathbf{e}^{(q)} \) associated to the coordinates \( q_i \) (or, in the case of rotational degrees of freedom, to the components of the angular momentum operator), and to the \( \alpha \)th nucleus of the molecule. The name ”measuring vector” originates from the fact that the vector \( \mathbf{e}^{(q)} \) gives the measure of the rate of change of the coordinate \( q_i(\mathbf{x}_a) \) for any given rate of the change \( d\mathbf{x}_a/dt \) of the nuclear position \( \mathbf{x}_a \) as \( dq_i/dt = \sum_{\alpha} \mathbf{e}^{(q)} \cdot (d\mathbf{x}_a/dt) \) (see page 108 in Ref. 3). In the case of the vibrational degrees of freedom, the measuring vectors are simply the gradients of the vibrational coordinates. Fortunately, they can be easily obtained for any geometrically defined shape coordinates by the methods of geometric algebra, either by the direct vectorial differentiation,\textsuperscript{1} or from the variation of the appropriate coordinate along the path of the particle.\textsuperscript{2} Besides, a sufficient shape coordinate system for an \( N \)-atomic molecule consists of \( N-1 \) mutual distances of nuclei, \( N-2 \) valence angles, and \( N-3 \) dihedral angles, (the polyspherical coordinates), whose \( g^{(q,q)} \) elements have already been derived.\textsuperscript{5} Unfortunately, it is more difficult to obtain the rotational and Coriolis part of the kinetic energy operator, when true curvilinear internal coordinates are used. In fact, the derivation of the rotational and Coriolis part of the kinetic energy operator becomes a serious algebraic problem even in the case of such a small system as a triatomic molecule, if any conventional Lagrangian based method is used. To my knowledge, no general method, which could be applied in practice (as opposed to in principle) to any
choice of body fixed frame, and to any choice of shape coordinates, has been presented in the literature. For some different approaches and applications, see Refs. 6–19 and the references therein.

In this article, I use the branch of mathematics called geometric algebra to obtain the measuring vectors for the rotational degrees of freedom. The rotational part of the kinetic energy operator (i.e., the rotational part of the reciprocal metric tensor \( g^{(q_i q_j)} \)) is given as the mass-weighted sum of the inner products of the rotational measuring vectors. The Coriolis part is given as the mass-weighted sum of the inner products of the rotational measuring vectors \( e_{L_i}^{(a)} \) with the vibrational measuring vectors \( e_{q_i}^{(a)} \). In the present work, I concentrate on the geometrical embeddings, where the body frame is a simple function of the internal nuclear position vectors. Even the experienced professional reader, who is not familiar with geometric algebra, should be pleasantly surprised at the number of fresh geometrical insights and simplified derivations.

In order to be able to follow the current presentation, the reader, who is not familiar with geometric algebra, should read at least the rudimentary introduction in Ref. 1. A more complete introduction approximately of the same level is given in Ref. 3, and an advanced treatment is given in Ref. 20. For a fast reference, a short introduction to the treatment given in Ref. 3, and an advanced treatment is given in Ref. 24. For a fast reference, a short introduction to the treatment of rotations in geometric algebra, as well as a short introduction to the directional derivation (used much in the present work) is given as supplementary material.

II. INTERNAL KINETIC ENERGY

The expectation value of the kinetic energy of an \( N \)-atomic molecule is

\[
\langle T \rangle = -\frac{\hbar^2}{2} \sum_{a}^{N} \int d\tau \Psi^{*} \frac{\nabla_{a}^{2}}{m_{a}} \Psi,
\]

where \( \Psi \) is the eigenfunction of the full Hamiltonian, \( m_{a} \) is the mass of the atom \( a \) and \( \nabla_{a} \) is the vector derivative (gradient) operator with respect to the spatial position \( x_{a} \) of the nucleus \( a \). The translation of the molecule as a whole is separated from the internal motion by introducing internal (center of the mass) positions

\[
y_{a} = x_{a} - X,
\]

where

\[
X = \sum_{a}^{N} \frac{m_{a} x_{a}}{M}
\]

is the center of the mass of the molecule \((M = \sum_{a}^{N} m_{a} \) is the mass of the molecule). The internal part of the total kinetic energy of Eq. (2) can be written in terms of the internal angular momentum operator

\[
\mathbf{L} = -i\hbar \sum_{a}^{N-1} y_{a} \times \nabla_{y_{a}}
\]

(note that only \( N - 1 \) internal positions are independent, because they are related as \( \sum_{a} m_{a} y_{a} = 0 \)) and the \( 3N-6 \) internal shape coordinates \( q_{1}, q_{2}, \ldots, q_{3N-6} \) as

\[
\langle T \rangle = -\frac{\hbar^2}{2} N^{3N-6} \sum_{ij} \left( \frac{\partial}{\partial q_{i}} + \frac{1}{J} \frac{\partial J}{\partial q_{j}} \right) \lambda_{i j} \lambda_{i j} \Psi
\]

\[
- \frac{1}{2} \sum_{i j} \left( \frac{\partial}{\partial q_{i}} + \frac{1}{J} \frac{\partial J}{\partial q_{j}} \right) \lambda_{i j} \lambda_{i j} \Psi
\]

\[
- \frac{\hbar}{2} \sum_{i j} \left( \frac{\partial}{\partial q_{i}} + \frac{1}{J} \frac{\partial J}{\partial q_{j}} \right) d_{i j} \lambda_{i j} \lambda_{i j} \Psi
\]

\[
- \frac{\hbar}{2} \sum_{i j} \left( \frac{\partial}{\partial q_{i}} + \frac{1}{J} \frac{\partial J}{\partial q_{j}} \right) \lambda_{i j} \lambda_{i j} \Psi
\]

\[
= \frac{1}{2} \int d\tau \Psi^{*} \sum_{i j} \left( \frac{\partial}{\partial q_{i}} + \frac{1}{J} \frac{\partial J}{\partial q_{j}} \right) g^{(q_{i} q_{j})} \lambda_{i j} \lambda_{i j} \Psi
\]

\[
(6)
\]

where \( l_{k} = \mathbf{u}_{k} \cdot \mathbf{L} \) is the \( k \)th scalar component of the dual \( \mathbf{L} \)

\[
= -i\mathbf{L}
\]

of the internal angular momentum operator \( \mathbf{L} \) in the orthonormal body-fixed frame \( \{ \mathbf{u}_{i}, \mathbf{u}_{j}, \mathbf{u}_{k} \} \) related to some standard laboratory-fixed frame of orthonormal vectors \( \{ \mathbf{u}_{1}, \mathbf{u}_{2}, \mathbf{u}_{3} \} \) by the rotation \( \mathbf{u}'_{i} = R_{i}^{j} \mathbf{u}_{j} R \).

In order to use the formalism of geometric algebra consistently, the angular momentum operator \( \mathbf{L} \) is treated as a bivector, i.e., we assume that \( i \) in Eq. (5) is the unit trivector, in contrast to the conventional treatments (such as Ref. 24) where no such interpretation is assigned to \( i \). Consequently, there is no (uninterpreted) imaginary unit in front of the Coriolis term in Eq. (6), as there would be in the conventional treatments. Incidentally, as shown explicitly in Ref. 3, the angular momentum in classical mechanics is better considered as a bivector rather than a vector quantity. However, the question of the deeper role of \( i \) in the Schrödinger (as well as Pauli and Dirac) theory is discussed elsewhere.

In the curvilinear case, the \( g^{(q_{i} q_{j})} \) elements are generally functions of the shape coordinates. The volume-element of the integration \( d\tau = J dq_{1} dq_{2} \ldots \) where \( J \) is the absolute value of the Jacobian of the coordinate transformation given by

\[
J = | \det g^{(q_{i} q_{j})} |^{-1/2} \sin \theta \prod_{a} m_{a}^{-3/2},
\]

where \( \theta \) is the Euler angle between \( \mathbf{u}_{i} \) and \( \mathbf{u}'_{i} \) (see Appendix A). If one wishes to integrate using the volume-element \( d\tau = w dq_{1} dq_{2} \ldots \) instead of the volume-element \( d\tau = J dq_{1} dq_{2} \ldots \), the corresponding kinetic energy operator \( \mathbf{T}_{w} \) is given as

\[
\mathbf{T}_{w} = J^{1/2} w^{-1/2} \mathbf{T} J^{-1/2}
\]

in terms of the kinetic energy operator

\[
\mathbf{T} = \sum_{ij} \left[ -\frac{\hbar^{2}}{2} \left( \frac{\partial}{\partial q_{i}} + \frac{1}{J} \frac{\partial J}{\partial q_{j}} \right) g^{(q_{i} q_{j})} \lambda_{i j} \lambda_{i j} \right. - \frac{1}{2} \left. g^{(L_{i} L_{j})} \lambda_{i j} \lambda_{i j} \right]
\]

\[
(9)
\]

of Eq. (6).

The vibrational elements of the mass weighted reciprocal metric tensor are given by

\[
g^{(q_{i} q_{j})} = \sum_{a}^{N} \frac{1}{m_{a}} \left( \nabla_{a} q_{i} \right) \cdot \left( \nabla_{a} q_{j} \right)
\]

\[
(10)
\]
for any vibrational coordinates \( q_i \), \( (i = 1, 2, \ldots, 3N - 6) \). Usually, these coordinates can be written straightforwardly as functions of the nuclear position vectors \( \mathbf{x}_a \), and the vibrational gradients \( \nabla_{q_i} \) are obtained by taking the vector derivative of the coordinate \( q_i \) with respect to the position vector of the nucleus \( \alpha \), i.e.,

\[
\nabla_{q_i} q_i = \nabla_{\mathbf{x}_a} q_i = \frac{\partial}{\partial \mathbf{x}_a} q_i = \mathbf{e}_a^{(L_k)} \nabla_{q_i} q_i \quad (11)
\]

or alternatively, they can be extracted from the variation

\[
\dot{q}_i = \sum_{a} \dot{x}_a(t) \cdot \nabla_{q_i} q_i \quad (12)
\]

of the coordinate \( q_i \) along the path \( \mathbf{x}_a(t) \) of the particle \( \alpha \) (now \( \dot{q} = dq/dt \), and \( t \) is some scalar parameter). Because the acceptable vibrational coordinates are functions of the molecule-fixed positions \( y_a \) (related to the laboratory-frame positions \( y_a \) by a rotation as \( y_a = R^s \cdot y_a^R \) ), they are translationally and rotationally invariant, and

\[
\nabla_{q_i} q_i = \nabla_{y_a} q_i \quad (13)
\]

holds as well.

It is much more difficult to find the rotational and the Coriolis part of the reciprocal metric tensor, because the components of the angular momentum operator \( \mathbf{L} \) are not conjugated to any rotational coordinate \( B_j \). However, with geometric algebra, one can show that the rotational \( g \)-elements are given as

\[
g_{(L_i, L_k)} = \sum_{a} \frac{1}{m_a} \mathbf{e}_a^{(L_i)} \cdot \mathbf{e}_a^{(L_k)} \quad (14)
\]

and the Coriolis \( g \) elements as

\[
g_{(L_i, q_k)} = \sum_{a} \frac{1}{m_a} \mathbf{e}_a^{(L_i)} \cdot (\nabla_{q_k} q_i) \quad (15)
\]

where

\[
\mathbf{e}_a^{(L_k)} = \nabla_{q_k} [ (\mathbf{a} \cdot \nabla_{q_k} \mathbf{u}_j^i) \cdot \mathbf{u}_j^i ] \quad (16)
\]

is the rotational measuring vector associated to the nucleus \( \alpha \) and \( k \)th component of the angular momentum \( \mathbf{L} \) (now the target of differentiation is implied by the parenthesis, and the indices \( i, j, \) and \( k \) are in cyclic order). A detailed derivation is presented in Appendix B.

The result presented in Eq. (16) enables one to obtain the rotational measuring vectors by directly manipulating the body-fixed axes. One simply calculates the directional derivatives \( \mathbf{a} \cdot \nabla_{q_k} \mathbf{u}_j^i \) of the body frame using the full machinery of geometric algebra. A practical introduction to directional derivation is given as supplementary material.\textsuperscript{23} Then one calculates the vector derivatives of \( (\mathbf{a} \cdot \nabla_{q_k} \mathbf{u}_j^i) \cdot \mathbf{u}_j^i \) with respect to the vector \( \mathbf{a} \). Because the subject of vectorial differentiation has been studied at sufficient depth for the present purpose in Ref. 1, no introduction in it is given here. However, some useful vector derivatives are tabulated in Appendix C. Because of the translational invariance of the rotational degrees of freedom, it is only necessary to calculate at most \( N - 1 \) rotational measuring vectors \( \mathbf{e}_a^{(L_k)} \) from the set \( \{ \mathbf{e}_1^{(L_k)}, \mathbf{e}_2^{(L_k)}, \ldots, \mathbf{e}_N^{(L_k)} \} \). The measuring vector \( \mathbf{e}_N^{(L_k)} \) is then given by

\[
\mathbf{e}_N^{(L_k)} = - (\mathbf{e}_1^{(L_k)} + \mathbf{e}_2^{(L_k)} + \ldots + \mathbf{e}_N^{(L_k)}) \quad (17)
\]

Last, a word about the notation of the measuring vectors followed here. I use the notation \( \mathbf{e}_a^{(L_k)} \) as the symbol of the rotational measuring vector, instead of \( \mathbf{s}_a^{(L_k)} \), because the rotational measuring vectors in Eq. (16) are exact, not just some approximations in the limit of infinitesimal vibration or rotation. On the other hand, the \( s \)-vector notation bears some infinitesimal connotations. For example, the vibrational \( s \)-vector \( \mathbf{s}_a^{(L_k)} \) stands for the value \( \nabla_{q_k} q_i \left( \mathbf{e}_1^{(L_k)}, \mathbf{e}_2^{(L_k)}, \ldots \right) \) of the gradient of the vibrational coordinate \( q_k \) at the reference configuration \( \{ \mathbf{q}_1^{(c)}, \mathbf{q}_2^{(c)}, \ldots \} \), instead of the gradient \( \nabla_{q_k} q_i \) itself (see Ref. 1).

### III. ROTATIONAL MEASURING VECTORS

In this section, the explicit formulas for the rotational measuring vectors are derived for the generic geometrically defined body frame. Interestingly enough, all the rotational measuring vectors of the geometrically defined body-frames derived in the literature before\textsuperscript{14–16} are obtained as special cases of the rotational measuring vectors of the generic geometric frame presented here. Some examples of this are given. Rotational measuring vectors are also derived for some \textit{new} triatomic, and general \textit{N}-atomic body frames. To my knowledge, these measuring vectors have not been presented before.

Let us choose one of the body axis, say \( \mathbf{u}_1^j \), to be in the direction of

\[
\mathbf{u}_1^j = \frac{\mathbf{r}}{r} \quad (18)
\]

where the coefficients \( c_a \) are known functions of the nuclear positions \( \mathbf{x}_1, \mathbf{x}_2, \ldots \). Thus,

\[
\mathbf{s} = \sum_{a} d_a \mathbf{x}_a \quad (19)
\]

By choosing another direction as

\[
\mathbf{u}_2^j = \frac{\mathbf{r} \times \mathbf{s}}{r \times \mathbf{s}} \quad (20)
\]

where the coefficients \( d_a \) are also known functions of the nuclear positions, and \( \mathbf{s} \) is not collinear with \( \mathbf{r} \) (i.e., \( \mathbf{r} \times \mathbf{s} \neq 0 \)), one can define the body-fixed axis \( \mathbf{u}_2^j \) as

\[
\mathbf{u}_2^j = \frac{\mathbf{r} \times \mathbf{s}}{r \times \mathbf{s}} \quad (21)
\]

and the body-fixed axis \( \mathbf{u}_1^j \) is given by

\[
\mathbf{u}_1^j = \mathbf{u}_2^j \times \mathbf{u}_1^j \quad (22)
\]

In order to preserve the translational invariance of the body-fixed frame, the coefficients \( c_a \) and \( d_a \) must fulfill

\[
\sum_{a} c_a = 0, \quad \sum_{a} d_a = 0 \quad (23)
\]
This guarantees that $\mathbf{r} = \sum \alpha \mathbf{a}_\alpha \mathbf{y}_\alpha$ and $\mathbf{s} = \sum \alpha d \mathbf{a}_\alpha \mathbf{y}_\alpha$.

It is an easy task to find the directional derivative $\mathbf{a} \cdot \nabla \mathbf{a}_3$ as

\[
\mathbf{a} \cdot \nabla \mathbf{a}_3 = \mathbf{a} \cdot \nabla \mathbf{a}_3 = \mathbf{a} \cdot \nabla \frac{\mathbf{r}}{r} + \mathbf{a} \cdot \nabla \frac{\mathbf{a} \cdot \mathbf{a}_3}{r}
\]

\[
= \mathbf{a} \cdot \nabla \frac{\mathbf{a} \cdot \mathbf{r}}{r} - \mathbf{a} \cdot \nabla \frac{\mathbf{a} \cdot \mathbf{a}_3}{r^2}
\]

\[
= \mathbf{a} \cdot \frac{\mathbf{r}}{r} - \mathbf{a} \cdot \frac{\mathbf{a} \cdot \mathbf{r}}{r^2} - \mathbf{a} \cdot \nabla \frac{\mathbf{a} \cdot \mathbf{a}_3}{r^3}, \tag{25}
\]

(\text{where } r = |\mathbf{r}|). Thus, the rotational measuring vector $\mathbf{e}_a^{(L_2)}$ is given by Eq. (16) as

\[
\mathbf{e}_a^{(L_2)} = \mathbf{a} \cdot \frac{\mathbf{r}}{r} - \mathbf{a} \cdot \frac{\mathbf{a} \cdot \mathbf{r}}{r^3} \cdot \mathbf{u}_1 = \nabla \frac{\mathbf{a} \cdot \mathbf{a}_3}{r}. \tag{26}
\]

Similarly, because

\[
\mathbf{a} \cdot \nabla \mathbf{a}_3 = \mathbf{a} \cdot \frac{\mathbf{r}}{r} - \frac{\mathbf{a} \cdot \mathbf{r}}{r^3} \cdot \mathbf{u}_1 = \nabla \frac{\mathbf{a} \cdot \mathbf{a}_3}{r}. \tag{27}
\]

The gradients $\nabla_a c \beta$ and $\nabla_a d \beta$ depend on the explicit formulas of coefficients $c \beta$ and $d \beta$. Typically, these coefficients are functions of the bond lengths, valence angles, etc. In any case, the gradients can be calculated by the methods of geometric algebra (see Ref. 1). These formulas cover many possible choices of the body frames: for example, all the rotational measuring vectors derived in Refs. 14–16 are obtained by the substitution of $\mathbf{r}$ and $\mathbf{s}$ to Eqs. (31)–(33).

A. Body frames for triatomic molecule

In this subsection, Eqs. (31)–(33) are applied to several triatomic body frames. In order to show that the results derived by the present method are correct, the rotational measuring vectors are rederived in some detail for the familiar bond-z frame and the angle bisector frame. The rotational measuring vectors are also derived for a new triatomic Jacobi vector embedding.

1. Bond-z frame

Let us index the nuclei with 1, 2, and 3, where the index 3 is reserved for the central nucleus, as in Ref. 14. Then,

\[
\mathbf{r} = \mathbf{x}_1 - \mathbf{x}_3, \tag{34}
\]

\[
\mathbf{s} = -(\mathbf{x}_2 - \mathbf{x}_1), \tag{35}
\]

and the only nonzero coefficients are $c_1 = 1, c_3 = -1, d_2 = -1, d_3 = 1$. Thus, all the gradients of the coefficients are zero (i.e., $\nabla_a c \beta = \nabla_a d \beta = 0$ for all $\alpha$ and $\beta$), and the formulas given in Table I of Ref. 14 follow by the substitution of Eqs. (31)–(33). For example,

\[
\mathbf{e}_a^{(L_2)} = \frac{\mathbf{u}_1}{r}, \tag{36}
\]

\[
\mathbf{e}_a^{(L_1)} = -\frac{\mathbf{u}_2}{r}, \tag{37}
\]

and

\[
\mathbf{e}_a^{(L_3)} = -\frac{\mathbf{s} \cdot \mathbf{u}_1}{r} \cdot \mathbf{u}_2 = \frac{s \cos \theta_{132} \mathbf{u}_2}{rs \sin \theta_{132}} = \frac{\cot \theta_{132} \mathbf{u}_2}{r}. \tag{38}
\]

2. Angle bisector frame

One of the simplest body frames, where coefficients $c_\alpha$ and $d_\alpha$ may depend on the nuclear positions, is the angle bisector frame, where

\[
\mathbf{r} = \frac{\mathbf{x}_1 - \mathbf{x}_3}{|\mathbf{x}_1 - \mathbf{x}_3|} + \frac{\mathbf{x}_2 - \mathbf{x}_3}{|\mathbf{x}_2 - \mathbf{x}_3|} = \frac{\mathbf{r}_{31}}{r_{31}} + \frac{\mathbf{r}_{32}}{r_{32}}, \tag{39}
\]

\[
\mathbf{s} = -(\mathbf{x}_2 - \mathbf{x}_1) = \mathbf{r}_{23}. \tag{40}
\]
In this frame, the nonzero coefficients are \( c_1 = 1/r_{31}, \ c_2 = 1/r_{32}, \ c_3 = 1/r_{33}, \ d_2 = -1, \) and \( d_3 = 1 \) and the nonzero gradients of the coefficients are (see Ref. 1)

\[
\nabla_1 c_1 = -\frac{\nabla 1 r_{31}}{r_{31}^2} = -\frac{r_{31}}{r_{31}^3} = -\nabla 3 c_1 = -\nabla 1 c_3,
\]

(41)

\[
\nabla_2 c_2 = -\frac{r_{32}}{r_{32}^3} = -\nabla 3 c_2 = -\nabla 2 c_3,
\]

(42)

\[
\nabla_3 c_3 = -\nabla 1 c_3 - \nabla 2 c_3 = -\frac{r_{31}}{r_{31}^3} - \frac{r_{32}}{r_{32}^3}.
\]

(43)

The rotational measuring vectors are given by a substitution of Eqs. (31)–(33). For example,

\[
e_2^{(L_2)} = \frac{1}{r} \left( u'_r \frac{r_{32}}{r_{32}^3} + r_{32} \frac{r_{31} \times r_{32}}{r_{32}^2} \right) = \frac{r_{32} \times (u'_r \times r_{32})}{r_{32}^2},
\]

(44)

By inserting

\[
u'_r = \frac{u_{r_{31}} - u_{r_{32}}}{\sqrt{2(1 - \cos \theta_{132})}}, \quad r = |u_{r_{31}} + u_{r_{32}}| = \sqrt{2(1 + \cos \theta_{132})},
\]

(45)

(46)

(where \( u_a \) is a unit vector in the direction of \( a, \) i.e., \( u_a = a / a \)), and \( \theta_{132} \) is the angle between vectors \( r_{a_1} \) and \( r_{a_2} \). Eq. (44) reads as

\[
e_2^{(L_2)} = \frac{r_{32} \times (u_{r_{31}} \times u_{r_{32}})}{2 r_{32} \sin \theta_{132}},
\]

(47)

which is the result derived in Ref. 14, because

\[
u_{r_{31}} \times u_{r_{32}} = \sin \theta_{132} u_{r_{31}} \times u_{r_{32}}.
\]

(48)

The reader may verify that the rest of the measuring vectors obtained by the present method also agree with the present results. \(^\text{14}^\)

3. Triatomic Jacobi vector embedding

The Jacobi vector \( j_i \) is defined as the difference of the position vectors of the first two particles, i.e.,

\[
j_i = x_2 - x_1,
\]

(49)

and the other Jacobi vectors \( j_i \) (\( i > 1 \)) are defined as vectors directed from the center of the mass of the previous \( i \) particles to the particle \( i + 1 \), i.e.,

\[
j_i = x_{i+1} - \frac{\sum_{a=1}^{i} m_a x_a}{\sum_{a=1}^{i} m_a}.
\]

(50)

Let us define the direction \( r \) and \( s \) as the Jacobi vectors

\[
r = x_2 - x_1,
\]

(51)

\[
s = x_3 - \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}.
\]

(52)

In this frame, the nonzero coefficients are \( c_1 = -1, \ c_2 = 1, \ d_1 = -m_1 / (m_1 + m_2), \ d_2 = -m_2 / (m_1 + m_2) \), and \( d_3 = 1 \) and all the gradients of the coefficients are zero (i.e., \( \nabla_a c_\beta = \nabla_a d_\beta = 0 \) for all \( a \) and \( \beta \)). Thus, by the direct substitution of Eqs. (31)–(33), the nonzero rotational measuring vectors are seen to be

\[
e_1^{(L_1)} = \frac{u'_r}{r} = -e_2^{(L_1)},
\]

(53)

\[
e_1^{(L_2)} = -\frac{u'_r}{r} = -e_2^{(L_2)},
\]

(54)

\[
e_1^{(L_3)} = \frac{r \cdot s - r m_1 / (m_1 + m_2) j'_i}{r},
\]

(55)

\[
e_2^{(L_3)} = \frac{r \cdot s - r m_2 / (m_1 + m_2) j'_i}{r},
\]

(56)

\[
e_3^{(L_3)} = \frac{r j'_i}{r},
\]

(57)

If these rotational measuring vectors are substituted to Eq. (14), it is seen that the rotational part of the internal kinetic energy in the Jacobi embedding is almost diagonal:

\[
g^{(L_1 L_1)} = \frac{1}{r^2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right),
\]

(58)

\[
g^{(L_1 L_2)} = 0,
\]

(59)

\[
g^{(L_1 L_3)} = \frac{r \cdot s}{r^2 |r \times s|} \left( \frac{1}{m_1} + \frac{1}{m_2} \right),
\]

(60)

\[
g^{(L_2 L_2)} = \frac{1}{r^2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right),
\]

(61)

\[
g^{(L_2 L_3)} = 0,
\]

(62)

\[
g^{(L_3 L_3)} = \left[ \frac{r \cdot s - r m_1 / (m_1 + m_2)}{m_1 |r \times s|^2} \right]^2
\]

\[
+ \left[ \frac{r \cdot s - r m_2 / (m_1 + m_2)}{m_2 |r \times s|^2} \right]^2
\]

\[
+ \frac{r^2}{m_3 |r \times s|^2},
\]

(63)

B. Simple body frames for \( N \)-atomic molecule

In this subsection, explicit formulas are derived for the rotational measuring vectors for a general \( N \)-atomic molecule \((N = 3,4,5,\ldots)\), with two different choices of the body frame.

1. \( N \)-atomic Jacobi vector embedding

The Jacobi embedding for the \( N \)-body system is a simple generalization of the triatomic Jacobi embedding. Now, let us define the directions \( r \) and \( s \) as

\[
r = \sum_{i=1}^{N-2} j_i,
\]

(64)

\[
s = j_{N-1},
\]

(65)
where $j_i$ ($i = 2, \ldots, N-1$) is the Jacobi vector of Eq. (50), and $j_1$ is given by Eq. (49). In this frame, the nonzero coefficients are

$$c_1 = -1 - m_1 \sum_{\beta=2}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1},$$

$$c_\alpha = -1 - m_\alpha \sum_{\beta=\alpha}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \quad \text{for} \quad 2 \leq \alpha < N-1,$$

$$c_{N-1} = 1,$$

(where $M$ is the mass of the molecule, as before, and it is understood that the sums equal to zero, if the lower limit of a summation is greater than the upper limit), and

$$d_\alpha = - \frac{m_\alpha}{M - m_N} \quad \text{for} \quad 1 \leq \alpha < N,$$

$$d_N = 1,$$

and all the gradients of the coefficients are zero (i.e., $\nabla_c e_\beta = \nabla_d e_\beta = 0$ for all $\alpha$ and $\beta$). By the direct substitution of Eqs. (31)–(33), the nonzero rotational measuring vectors $e^{(L_1)}_\alpha$ are seen to be

$$e^{(L_1)}_1 = - \frac{u'_1}{r} \left[ -1 - m_1 \sum_{\beta=2}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right],$$

$$e^{(L_1)}_\alpha = - \frac{u'_\alpha}{r} \left[ -1 - m_\alpha \sum_{\beta=\alpha}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right] \quad \text{for} \quad 2 \leq \alpha < N-1,$$

$$e^{(L_1)}_{N-1} = - \frac{u'_1}{r}.$$  

Similarly, the nonzero measuring vectors $e^{(L_2)}_\alpha$ are

$$e^{(L_2)}_1 = \frac{u'_1}{r} \left[ -1 - m_1 \sum_{\beta=2}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right],$$

$$e^{(L_2)}_\alpha = \frac{u'_\alpha}{r} \left[ -1 - m_\alpha \sum_{\beta=\alpha}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right] \quad \text{for} \quad 2 \leq \alpha < N-1,$$

$$e^{(L_2)}_{N-1} = \frac{u'_1}{r}.$$  

and the measuring vectors $e^{(L_3)}_\alpha$ are

$$e^{(L_3)}_1 = \frac{s u_1' u'_2}{rXs} \left[ -1 - m_1 \sum_{\beta=2}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right]$$

$$- \frac{rm_1 u'_2}{rXs(M-m_N)},$$

$$e^{(L_3)}_{N-1} = \frac{s u_1' u'_2}{rXs} \left[ -1 - m_1 \sum_{\beta=2}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right]$$

$$- \frac{rm_1 u'_2}{rXs(M-m_N)},$$

$$e^{(L_3)}_\alpha = \frac{s u_1' u'_2}{rXs} \left[ -1 - m_\alpha \sum_{\beta=\alpha}^{N-2} \left( M - \sum_{\gamma=\beta+1}^{N} m_{\gamma} \right)^{-1} \right]$$

$$- \frac{r m_\alpha u'_2}{rXs(M-m_N)} \quad \text{for} \quad 2 \leq \alpha < N-1.$$  

2. Another N-body Frame

Let us choose the directions $r$ and $s$ as

$$r = x_1 + x_2 + x_3 + \cdots - (N-1)x_N,$$

$$s = x_1 - x_2.$$  

Then, the nonzero coefficients are $c_\alpha = 1$ for $1 \leq \alpha < N$, $c_N = -(N-1)$, $d_1 = 1$, and $d_2 = -1$ and all the gradients of the coefficients are zero (i.e., $\nabla_c e_\beta = \nabla_d e_\beta = 0$ for all $\alpha$ and $\beta$). By the direct substitution of Eqs. (31)–(33), the rotational measuring vectors $e^{(L_1)}_\alpha$ are seen to be

$$e^{(L_1)}_1 = - \frac{u'_1}{r} \quad \text{for} \quad 1 \leq \alpha < N,$$

$$e^{(L_1)}_{N-1} = (N-1) \frac{u'_1}{r}.$$  

Similarly, the measuring vectors $e^{(L_2)}_\alpha$ are

$$e^{(L_2)}_1 = \frac{u'_1}{r} \quad \text{for} \quad 1 \leq \alpha < N,$$

$$e^{(L_2)}_{N-1} = -(N-1) \frac{u'_1}{r}.$$  

and the measuring vectors $e^{(L_3)}_\alpha$ are

$$e^{(L_3)}_1 = \frac{\langle s \cdot u_1' - r \rangle u'_2}{rXs},$$

$$e^{(L_3)}_2 = \frac{\langle s \cdot u_1' + r \rangle u'_2}{rXs},$$

$$e^{(L_3)}_{N-1} = \frac{s u_1' u'_2}{rXs} \quad \text{for} \quad 3 \leq \alpha < N,$$

$$e^{(L_3)}_\alpha = \frac{s u_1' u'_2}{rXs} \quad \text{for} \quad 2 \leq \alpha < N-1.$$  

IV. COMPARISON TO OTHER APPROACHES

The geometric algebra approach has some advantages over conventional methods. First of all, no analytic matrix inversions are needed, unlike in the Lagrangian based approach, where the matrix containing the covariant $g_{q,q'}$ elements must be inverted to obtain the $g^{(q,q')}$ elements which appear in the quantum mechanical kinetic energy operator. Even though the problem can be simplified by the
judicious factorization of the matrix $g_{q_i q_j}$ and by the direct use of the vibrational elements $g^{q_i q_j}$, one must still be able to invert at least one $3 \times 3$ matrix, whose elements can be complicated functions of nuclear positions. Thus, it is no surprise that the Lagrangian based method is most appropriate in the cases where the shape of the system is described in terms of rectilinear coordinates, or orthogonal (or nearly orthogonal) curvilinear coordinates, such as the hyperspherical coordinates, and the principal axis system is used as the body-frame.\textsuperscript{8,9} In the geometric algebra approach, the molecule-fixed frame is also directly manipulated instead of its components, and hence the expressions are simple at each stage of the derivation. For example, when the Cartesian components of the molecule-fixed frame are expressed as a function of the Euler angles, and the Euler angle derivative operators as functions of the angular momentum operators, the intermediate expressions are more complicated. As a consequence, this method has not been applied to larger than tetra-atomic systems.\textsuperscript{10,12} In the geometric algebra approach, it is also unnecessary to calculate the inverse of the inertia tensor to obtain the rotational measuring vectors, unlike in the approach where the rotational basis vectors are read off from the components of the rotational velocity.\textsuperscript{13} Finally, as the reader has no doubt noticed, the current method applies straightforwardly to any system: there is no restriction in the number of particles involved.

It is interesting to compare the present treatment to the approach of Lukka,\textsuperscript{14} which also produces explicit expressions for the rotational measuring vectors. In that approach, one calculates the rotational measuring vector $\mathbf{e}_a^{(L_i)}$ as the gradient of the infinitesimal rotation angle $\epsilon_k$ as

$$ e_a^{(L_i)} = \nabla_a \epsilon_k. \quad (91) $$

In the original approach of Lukka,\textsuperscript{14} the directions of the gradients of $\epsilon_k$ are determined heuristically, and the gradient $\nabla_a \epsilon_k$ is calculated from the change in $\epsilon_k$ produced by an infinitesimal displacement of the nucleus $a$ to the direction of $\nabla_a \epsilon_k$. In this respect, this method is similar to “Wilson’s $s$-vector method” used to determine the gradients of the vibrational coordinates (see Ref. 1). Lukka’s approach has gained popularity recently (see e.g., Refs. 15–17), because it is simpler than other methods. The conventional algebraic expression for the gradient of the rotation is

$$ \nabla_a \epsilon_k = \sum_j u_j \frac{\partial \epsilon_k}{\partial \alpha_{ak}} = \sum_k u_k \frac{\partial \epsilon_k}{\partial \epsilon_{ak}} \cdot u_j. \quad (92) $$

In the coordinate free language of geometric algebra, this gradient reads as

$$ \nabla_a \epsilon_k = \nabla_a \mathbf{u}_i \cdot \mathbf{u}_j, \quad (93) $$

(where the subscripts $i$, $j$, and $k$ are in cyclic order, and the target of differentiation is implied by the accent). The operator equation\textsuperscript{20,21,23}

$$ \nabla_a = \nabla_a \mathbf{a} \cdot \nabla_a \quad (94) $$

reveals, that Eq. (93) is exactly the result presented in Eq. (16). Thus, one may say that the result of the current work generalizes the result in Ref. 14. It should be emphasized that it is the use of geometric algebra, and especially the operator equation (94) (which does not exist in the conventional vector calculus), which makes the result in Eq. (16) useful in the practical calculations.

V. CONCLUSION

I have presented a general and practical way to obtain the rotational measuring vectors $\mathbf{e}_a^{(L_i)}$, whose inner products with other rotational measuring vectors, and with the gradients of the vibrational coordinates give the exact vibration–rotation kinetic energy operator of polyatomic molecules. In this treatment, a useful algebraic formula [Eq. (16)] is given for the $\mathbf{e}_a^{(L_i)}$, which is presented as a function of the directional derivatives of the body frame vectors (not their components). The presentation underlies the utility of geometric algebra in the derivation, and the actual use of Eq. (16). This formula has not been presented before in a proper algebraic form: there is no analogue to the operator equation (94), nor is there an analogue to the derivation presented in Appendix B, if one uses the ordinary vector calculus (or any other conventional mathematical system invented to supplement it, such as tensor calculus, or calculus of forms).

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APPENDIX A: EULER ANGLE CONVENTION

The rotor $R$ can be parametrized with many different ways. The Euler angles $\phi$, $\theta$ and $\chi$ are popular among physicists and astronomers. The laboratory-fixed frame $\{\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3\}$ can be made to coincide with the body-fixed frame $\{\mathbf{u}_1', \mathbf{u}_2', \mathbf{u}_3'\}$ by three successive rotations

$$ \mathbf{u}_1' = R_{\phi}^t R_{\theta}^t R_{\chi}^t \mathbf{u}_1. \quad (A1) $$

The rotation is composed as follows:

1. First, \( \mathbf{u}_1 \) is rotated right-handedly by $R_{\phi} = R(i \phi \mathbf{u}_3)$

$$ = e^{i \phi \mathbf{u}_3} \mathbf{u}_1 \quad (A2) $$

about the laboratory-fixed axis $\mathbf{u}_3$.

2. Second, the resulting vector is rotated right-handedly by $R_{\theta} = R(i \theta \mathbf{u}_1)$

$$ = e^{i \theta \mathbf{u}_1} \mathbf{u}_1' \quad (A2) $$

about the line of nodes $\mathbf{n} = R_{\phi}^t \mathbf{u}_1 R_{\phi} = \mathbf{u}_1 e^{i \phi \mathbf{u}_3} = \mathbf{u}_1 \times \mathbf{u}_3'$.\( (A2) $$

3. Finally, the resulting vector is rotated right-handedly by $R_{\chi} = R(i \chi \mathbf{u}_3')$

$$ = e^{i \chi \mathbf{u}_3'} \mathbf{u}_1' \quad (A2) $$

about the body-fixed axis $\mathbf{u}_3'$.\( (A2) $$

However, this *hybrid* interpretation is not unique, but the same rotation is achieved as a product of rotations about the laboratory-fixed axes $\mathbf{u}_1$ and $\mathbf{u}_3$ as

$$ \mathbf{u}_1' = R_{\phi}^t Q_{\chi}^t R_{\theta}^t \mathbf{u}_1, \quad (A3) $$

where $Q_{\chi} = e^{i \chi \mathbf{u}_3'}$ and $Q_{\theta} = e^{i \theta \mathbf{u}_1}$, or as a product of rotations about the body-fixed axes $\mathbf{u}_1'$ and $\mathbf{u}_3'$ as

$$ \mathbf{u}_1' = R_{\phi}^t Q_{\chi}^t R_{\theta}^t \mathbf{u}_1. \quad (A3) $$


\[ \mathbf{u}'_i = R_{\phi}^i Q'_{\phi} R_{\phi}^i \mathbf{u}_1 R_{\phi} Q'_{\phi} R_{\phi} \]  

(A4)

where \( R_{\phi}^i = e^{i\omega_{a'i}/2} \) and \( Q'_{\phi} = e^{i\omega_{a'i}/2} \). Note finally that the definition of the Euler angles differs in different references. The one used here follows the convention adopted in Ref. 3, but it differs from the convention in Ref. 24, where the line of nodes is defined as \( \mathbf{n} = R_{\phi} R_{\phi} R_{\phi} \) (but the rotation is otherwise the same \( R = R_{\phi} R_{\phi} R_{\phi} \)).

**APPENDIX B: ROTATIONAL PART OF GRADIENT**

The derivative of an arbitrary multivector field \( M(y_1,y_2,\ldots) \) of vector variables \( y_1,y_2,\ldots \) with respect to the (magnitude of the) \( i \)th rotation angle \( B_i \) is

\[
\frac{\partial M}{\partial B_i} = \left[ M(y_1,y_2,\ldots) \right] \frac{i}{2} \sum_{\alpha} \mathbf{n} \cdot \mathbf{y}_\alpha \nabla_{y_\alpha} M(y_1,y_2,\ldots),
\]

(B1)

where \( \mathbf{n} \) is the \( i \)th hybrid unit rotation axis, \([A,B]=AB-BA\) stands for the commutator product of \( A \) and \( B \), and \( i \) is the unit bivector of the rotation plane.\(^{27}\) If \( M=\Psi \) is a scalar function, the right-hand side of Eq. (B1) is proportional to the scalar product of the hybrid axis \( \mathbf{n} \) with the dual \( 1=-i\mathbf{L} \) of the angular momentum operator \( \mathbf{L} \), i.e.,

\[
\hbar \frac{\partial}{\partial B_i} \Psi = \mathbf{n} \cdot \mathbf{L} \Psi,
\]

(B2)

where it is understood that \( B_1 = \phi, \ B_2 = \theta \), and \( B_3 = \chi \) and \( \mathbf{n}_1 = \mathbf{u}_1, \ \mathbf{n}_2 = \mathbf{n}, \) and \( \mathbf{n}_3 = \mathbf{u}_3 \) (see Appendix A). When \( \mathbf{n} \) is expressed in terms of the body-fixed frame \( \{ \mathbf{u}'_1, \mathbf{u}'_2, \mathbf{u}'_3 \} \) as

\[
\mathbf{n}_i = \sum_k \mathbf{n}_i \cdot \mathbf{u}'_k \mathbf{u}'_k
\]

(B3)

one can write

\[
\hbar \frac{\partial}{\partial B_i} \Psi = \sum_k \mathbf{n}_i \cdot \mathbf{u}'_k \mathbf{u}'_k \cdot 1 = \sum_k \mathbf{n}_i \cdot \mathbf{u}'_k \mathbf{u}'_k.
\]

(B4)

Thus,

\[
\hbar \nabla_{\alpha} B_i \frac{\partial}{\partial B_i} \nabla_{\alpha} B_i \mathbf{u}'_k = \sum_k \mathbf{u}'_k \cdot \mathbf{n} \nabla_{\alpha} B_i \mathbf{u}'_k.
\]

(B5)

On the other hand, when the operator equation (94) is used, the gradient of the \( i \)th rotation angle can be written in terms of the rotational velocity (derived explicitly in Appendix)

\[
\mathbf{\omega}^{(a)}(\mathbf{a}) = \frac{i}{2} \sum_j \mathbf{u}'_j \cdot \mathbf{a} \nabla_{\alpha} \mathbf{u}'_j = \frac{i}{2} \sum_j \mathbf{u}'_j \times (\mathbf{a} \cdot \nabla_{\alpha} \mathbf{u}'_j)
\]

(B6)

of the body frame caused by the displacement of the particle \( a \) (and evaluated at the position \( a \)) as

\[
\nabla_{\alpha} B_i = \nabla_{\alpha} \mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}).
\]

(B7)

Now, \( \mathbf{n}(\mathbf{a}) \) is the vector reciprocal to the hybrid axis \( \mathbf{n} \), i.e.,

\[
\mathbf{n}(\mathbf{a}) = \delta^{(j)}_i
\]

(B8)

(\( \delta^{(j)}_i = 1 \) if \( i = j \) and zero otherwise). See Appendix B2 for the detailed derivation of Eq. (B7). Thus, when Eq. (B7) is inserted to Eq. (B5),

\[
\hbar \nabla_{\alpha} B_i \frac{\partial}{\partial B_i} \nabla_{\alpha} B_i = \frac{1}{4} \sum_k \mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) l_k
\]

(B9)

follows. The vector derivative operator \( \nabla_{\alpha} \) can be moved in front of \( \mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) \) because \( \mathbf{u}'_k \cdot \mathbf{n} \) and \( \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) \) are scalars, and only the vector \( \mathbf{\omega}^{(a)}(\mathbf{a}) \) depends on \( \mathbf{a} \). Equation (B9) can in turn be expressed as

\[
\hbar \nabla_{\alpha} B_i \frac{\partial}{\partial B_i} \nabla_{\alpha} B_i = \frac{1}{4} \sum_k \nabla_{\alpha} (\mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a})) l_k \\
= \frac{1}{4} \sum_k \nabla_{\alpha} \mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) + \mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) l_k
\]

(B10)

If both sides of this expression are summed over index \( i \), then

\[
\hbar \sum_i \nabla_{\alpha} B_i \frac{\partial}{\partial B_i} \nabla_{\alpha} B_i = \frac{1}{4} \sum_k \nabla_{\alpha} (\mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a})) l_k \\
= \nabla_{\alpha} \mathbf{u}'_k \cdot \mathbf{n}\mathbf{n}(\mathbf{a}) \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) l_k
\]

(B11)

follows as a consequence of the general formula

\[
\sum_i \mathbf{n}(\mathbf{a}) A_i n_i = (-1)^r(3-2r)A_r,
\]

(B12)

where \( A_r \) is an \( r \) blade \( (r=0,1,2,3) \), and 3 is the dimension of the space. With the help of Eqs. (B6) and (B18), one can find \( \mathbf{u}'_k \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) = \mathbf{\omega}^{(a)}(\mathbf{a}) \cdot \mathbf{u}'_k \) as

\[
\mathbf{u}'_k \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) = \mathbf{\omega}^{(a)}(\mathbf{a}) \cdot \mathbf{u}'_k - i \mathbf{\omega}^{(a)}(\mathbf{a}) \times \mathbf{u}'_k
\]

\[
= -\frac{i}{2} \mathbf{a} \cdot \nabla_{\alpha} u'_k - \frac{1}{2} \sum_j (\mathbf{a} \cdot \nabla_{\alpha} u'_j) u'_k \times u'_j
\]

(B13)

Because

\[
\mathbf{a} \cdot \nabla_{\alpha} u'_k = (\mathbf{a} \cdot \nabla_{\alpha} u'_j) u'_k + u'_k \times (\mathbf{a} \cdot \nabla_{\alpha} u'_j)
\]

\[
= -i[(\mathbf{a} \cdot \nabla_{\alpha} u'_j) \cdot (u'_k \times u'_j)]
\]

(B14)

(indices \( i,j,k \) in cyclic order), it is seen that the bivector terms on the right-hand side of Eq. (B13) cancel (as they must, because \( \mathbf{u}'_k \cdot \mathbf{\omega}^{(a)}(\mathbf{a}) \) is a scalar), and Eq. (B10) can be written as
\[
\sum_{i=1}^{3} \nabla_{a} B_{i} \frac{\partial}{\partial B_{i}} = \frac{3}{2} \sum_{jk} \nabla_{a} \left[ (a \cdot \nabla_{a} u_{i}) \cdot (u_{j} \times u_{k}) \right] l_{k}.
\]

(B15)

However, because \( u_{i} \times u_{j} = u_{j} \) (indices \( i, j \)), and \( k \) in cyclic order, and \( (a \cdot \nabla_{a} u_{i}) \cdot u_{j} = - (a \cdot \nabla_{a} u_{j}) \cdot u_{i} \) as is seen by taking the directional derivative of \( u_{i} \cdot u_{j} = 0 \), the summation over the index \( j \) may be omitted, and Eq. (B15) can be written in a shorter form as

\[
\sum_{i=1}^{3} \nabla_{a} B_{i} \frac{\partial}{\partial B_{i}} = \frac{3}{2} \sum_{k} \nabla_{a} \left[ (a \cdot \nabla_{a} u_{i}) \cdot u_{j} \right] l_{k},
\]

(B16)

where the indices \( i, j, \) and \( k \) on the right-hand side of Eq. (B16) are in the cyclic order. The left-hand side of Eq. (B16) is the part of the gradient operator (multiplied by \( \hbar \)), that depends on the rotation only. Because of the chain rule (Ref. 22, page 35), one can write the gradient operator \( \nabla_{a} \) in terms of the three position coordinates \( X_{i} \) of the center of the mass, \( 3N-6 \) shape coordinates \( q_{i} \), and the three rotational angles \( B_{i} \) as

\[
\nabla_{a} = \sum_{i=1}^{3} \nabla_{a} X_{i} \frac{\partial}{\partial X_{i}} + \sum_{i=1}^{3} \nabla_{a} q_{i} \frac{\partial}{\partial q_{i}} + \sum_{i=1}^{3} \nabla_{a} B_{i} \frac{\partial}{\partial B_{i}}.
\]

(B17)

The representation of the internal kinetic energy in Eq. (6) follows, when Eq. (B17) is substituted to Eq. (2). Equation (16) can also easily be read off from Eq. (B16). Finally, it should be noted that Eq. (B17) restricts somewhat the possible choices of the body frame \( \{ u_{i}, u_{j}, u_{k} \} \). Even when the shape coordinates \( q_{i} \) are fixed at some configuration \( \{ q_{1}, q_{2}, \ldots \} \), and the center of mass is kept frozen, the orientation of the particles may still change. Because two angles are needed to describe the orientation of any position \( x_{a} \), at least two rotational angles \( B_{i} \) must depend on the positions of the particle \( \alpha \) \( (\alpha = 1, 2, \ldots, N) \), if Eq. (B17) is to be valid for \( \alpha \) any value of the particle index. This is achieved, if the position vector \( x_{a} \) \( (\alpha = 1, 2, \ldots, N) \) is an argument to at least one of the body axes. If one likes to be on the safe side, it is clearly sufficient (but it is not necessary) to choose two of the body-fixed axes to depend on the positions of all of the particles. In terms of the directions \( r \) of Eq. (18) and \( s \) of Eq. (20), this can done choosing their cross product \( r \times s \) to depend on all of the nuclear positions, which results in \( c_{a} d_{b} - c_{b} d_{a} \neq 0 \) for \( \alpha < \beta, 2, \ldots, N \).

1. Rotational velocity

The directional derivative of the \( i \)th body-fixed axis \( u_{i} \) (with respect to the displacement of the particle \( \alpha \)) evaluated at the position \( a \) can be written as \( a \cdot \nabla_{a} u_{i} = \omega^{(a)}(a) \times u_{i} \),

(B18)

where the rotational velocity \( \omega^{(a)}(a) \) is given by Eq. (B6). To derive Eq. (B6), write the right-hand side of Eq. (B18) as

\[
\omega^{(a)}(a) \times u_{i} = i \frac{1}{2} [u_{i} \omega^{(a)}(a) - \omega^{(a)}(a) u_{i}].
\]

(B19)

multiply this from the left with \( u_{j} \), and sum over \( j \). Then, by Eq. (B18), and the identity

\[
\sum_{j=1}^{3} u_{j} \omega^{(a)}(a) u_{j} = -i \omega^{(a)}(a).
\]

(B20)

Eq. (B6) follows. The last form of Eq. (B6) follows from the fact that the directional derivative of any vector of the constant length is always at the right angle to that vector.

2. Gradients of rotational angles

The rotational velocity can also be written as (see especially pages 306–315 of Ref. 3)

\[
\omega^{(a)}(a) = 2i (a \cdot \nabla_{a} R^{\phi}) \hat{R} = -2i R^a \cdot \nabla_{a} R.
\]

(B21)

where the target of directional differentiation is implied by the parentheses. In terms of the present Euler angle convention, the rotational velocity reads as

\[
\omega^{(a)}(a) = \hat{u}_{a} \alpha \cdot \nabla_{\chi} \phi + \hat{u}_{b} \alpha \cdot \nabla_{\theta} \alpha + \hat{u}_{c} \alpha \cdot \nabla_{\chi} \alpha.
\]

(B22)

The easiest way to derive Eq. (B22) is to insert the directional derivative of \( R = e^{i \omega^{(a)}(a)} e^{i \omega^{(a)}(a)} e^{i \omega^{(a)}(a)} = Q_{s} Q_{d} R_{d} \) to Eq. (B21). The end result follows, because \(-2i \alpha \cdot \nabla_{a} R = (\alpha \cdot \nabla_{a} \chi) u_{a} R + (\alpha \cdot \nabla_{a} \theta) Q_{d} Q_{d} \alpha \cdot \nabla_{d} \phi \) and \( Q_{a} = R_{a} R_{a} R_{d} \) and \( Q_{a} = R_{a} R_{a} R_{a} \) (see Appendix A). When Eq. (B22) is dotted with the reciprocal vectors

\[
n^{(i)} = \frac{n_{i} \times n_{k}}{n_{1} n_{2} n_{3}}
\]

(B23)

(indices \( i, j, \) and \( k \) in cyclic order), Eq. (B7) follows.

APPENDIX C: USEFUL VECTOR DERIVATIVES

Let \( b, c, \) and \( d \) be vectors and \( B_{i} = b_{i} \wedge \ldots \wedge b_{j} \) be a \( p \) blade independent of a vector \( a (p = 1, 2, \ldots) \). Then, \( f \)

\[
\nabla_{a} f
\]

\[
a = 3
\]

\[
ab = 3 b
\]

\[
ba = - b
\]

\[
a \cdot B_{i} = p B_{i}
\]

\[
a^{\wedge} B_{i} = (3 - p) B_{i}
\]

\[
(a \times b) \cdot c = b \times c
\]

\[
(a \times b) \times (c \times d) = c b - d b - c b
\]

See Ref. 1 to determine how these formulas are derived. Here, only one derivation is given as an example:

\[
\nabla_{d} [(a \times b) \cdot c] = \nabla_{d} [a \cdot (b \times c)] = b \times c.
\]

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23 See EPAPS Document No. E-JCPSA6-114-004124 for latex file containing the sections *Rotations in geometric algebra* and *Directional derivative in geometric algebra*. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.