Application of geometric algebra to theoretical molecular spectroscopy

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Academic dissertation

To be presented, with the permission of the Faculty of Science of the University of Helsinki for public criticism in the Main lecture hall A110 of the Department of Chemistry (A.I. Virtasen aukio 1, Helsinki) December 13th, 2001, at 10 o'clock.

Helsinki 2001

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Abstract

In this work, *geometric algebra* has been applied to construct a general yet practical way to obtain molecular vibration-rotation kinetic energy operators, and related quantities, such as Jacobians.

The contravariant metric tensor appearing in the kinetic energy operator is written as the mass-weighted sum of the inner products of measuring vectors associated to the nuclei of the molecule. By the methods of geometric algebra, both the vibrational and rotational measuring vectors are easily calculated for any geometrically defined shape coordinates and body-frames, without any restrictions to the number of nuclei in the molecule. The kinetic energy operators produced by the present approach are in perfect agreement with the previously published results.

The volume-element of integration is derived as a product of N volume-elements, each associated to a set of three coordinates. The method presented has several advantages. For example, one does not need to expand any determinants, and all calculations are performed in the 3-dimensional physical space (not in some $3N$-dimensional abstract configuration space).

The methods of geometric algebra are applied with good success to the description of the large amplitude inversion vibration of ammonia.

Contents

List of publications

1. J. Pesonen, Vibrational coordinates and their gradients: A geometric algebra approach. J. Chem. Phys. **112**, 3121-3132 (2000).

2. J. Pesonen, Gradients of vibrational coordinates from the variation of coordinates along the path of a particle. J. Chem. Phys. **115**, 4402-4403 (2001).

3. J. Pesonen, A. Miani, and L. Halonen, New inversion coordinate for ammonia: Application to a CCSD(T) bidimensional potential energy surface. J. Chem. Phys. **115**, 1243-1250 (2001).

4. J. Pesonen, Vibration-rotation kinetic energy operators: A geometric algebra approach. J. Chem. Phys. **114**, 10598-10607 (2001).

5. J. Pesonen and L. Halonen, Volume-elements of integration: A geometric algebra approach. J. Chem. Phys, accepted for publication.

1   Introduction

I became first interested in molecular Hamiltonian operators while I browsed through the book *Molecular vibrations* by Wilson, Decius and Cross. [1] The authors present an "s-vector" method for obtaining coordinate gradients (needed to represent Laplacian operators in the Schrödinger equation) for standard shape coordinates, such as bond lengths and valence angles. The gradients of the coordinates $\nabla_\alpha q_i$ were deduced from the change of the coordinate caused by the displacement of the nucleus in question. But I was puzzled by two things. First, the nuclei were assumed to move by unit displacements. But the authors were talking about infinitesimal displacements, in which case there should not be any *unit* of displacement! Second, I could not see if this method really produced a general expression for the gradient of the coordinate, or only the value $\nabla_\alpha q_i \left(q_1^{(e)}, q_2^{(e)}, \ldots \right)$ of the gradient in terms of a reference configuration $q_1^{(e)}, q_2^{(e)}, \ldots$ used at the point of displacement. Third, for a practical point of view this "s-vector method" seemed unsatisfactory, because the success of the method would depend if one could somehow deduce the direction of greatest change in the coordinate caused by the displacement of the nucleus in question. While this was easy for some simple coordinates, it could be difficult for some more complicated coordinates.

The second impetus for my work was the inherent difficulties in finding the rotation-vibration parts of kinetic energy operators. There existed a vast amount of literature on the subject, but most of the solutions were solutions only in principle, not in practice. This is especially true for those approaches concentrating on the transformation from Lagrangian to (quantum mechanical) Hamiltonian. They could in most cases be applied only to triatomic molecules. Some approaches for finding the vibration-rotation kinetic energy operator of an N-atomic molecule appeared reasonable, because the body-fixed axes had been chosen in terms of a tri-atomic fragment of the molecule. The only practical way presented in the literature for finding the vibration-rotation kinetic energy operator (in bond lengths and valence angles) was analogous to Wilson's s-vector method. This approach was invented by T. Lukka. It was based on the concept of infinitesimal rotations. [2] But for me the mathematical ground of the success of this method was something of a mystery.

I finally concluded that the difficulties had their origin in the mathematical tools used in finding vibration-rotation kinetic energy operators. The tensor analysis concentrates on coordinate transformations, which most part play no

intrinsic role in the problem at hand. Although solution could be obtained in principle using tensor analysis, the intermediate expressions would fast become intractable. On the other hand, the ordinary vector calculus is inappropriate for the handling of rotations and just as in the case of tensor analysis the physical concept of direction is separated from the algebraic operations. Thus, all the approaches utilizing physical displacement vectors or rotations as geometric entities had to contain some heuristic steps to compensate the algebraic shortcomings in the vector algebra. Clearly, to make any true progress, one would have to find better mathematical tools. *Geometric algebra*, developed in the sixties by David Hestenes, turned out to be such an ideal instrument. It also gave me the chance to clearly pinpoint the conditions under which the "s-vector" method would work or fail in finding the coordinate gradients.

In this thesis, I apply geometric algebra to construct a general yet practical way to obtain vibration-rotation kinetic energy operators and related quantities, such as Jacobians. Paper 1 is devoted to the application of geometric algebra to construction of exact vibrational kinetic energy operators. Geometric algebra is used both to design suitable shape coordinates and to obtain the measuring vectors needed to form the exact kinetic energy operators by the direct vectorial differentiation of the coordinates. An alternative method to obtain the measuring vectors is represented in Paper 2. An application of the method developed in Paper 1 to the symmetric vibrational modes of ammonia is given in Paper 3. In Paper 4, geometric algebra is used to obtain general yet practical formulas for the rotational measuring vectors for *any* body-frame, without any restrictions to the number of particles used to define the body-frame. In Paper 5, geometric algebra is applied to find a practical way to obtain the volume-element of integration for the 3 Cartesian coordinates of the center of mass, 3 Euler angles, and $3N - 6$ shape coordinates needed to describe the position, orientation, and shape of an N-atomic molecule.

2 Geometric algebra

Many distinct algebraic systems have been developed to express geometric relations. Among these are the well-established branches of complex analysis, matrix, vector, and tensor algebras, and the less known calculus of differential forms, the quaternion, and spinor algebras. Each of them has some advantage in certain ap-

plications and at the same time they overlap significantly, i.e. they provide several mathematical representations of the same geometrical ideas. Geometric algebra integrates all these algebraic systems to a coherent mathematical language which retains the advantages of each of these subalgebras, but also possesses powerful new capabilities [3]-[11]. It also integrates the projective geometry fully into its formalism, unlike the other algebraic systems [11]-[13]. To put it shortly, geometric algebra is an extension of the real number system to incorporate the geometric concept of direction, i.e. it is a system of directed numbers.

2.1 Introduction to basic concepts

The rules to combine real numbers by adding and multiplying them can be expanded to include the ordinary complex numbers. Two complex numbers $a + bi$ and $c + di$ are added as $(a + bi) + (c + di) = a + c + (b + d)\,i$ and they are multiplied as $(a + bi)\,(c + di) = ac - bd + (ad + bc)\,i$. The addition and multiplication of complex numbers are distributive, associative and commutative. The addition of two complex numbers resembles to that of the two vectors, if the complex numbers are illustrated by an Argand diagram. As generally known, the sum $\mathbf{a} + \mathbf{b}$ of the vectors $\mathbf{a}$ and $\mathbf{b}$ is found by joining the head of the vector $\mathbf{a}$ to the tail of the vector $\mathbf{b}$ (see Fig. 1). This parallelogram rule is associative, distributive, and commutative. Ordinarily, there is no clear connection between vectors and
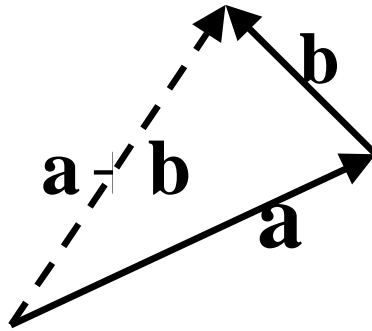

Figure 1: Vector addition

complex numbers. One is unlikely to find any proper geometrical interpretation

for a "complex vector" quantity such as $i\mathbf{a}$ in the standard textbooks. On the contrary, complex numbers are introduced as scalars and their directional properties are hardly ever utilized. Thus, it may become a surprise to learn that in most physical applications the unit imaginary i possesses a definite geometric interpretation [4, 18, 19] and that there exists more than one type of unit imaginaries, i.e. unit quantities with the square -1. It is this interpretation which distinquishes geometric algebra from the conventional complex analysis, where the complex numbers are introduced as a purely algebraic extension of the real number system.

As a starting point in order to unite vectors, complex numbers, and quaternions, among others, into a single algebraic system, one needs a *geometric product* $\mathbf{ab}$, which should be distributive and associative, i.e. for which it holds

$$\mathbf{a}\,(\mathbf{b}+\mathbf{c}) \;=\; \mathbf{ab}+\mathbf{ac} \tag{1}$$

$$\mathbf{abc} \;=\; \mathbf{a}\,(\mathbf{bc}) = (\mathbf{ab})\,\mathbf{c} \tag{2}$$

All other products (such as the inner and cross products) can be derived from the geometric product. Thus, the geometric product can be regarded as the most fundamental product. Its plausibility can be argumented by starting from the requirement that the square of any vector is a scalar. This is needed, if we want to denote Laplace's operator as the square of the gradient operator ∇. In physical (i.e. in the Euclidean 3-dimensional) space, the square of a vector $\mathbf{a}$ is equal to the square of its length, i.e.

$$\mathbf{a}^2 = |\mathbf{a}|^2 \geq 0 \tag{3}$$

The square of the sum of two vectors is similarly

$$(\mathbf{a}+\mathbf{b})^2 = |\mathbf{a}|^2 + |\mathbf{b}|^2 + \mathbf{ab} + \mathbf{ba} \tag{4}$$

By the Pythagorean theorem, one can also write

$$|\mathbf{a}+\mathbf{b}|^2 = |\mathbf{a}|^2 + |\mathbf{b}|^2 + 2\mathbf{a}\cdot\mathbf{b} \tag{5}$$

Thus, it is possible to define the inner product of any two vectors $\mathbf{a}$ and $\mathbf{b}$ in terms of a yet unknown product $\mathbf{ab}$ as

$$\mathbf{a}\cdot\mathbf{b} = \frac{\mathbf{ab}+\mathbf{ba}}{2} \tag{6}$$

Note that it is not assumed that the product $\mathbf{ab}$ would be commutative. On the contrary, if $\mathbf{a}$ is perpendicular to $\mathbf{b}$, then $\mathbf{a}\cdot\mathbf{b} = 0$ and it follows that for any two

perpendicular vectors $\mathbf{ab} = -\mathbf{ba}$. These properties can be combined by defining a geometric product for arbitrary vectors $\mathbf{a}$ and $\mathbf{b}$ as [4, 5]

$$\mathbf{ab} = \mathbf{a} \cdot \mathbf{b} + \mathbf{a} \wedge \mathbf{b} \tag{7}$$

where

$$\mathbf{a} \wedge \mathbf{b} = \frac{\mathbf{ab} - \mathbf{ba}}{2} = -\mathbf{b} \wedge \mathbf{a} \tag{8}$$

is the antisymmetric part of the geometric product. This entity cannot be a scalar, because it anticommutes with the vector $\mathbf{a}$:

$$
\begin{aligned}
\mathbf{a} \, (\mathbf{a} \wedge \mathbf{b}) & = \mathbf{a} \frac{\mathbf{ab} - \mathbf{ba}}{2} = \frac{|\mathbf{a}|^2 \mathbf{b} - \mathbf{aba}}{2} = \frac{\mathbf{b} \, |\mathbf{a}|^2 - \mathbf{aba}}{2} = \frac{\mathbf{ba}^2 + \mathbf{aba}}{2} \\
& = (\mathbf{b} \wedge \mathbf{a}) \, \mathbf{a} = -(\mathbf{a} \wedge \mathbf{b}) \, \mathbf{a}
\end{aligned}
\tag{9}
$$

Nor is $\mathbf{a} \wedge \mathbf{b}$ a vector, because its square is *negative*, as seen by

$$
\begin{aligned}
(\mathbf{a} \wedge \mathbf{b})^2 & = \left(\frac{\mathbf{ab} - \mathbf{ba}}{2} \right)^2 = \frac{(\mathbf{ab})^2 - 2 \, |\mathbf{a}|^2 \, |\mathbf{b}|^2 + (\mathbf{ba})^2}{4} \\
& = \frac{(\mathbf{a} \cdot \mathbf{b} + \mathbf{a} \wedge \mathbf{b})^2 - 2 \, |\mathbf{a}|^2 \, |\mathbf{b}|^2 + (\mathbf{a} \cdot \mathbf{b} - \mathbf{a} \wedge \mathbf{b})^2}{4} \\
& = \frac{(\mathbf{a} \wedge \mathbf{b})^2 + (\mathbf{a} \cdot \mathbf{b})^2 - |\mathbf{a}|^2 \, |\mathbf{b}|^2}{2}
\end{aligned}
\tag{10}
$$

(because $(\mathbf{a} \cdot \mathbf{b})^2 \leq |\mathbf{a}|^2 \, |\mathbf{b}|^2$, where the equality holds only for $\mathbf{a}$ which is collinear with $\mathbf{b}$). Also, its direction does not change when its vector factors $\mathbf{a}$ and $\mathbf{b}$ are both multiplied by -1. It is a *bivector*, a new kind of entity. It can be pictured as an oriented parallelogram with sides $\mathbf{a}$ and $\mathbf{b}$ (See Fig. 2). Note, however, that
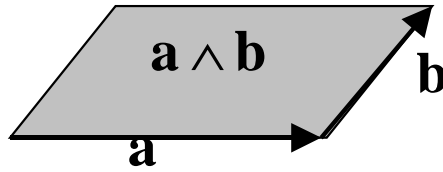

Figure 2: Bivector $\mathbf{a} \wedge \mathbf{b}$

the same bivector could as well be pictured as any other planar object with the

same orientation and area: the particular shape is unimportant. If the bivector is multiplied by the scalar λ, its area is dilated by the factor $|\lambda|$. If the scalar is negative, the orientation also changes to opposite.

One can define a *trivector* $\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}$ as

$$\mathbf{a} \wedge (\mathbf{b} \wedge \mathbf{c}) = \frac{\mathbf{ab} \wedge \mathbf{c} + \mathbf{b} \wedge \mathbf{ca}}{2} = (\mathbf{a} \wedge \mathbf{b}) \wedge \mathbf{c} \tag{11}$$

which shows that the outer product of a vector with a bivector is symmetric. As emphasized in the last equality, the outer product is associative in each of its vector factors. The trivector $\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}$ can be pictured as an oriented parallelepiped with sides $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ (see Fig. 3). The outer product $\mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \ldots \wedge \mathbf{a}_k$ is zero for $k > 3$ in the 3-dimensional space, and any trivector can be expressed as a multiple of a unit trivector i. As implied by its name, the unit trivector i is of the unit magnitude, i.e. $i^\dagger i = 1 = |i|$, where the superscript dagger signifies the change of the order of the vector factors, i.e. $(\mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \ldots \wedge \mathbf{a}_k)^\dagger = \mathbf{a}_k \wedge \mathbf{a}_{k-1} \wedge \ldots \wedge \mathbf{a}_1$. On the other hand, $i^2 = -1$. The unit trivector commutes with all other elements of the algebra in the 3-dimensional space. Hence, it is justifiable to say that the
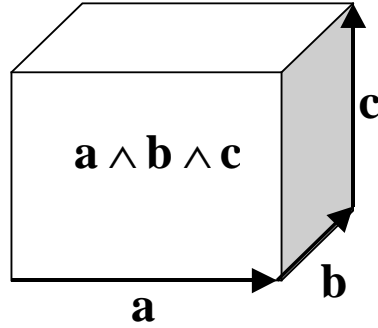

Figure 3: Trivector $\mathbf{a} \wedge \mathbf{b} \wedge \mathbf{c}$

unit trivector i plays the role of the imaginary unit in the 3-dimensional space. The vector cross product $\mathbf{a} \times \mathbf{b}$ is related to the bivector $\mathbf{a} \wedge \mathbf{b}$ as

$$\mathbf{a} \times \mathbf{b} = -i \, (\mathbf{a} \wedge \mathbf{b}) \tag{12}$$

where $\mathbf{a} \times \mathbf{b}$ is a vector perpendicular to the plane $\mathbf{a} \wedge \mathbf{b}$ (see Fig. 4). By using
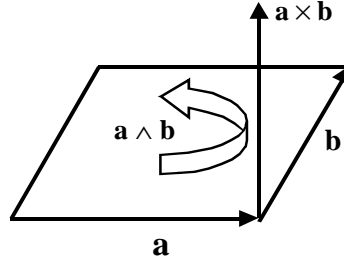
Figure 4: Cross product $\mathbf{a} \times \mathbf{b}$

this duality relation, any multivector A in a 3-dimensional space can be written as

$$A = \alpha + i\beta + \mathbf{a} + i\mathbf{b}$$

where $\alpha = \langle A \rangle_{\bar{0}}$ is the scalar part of A, $\mathbf{a} = \langle A \rangle_{\bar{1}}$ is the vector part of A, $i\mathbf{b} = \langle A \rangle_{\bar{2}}$ is the bivector part of A, and $i\beta = \langle A \rangle_{\bar{3}}$ is the trivector part of A (generally, $\langle A \rangle_{\bar{m}}$ denotes the m-blade part of A).

There are only three linearly independent bivectors $\{\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3\}$ in the 3-dimensional space. They can be represented in terms of some orthonormal set of vectors $\{\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3\}$ as

$$\mathbf{i}_1 = \mathbf{u}_2 \mathbf{u}_3 = i\mathbf{u}_1 \tag{13}$$

$$\mathbf{i}_2 = \mathbf{u}_3 \mathbf{u}_1 = i\mathbf{u}_2 \tag{14}$$

$$\mathbf{i}_3 = \mathbf{u}_1 \mathbf{u}_2 = i\mathbf{u}_3 \tag{15}$$

where the set $\{\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3\}$ is right-handed. Any bivector $\mathbf{B}$ can be expanded in this bivector basis as

$$\mathbf{B} = B_1 \mathbf{i}_1 + B_2 \mathbf{i}_2 + B_3 \mathbf{i}_3 \tag{16}$$

where $B_i = \mathbf{B} \cdot \mathbf{i}_i^{\dagger}$. It can be shown that

$$\mathbf{i}_1^2 = \mathbf{i}_2^2 = \mathbf{i}_3^2 = -1 \tag{17}$$

$$\mathbf{i}_1 \mathbf{i}_2 \mathbf{i}_3 = -i\mathbf{u}_1 \mathbf{u}_2 \mathbf{u}_3 = 1 \tag{18}$$

The inner, outer, and geometric products are generalized in Ref. [5] as

$$\mathbf{a} \cdot A_{\bar{k}} = \frac{1}{2} \left(\mathbf{a} A_{\bar{k}} - (-1)^k A_{\bar{k}} \mathbf{a} \right) = (-1)^{k+1} A_{\bar{k}} \cdot \mathbf{a} \tag{19}$$

$$\mathbf{a} \wedge A_{\bar{k}} = \frac{1}{2} \left(\mathbf{a} A_{\bar{k}} + (-1)^k A_{\bar{k}} \mathbf{a} \right) = (-1)^k A_{\bar{k}} \wedge \mathbf{a} \tag{20}$$

$$\mathbf{a} A_{\bar{k}} = \mathbf{a} \cdot A_{\bar{k}} + \mathbf{a} \wedge A_{\bar{k}} \tag{21}$$

for a vector $\mathbf{a}$ and any k-blade $A_{\bar{k}} = \mathbf{a}_1 \wedge \mathbf{a}_2 \wedge \ldots \wedge \mathbf{a}_k$ $(k = 1, 2, \ldots)$. The inner product $\mathbf{a} \cdot A_{\bar{k}}$ is a $k-1$ blade and the outer product $\mathbf{a} \wedge A_{\bar{k}}$ is a $k+1$ blade. The geometric product of two blades $A_{\bar{k}}$ and $B_{\bar{l}}$ is generally *not* related by the formula analogous to Eq. (21), if both $k, l > 1$. Generally, the geometric product $A_{\bar{k}} B_{\bar{l}}$ results in the terms of an intermediate grade from $|k - l|$ to $k + l$ in the steps of two, i.e.

$$A_{\bar{k}} B_{\bar{l}} = \sum_{m=0}^{(k+l-|k-l|)/2} \langle A_{\bar{k}} B_{\bar{l}} \rangle_{\overline{|k-l|+2m}} \tag{22}$$

One can write

$$A_{\bar{k}} \cdot B_{\bar{l}} = \langle A_{\bar{k}} B_{\bar{l}} \rangle_{\overline{|k-l|}} \text{ if } k, l > 0 \tag{23}$$

$$A_{\bar{k}} \cdot B_{\bar{l}} = 0 \text{ if } k = 0 \text{ or } l = 0 \tag{24}$$

$$A_{\bar{k}} \wedge B_{\bar{l}} = \langle A_{\bar{k}} B_{\bar{l}} \rangle_{\overline{k+l}} \tag{25}$$

where $\langle A_{\bar{k}} B_{\bar{l}} \rangle_{\bar{m}}$ denotes the m-blade part of $A_{\bar{k}} B_{\bar{l}}$. The exception in Eq. (24) to the definition of Eq. (23) sometimes complicates the otherwise simple algebraic manipulations. This defect can be corrected [6] by slightly modifying the concept of inner product by defining the left contraction (or contraction onto) of two arbitrary multivectors A and B as

$$A \rfloor B = \sum_{kl} \langle \langle A \rangle_{\bar{k}} \langle B \rangle_{\bar{l}} \rangle_{\overline{k-l}} \tag{26}$$

and the right contraction (or contraction by) as

$$A \lfloor B = \sum_{kl} \langle \langle A \rangle_{\bar{k}} \langle B \rangle_{\bar{l}} \rangle_{\overline{l-k}} \tag{27}$$

If A is a pure k-blade $A_{\bar{k}}$, and B is a pure l-blade $B_{\bar{l}}$, the contractions are given by

$$A_{\bar{k}} \rfloor B_{\bar{l}} = \langle A_{\bar{k}} B_{\bar{l}} \rangle_{\overline{k-l}} \tag{28}$$

and

$$A_{\bar{k}} \lfloor B_{\bar{l}} = \langle A_{\bar{k}} B_{\bar{l}} \rangle_{\overline{l-k}} \tag{29}$$

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These rules are the counterparts of the analogous rule in Eqs. (23) for the inner product. Unlike Eq. (23), these rules are also valid if A or B or both are zero-blades (scalars). This is an advantage, because it enables to define rewriting rules, such as

$$(A \wedge B) \rfloor C = A \rfloor (B \rfloor C) \tag{30}$$

which are valid for any A, B, and C. A similar rewriting rule for $(A \wedge B) \cdot C$ breaks into several grade depending cases. [5] Both the left and right contraction of two k-blades $A_{\bar{k}}$ and $B_{\bar{k}}$ with $k > 0$ are equivalent to that of the inner product, i.e.

$$A_{\bar{k}} \rfloor B_{\bar{k}} = A_{\bar{k}} \lfloor B_{\bar{k}} = A_{\bar{k}} \cdot B_{\bar{k}} \text{ for } k > 0 \tag{31}$$

Analogous to the standard inner product, one can write for the vector $\mathbf{x}$ and arbitrary multivector A

$$\mathbf{x}A = \mathbf{x} \rfloor A + \mathbf{x} \wedge A \tag{32}$$

$$A\mathbf{x} = A \lfloor \mathbf{x} + A \wedge \mathbf{x} \tag{33}$$

Because $A \lfloor \mathbf{x} = -\mathbf{x} \rfloor \breve{A}$, one can solve

$$\mathbf{x} \rfloor A = \frac{1}{2} \left(\mathbf{x}A - \breve{A}\mathbf{x} \right) \tag{34}$$

$$A \lfloor \mathbf{x} = \frac{1}{2} \left(A\mathbf{x} - \mathbf{x}\breve{A} \right) \tag{35}$$

where the accent above implies the reversion of the sign for odd blades, i.e.

$$\breve{A}_{\bar{k}} = (-1)^k A_{\bar{k}} \tag{36}$$

2.2 Geometric transformations and relations

In the geometric algebra, each geometrical point is represented by a vector, and any geometric quantity can be described in terms of its intrinsic properties alone, without introducing any external coordinate frames. An unlimited number of *geometrical* relations can be extracted by simple algebraic manipulation of the rules given above. For example, any vector $\mathbf{a}$ can be decomposed to the components parallel and orthogonal to some given vector $\mathbf{b}$ by simply multiplying it by $1 = \mathbf{b}\mathbf{b}^{-1}$. This results

$$\mathbf{a}\mathbf{b}\mathbf{b}^{-1} = \frac{\mathbf{a}\mathbf{b}\mathbf{b}}{b^2} = \frac{(\mathbf{a}\mathbf{b})\,\mathbf{b}}{b^2} = \frac{1}{b^2} \left(\mathbf{a} \cdot \mathbf{b} + \mathbf{a} \wedge \mathbf{b} \right) \mathbf{b} = \mathbf{a}_{\parallel} + \mathbf{a}_{\perp} \tag{37}$$

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where $\mathbf{a}_\parallel = \mathbf{a} \cdot \mathbf{b}\mathbf{b}/b^2$ is the parallel and $\mathbf{a}_\perp = \mathbf{a} \wedge \mathbf{b}\mathbf{b}/b^2$ is the perpendicular component (see Fig. 5). Similarly, any vector $\mathbf{a}$ can be decomposed to the components parallel ($\mathbf{a}_\parallel$) and orthogonal ($\mathbf{a}_\perp$) to some given plane $\mathbf{A} = \mathbf{b} \wedge \mathbf{c}$ as

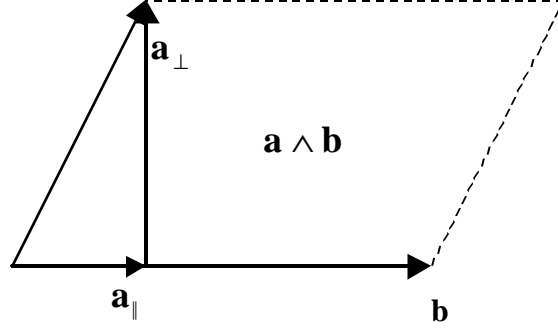

Figure 5: Decomposition of a vector $\mathbf{a}$ to components along and perpendicular to a vector $\mathbf{b}$

$$\mathbf{a}_\parallel = \mathbf{a} \cdot \mathbf{A}\mathbf{A}^{-1} \tag{38}$$
$$\mathbf{a}_\perp = \mathbf{a} \wedge \mathbf{A}\mathbf{A}^{-1} \tag{39}$$

Generally, the projection $\hat{P}_{B_{\bar{l}}}(A_{\bar{k}})$ of any k-blade $A_{\bar{k}}$ to an l-blade $B_{\bar{l}}$ is [6]

$$\hat{P}_{B_{\bar{l}}}(A_{\bar{k}}) = \left(A_{\bar{k}} \rfloor B_{\bar{l}}^{-1}\right) \rfloor B_{\bar{l}} \tag{40}$$

It is worth emphasizing that this rule holds without exceptions, unlike those utilizing the standard inner product.

A vector $\mathbf{a}$ can be reflected along a unit vector $\mathbf{u}$ to $\mathbf{a}'$ by

$$\mathbf{a}' = -\mathbf{u}\mathbf{a}\mathbf{u} \tag{41}$$

(see Fig. 6). The vector $\mathbf{a}$ can be rotated in the plane $\mathbf{i} = \mathbf{u} \wedge \mathbf{v}/|\mathbf{u} \wedge \mathbf{v}|$ through the bivector angle $\mathbf{A} = A\mathbf{i}$ ($A = |\mathbf{A}| \geq 0$ is the magnitude of the rotation angle) between the unit vectors $\mathbf{u}$ and $\mathbf{v}$ by reflecting it twice, first along the unit vector $\mathbf{u}$, then along the unit vector $\mathbf{v}$ as

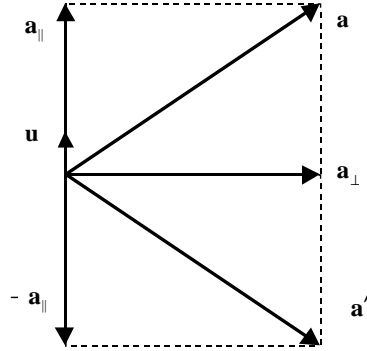$$\mathbf{a}' = \mathbf{v}\mathbf{u}\mathbf{a}\mathbf{u}\mathbf{v} \tag{42}$$

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Figure 6: Reflection of **a** along **u**.

(See Fig. 7). The product $\mathbf{uv} = \mathbf{u} \cdot \mathbf{v} + \mathbf{u} \wedge \mathbf{v}$ is a spinor, i.e. it is a sum of scalar and a bivector. It can be written as an exponential

$$\mathbf{uv} = e^{\mathbf{A}/2} = \cos\frac{A}{2} + \mathbf{i}\sin\frac{A}{2} \qquad (43)$$

The same formula applies to the rotation of *any* multivector M (a vector, a bivector etc. or any of their combination). If M' is the multivector M rotated
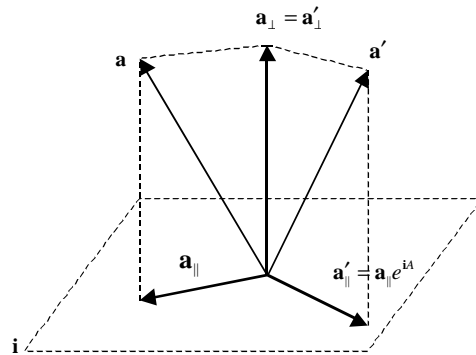

Figure 7: Rotation of a vector **a** in the plane **i**.

through a bivector angle $\mathbf{A}$, then M' is given by sandwiching the multivector M

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between exponentials of the rotation plane $\mathbf{A}$, [4]

$$M' = e^{-\mathbf{A}/2} M e^{\mathbf{A}/2} \tag{44}$$

Such a simple expression does not exist in the ordinary vector algebra, where supplementary algebraic structures in the form of the rotation matrices are needed. It can be said that geometric algebra offers the most effective way of describing rotations. For example, the spinor $e^{\mathbf{C}/2}$ describing the net rotation of two successive rotations, first $e^{\mathbf{A}/2}$ then $e^{\mathbf{B}/2}$, is found by multiplying

$$e^{\mathbf{C}/2} = e^{\mathbf{A}/2} e^{\mathbf{B}/2} \tag{45}$$

2.3 Quaternions

A comparison of the multiplication table of the unit bivectors in Eqs. (17) and (18) with the quaternionic multiplication table

$$\mathsf{i}^2 = \mathsf{j}^2 = \mathsf{k}^2 = -1 \tag{46}$$
$$\mathsf{ijk} = -1 \tag{47}$$

reveals that Hamilton's unit quaternions $\{\mathsf{i}, \mathsf{j}, \mathsf{k}\}$ are a set of left-handed orthonormal unit bivectors (i.e. $\mathsf{i} = -\mathbf{i}_1$, $\mathsf{j} = -\mathbf{i}_2$, and $\mathsf{k} = -\mathbf{i}_3$), and any quaternion

$$\mathsf{Q} = \alpha + x\mathsf{i} + y\mathsf{j} + z\mathsf{k} \tag{48}$$

(where α, x, y, and z are real numbers) is an even-graded multivector (i.e. a multivector, which possesses a scalar plus a bivector part), and the product between two quaternions is equal to their geometric product.

2.4 Geometric calculus

The machinery of geometric algebra makes it possible to differentiate and integrate functions of vector variables in a coordinate-free manner. The conventionally separated concepts of a gradient, a divergence and a curl are obtainable from a single vector derivative. Geometric algebra also enables one to generalize the results of complex analysis (such as Cauchy's integral formula) to higher dimensions. [5, 8, 10]

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Conventionally, the vector derivative $\nabla_\alpha F$ of a function $F(\mathbf{x}_\alpha)$ of a vector variable $\mathbf{x}_\alpha$ is defined only for scalar valued functions F, and the vector derivative operator ∇_α is expressed in some coordinates using the chain rule as

$$\nabla_\alpha = \sum_i (\nabla_\alpha q_i) \frac{\partial}{\partial q_i} \qquad (49)$$

where I use the subscript α in the vector variable $\mathbf{x}$ to emphasize that these results are applicable in the case of several vector variables $\mathbf{x}_1, \mathbf{x}_2, \ldots$. If F is a vector, i.e. if $F = \mathbf{f}(\mathbf{x}_\alpha)$, its divergence and curl are defined as

$$\operatorname{div}_\alpha \mathbf{f} = \nabla_\alpha \cdot \mathbf{f} \qquad (50)$$
$$\operatorname{curl}_\alpha \mathbf{f} = \nabla_\alpha \times \mathbf{f} \qquad (51)$$

By using the definition of the geometric product, we can write

$$\nabla_\alpha \mathbf{f} = \nabla_\alpha \cdot \mathbf{f} + \nabla_\alpha \wedge \mathbf{f} = \nabla_\alpha \cdot \mathbf{f} + i \nabla_\alpha \times \mathbf{f} \qquad (52)$$

so the divergence is the scalar part and the curl is the dual of the bivector part of the vector derivative of $\mathbf{f}$. Because the last form is restricted to a 3-dimensional space only, it is more appropriate to regard the curl as the bivector part of the vector derivative. The vector derivative $\nabla_\alpha F$ is defined for all elements F, not just for scalars and vectors, i.e. generally

$$\nabla_\alpha F = \nabla_\alpha \cdot F + \nabla_\alpha \wedge F \qquad (53)$$

It follows from Eq. (53) that the vector derivative operator changes the grade of the object it operates on by ± 1. For example, the vector derivative of the scalar $\lambda(\mathbf{x}_\alpha)$ is a vector (because $\mathbf{a} \cdot \lambda \equiv 0$ for any scalar λ, so $\mathbf{a}\lambda = \mathbf{a} \wedge \lambda$), and the vector derivative of the vector $\mathbf{f}(\mathbf{x}_\alpha)$ is a scalar plus a bivector. The differentiation with respect to the vector variable $\mathbf{x}_\alpha$ resembles much the differentiation with respect to some scalar variable x_α. For example, the vector differentiation is distributive,

$$\nabla_\alpha (F + G) = \nabla_\alpha F + \nabla_\alpha G \qquad (54)$$

for any F and G. If $\lambda = \lambda(\mathbf{x}_\alpha)$ is a scalar valued function, then

$$\nabla_\alpha (\lambda G) = (\nabla_\alpha \lambda) G + \lambda \nabla_\alpha G \qquad (55)$$

However, in the general case, the vector derivative operator does not commute with multivectors, and the product rule can be written as

$$\nabla_\alpha (FG) = \grave{\nabla}_\alpha \grave{F} G + \grave{\nabla}_\alpha F \grave{G} \qquad (56)$$

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where the target of differentiation is implicated by the accents.

I have not yet discussed how to find the vector derivative $\nabla_\alpha F$ in practice. It suffices to use the following simple vector derivatives

$$\nabla_\alpha \mathbf{x}_\alpha = \sum_{k,j}^{3} \mathbf{u}_k \mathbf{u}_j \frac{\partial x_{\alpha_j}}{\partial x_{\alpha_k}} = \sum_{k}^{3} \frac{\partial x_{\alpha_k}}{\partial x_{\alpha_k}} = 3 \tag{57}$$

$$\nabla_\alpha \mathbf{a} \cdot \mathbf{x}_\alpha = \sum_{k}^{3} \mathbf{u}_k \left(\mathbf{a} \cdot \frac{\partial \mathbf{x}_\alpha}{\partial x_{\alpha_k}} \right) = \sum_{k}^{3} \mathbf{u}_k \mathbf{a} \cdot \mathbf{u}_k = \mathbf{a} = \nabla_\alpha \mathbf{x}_\alpha \cdot \mathbf{a} \tag{58}$$

(for any $\mathbf{a}$ independent of $\mathbf{x}_\alpha$) and to combine them with the product and the chain rule to allow the evaluation of the vector derivative of any function.

Example 1 *By the product rule,*

$$\nabla_\alpha x_\alpha^2 = \nabla_\alpha \mathbf{x}_\alpha \cdot \mathbf{x}_\alpha = \dot{\nabla}_\alpha \dot{\mathbf{x}}_\alpha \cdot \mathbf{x}_\alpha + \dot{\nabla}_\alpha \mathbf{x}_\alpha \cdot \dot{\mathbf{x}}_\alpha = 2\mathbf{x}_\alpha \tag{59}$$

(where $x_\alpha = |\mathbf{x}_\alpha|$).

Some other rules are also useful. For example, if $F(\lambda(\mathbf{x}_\alpha))$ is a multivector function of the scalar argument $\lambda(\mathbf{x})$, then

$$\nabla_\alpha F(\lambda(\mathbf{x}_\alpha)) = \nabla_\alpha (\lambda(\mathbf{x}_\alpha)) \frac{\partial F}{\partial \lambda} \tag{60}$$

The use of this chain rule is illustrated in the next example:

Example 2 *The left-hand side of Eq. (59) can be written as*

$$\nabla_\alpha x_\alpha^2 = 2x_\alpha \nabla_\alpha x_\alpha \tag{61}$$

where by Eq. (59) the derivative $\nabla_\alpha x_\alpha$ can be solved as

$$\nabla_\alpha x_\alpha = \frac{\mathbf{x}_\alpha}{x_\alpha} \tag{62}$$

In some cases, one can find the vector derivative $\nabla_\alpha F$ as

$$\nabla_\alpha F = \nabla_\mathbf{a} \mathbf{a} \cdot \nabla_\alpha F \tag{63}$$

where $\mathbf{a} \cdot \nabla_\alpha F$ is the directional derivative defined [4] as

$$\mathbf{a} \cdot \nabla_\alpha F(\mathbf{x}_\alpha) = \lim_{\delta \to 0} \frac{F(\mathbf{x}_\alpha + \delta \mathbf{a}) - F(\mathbf{x}_\alpha)}{\delta} = \left. \frac{d}{d\delta} F(\mathbf{x}_\alpha + \delta \mathbf{a}) \right|_{\delta \to 0} \tag{64}$$

The chain rule in Eq. (63) may appear at first sight peculiar to the reader unfamiliar with geometric algebra (such an expression does not exist in ordinary vector algebra). As a hopefully useful example,

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Example 3 *As seen from Eq. (64), the directional derivative of $\mathbf{x}_\alpha$ is*

$$\mathbf{a} \cdot \nabla_\alpha \mathbf{x}_\alpha = \frac{d}{d\delta} \left. (\mathbf{x}_\alpha + \delta\mathbf{a}) \right|_{\delta \to 0} = \mathbf{a} \tag{65}$$

and the directional derivative of $\mathbf{x}_\alpha^2$ is

$$\mathbf{a} \cdot \nabla_\alpha \mathbf{x}_\alpha^2 = \mathbf{a} \cdot \nabla_\alpha (\mathbf{x}_\alpha \cdot \mathbf{x}_\alpha) = 2\mathbf{a} \cdot \mathbf{x}_\alpha \tag{66}$$

because the directional derivative operator $\mathbf{a} \cdot \nabla_\alpha$ is a scalar operator and consequently the directional derivative of $F \cdot G$ is found by $\mathbf{a} \cdot \nabla_\alpha F \cdot G = (\mathbf{a} \cdot \nabla_\alpha F) \cdot G + F \cdot (\mathbf{a} \cdot \nabla_\alpha G)$. Thus, by Eq. (63),

$$\nabla_\alpha x_\alpha^2 = \nabla_\mathbf{a} \mathbf{a} \cdot \nabla_\alpha x_\alpha^2 = \nabla_\mathbf{a} (2\mathbf{a} \cdot \mathbf{x}_\alpha) = 2\mathbf{x}_\alpha \tag{67}$$

which agrees with Eq. (59).

If $F(\mathbf{x}_\alpha)$ is a scalar valued function, the vector derivative $\nabla_\alpha F$ can be extracted from the variation

$$\dot{F} = \sum_\alpha^N \dot{\mathbf{x}}_\alpha(t) \cdot \nabla_\alpha F \tag{68}$$

of F along the path $\mathbf{x}_\alpha(t)$ [4]. Now, t is some scalar parameter, and the overdot implies the differentiation with respect to t, i.e. $\dot{F} = dF/dt$. This method has the advantage of reducing the calculation of the vector derivative of a scalar valued function to an ordinary scalar differentiation. As an example,

Example 4 *Because*

$$\frac{dx_\alpha^2}{dt} = 2x_\alpha \frac{dx_\alpha}{dt} = \frac{d\mathbf{x}_\alpha \cdot \mathbf{x}_\alpha}{dt} = 2\mathbf{x}_\alpha \cdot \frac{d\mathbf{x}_\alpha}{dt} \tag{69}$$

or

$$\frac{dx_\alpha}{dt} = \frac{\mathbf{x}_\alpha}{x_\alpha} \cdot \frac{d\mathbf{x}_\alpha}{dt} \tag{70}$$

the gradient $\nabla_\alpha x_\alpha$ can be picked by Eq. (68) as

$$\nabla_\alpha x_\alpha = \frac{\mathbf{x}_\alpha}{x_\alpha} \tag{71}$$

By using the above rules, the following results can be proved:

$$
\begin{array}{ll}
F & \nabla_\alpha F \\
\mathbf{x}_\alpha & 3 \\
\mathbf{x}_\alpha \mathbf{b} & 3\mathbf{b} \\
\mathbf{b}\mathbf{x}_\alpha & -\mathbf{b} \\
\mathbf{x}_\alpha \cdot B_{\bar{p}} & pB_{\bar{p}} \\
\mathbf{x}_\alpha \wedge B_{\bar{p}} & (3-p)\,B_{\bar{p}} \\
(\mathbf{x}_\alpha \times \mathbf{b}) \cdot \mathbf{c} & \mathbf{b} \times \mathbf{c} \\
(\mathbf{x}_\alpha \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) & \mathbf{c}\mathbf{b}\cdot\mathbf{d} - \mathbf{d}\mathbf{b}\cdot\mathbf{c} \\
|\mathbf{x}_\alpha - \mathbf{b}|^k & k\,|\mathbf{x}_\alpha - \mathbf{b}|^{k-2}\,(\mathbf{x}_\alpha - \mathbf{b}) \\
|\mathbf{x}_\alpha - \mathbf{b}|^k\,(\mathbf{x}_\alpha - \mathbf{b}) & (k+3)\,|\mathbf{x}_\alpha - \mathbf{b}|^k
\end{array}
$$

where $\mathbf{b}$, $\mathbf{c}$, and $\mathbf{d}$ are vectors, $B_{\bar{p}} = \mathbf{b}_1 \wedge \ldots \wedge \mathbf{b}_p$ is a p-blade independent of a vector $\mathbf{x}_\alpha$ ($p = 1$, 2, and 3), and $k = 0, \pm1, \pm2, \pm3, \ldots$.

2.5   Some history and present

Much of the geometric algebra is based on the work done as early as in the mid nineteenth century. W. R. Hamilton had created his algebra of the quaternions by that time. He started from the observation that if the complex numbers are represented (conventionally) as a vector in the plane with the real part along the x-axis, and the imaginary part along the y-axis, the multiplication of a vector (or a complex number) z by the unit imaginary i produces a new vector (or complex number) at the right angle to z. In 1834, Hamilton invented quaternions to possess a similar application to the geometry of the 3-dimensional space. H. G. Grassman had discovered his exterior algebra at the same time, starting from the simple idea that a product of two non-collinear vectors produces an area. W. K. Clifford united both quaternion and exterior algebra via the geometric product little later. Unfortunately, the development of geometric algebra has been far from a straightforward evolution. For example, Hamilton wanted to represent his unit quaternions i, j, and k as a left-handed set of vectors, instead of a left-handed set of bivectors. Due to the duality relations of vectors and bivectors of Eq. (12), this is indeed possible in the 3-dimensional space. Unfortunately, if unit quaternions are interpreted as unit vectors, one cannot generalize the quaternion products of the type ij = k to higher dimensional spaces. Furthermore, the inner product of a vector with itself possesses in this case a negative sign which

was considered somewhat unnatural by many, leading Gibbs and others to ultimately abolish the quaternion product altogether, and define the scalar and the cross-product separately. [14, 15] As a result, the relation of quaternions to vectors is obscured in the conventional textbooks, which often introduce them in their matrix representations. In the modern form, geometric algebra was discovered in the sixties by David Hestenes, who seeked the geometric significance of Dirac's gamma-matrices, and found, in effect, geometric algebra. [16] Since then, geometric algebra has found applications to such diverse fields as relativistic quantum physics [17, 18], classical mechanics [4], classical electrodynamics [19], Lagrangian field theory [20], gravity [21], error correction of NMR signals [22], theory of molecular conformation [23, 24], representation of point and space groups [25], and modeling of elastically coupled rigid bodies [26], to name only a few of them.

3 Molecular Schrödinger equation

The state of a molecule consisting of N nuclei and P electrons is described in the fullest possible details by its wave function Ψ. In principle, all the molecular properties, such as energy states and dipole moments, can be obtained from the wave function. The molecular wave function and the energies E can in turn be solved from the Schrödinger equation

$$\left(\hat{T} + \hat{V} \right) \Psi = E\Psi \tag{72}$$

when the appropriate boundary conditions are taken into account. The kinetic energy operator $\hat{T}$ and the potential energy operator $\hat{V}$ depend both on the positions $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$ of the nuclei, and on the positions $\mathbf{x}_{N+1}, \mathbf{x}_{N+2}, \ldots, \mathbf{x}_{N+P}$ of the electrons. When the relativistic effects and the spin are ignored, the kinetic energy operator is given as the mass-weighted sum of the Laplace's operators [27, 28]

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N+P} \frac{\nabla_\alpha^2}{m_\alpha} \tag{73}$$

where ∇_α is the vector derivative operator with respect to the position $\mathbf{x}_\alpha$, and m_α is the mass of the particle α. Because both the electrons and the nuclei are considered as point charges, the potential energy operator is (again ignoring the

relativistic effects and the spin)

$$\hat{V} = \frac{e^2}{8\pi\epsilon_0} \sum_{\alpha=1}^{N+P} \sum_{\beta\neq\alpha}^{N+P} \frac{Z_\alpha Z_\beta}{|\mathbf{x}_\alpha - \mathbf{x}_\beta|} \tag{74}$$

where $e = 1.6019 \times 10^{-19}$C is the unit charge, $\epsilon_0 = 8.854 \times 10^{-12}$J^{-1}C^{2}m^{-1} is the vacuum permittivity, and Z_α is the charge number of the particle α (it is -1 for an electron).

3.1   Born-Oppenheimer approximation

In practice, it is impossible to solve Eq. (72) analytically for molecules (analytical solutions exist only for two-body systems such as the hydrogen atom), but some simplications must be made. In the Born-Oppenheimer approximation, one takes into account the large difference in the masses of the nuclei and the electrons. Because of this difference, the motion of the nuclei is much slower than the motion of the electrons, which can respond almost immediately to the displacements of the nuclei. In effect, one can view the motion of the electrons as if the nuclei were fixed in space and one solves the electronic Schrödinger equation separately for each value of the nuclear coordinates. This is also known as the adiabatic approximation. The electronic energy $E^{(\mathrm{el})}$ obtained from the solution of the electronic Schrödinger equation at the nuclear configuration $\{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\}$, together with the value of the nuclear repulsion energy, is equal to the value of the potential $V^{(\mathrm{nucl})}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$, which the nuclei feel due to their mutual repulsion and the rapid motion of the electrons [28]. The translational, vibrational, and rotational states and energies of the molecule under study are then found by solving the Schrödinger equation

$$\left[\hat{T}^{(\mathrm{nucl})}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) + \hat{V}^{(\mathrm{nucl})}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right] \Psi^{(\mathrm{nucl})} = E^{(\mathrm{nucl})}\Psi^{(\mathrm{nucl})} \tag{75}$$

which depends only on the coordinates of the nuclei, instead of the full equation (72) depending both on the coordinates of the nuclei *and* the electrons.

4   Kinetic energy operators for polyatomic molecules

The subject of quantizing the Hamiltonians of many particle systems (such as polyatomic molecules) has been of great interest since the birth of the modern

quantum theory. Many different approaches have been proposed. While the potential energy operator is the same as in the classical case, the quantization of the kinetic energy operator is more demanding, especially for constrained systems.

The difficulties are mostly due to operator ordering and finding the quantum mechanical equivalents of classical quantities. Most prescriptions do not produce, in general, a correct representation of the quantum mechanical kinetic energy operator. This is the case, if the representation is sought by using correspondence principles [29, 30], such as Weyl's rule or Born-Jordan ordering. Neither the correct representation is found by substituting the generalized momentum p_i in the classical Hamiltonian by the partial derivative operator $-i\hbar\partial/\partial q_i$, or by its Hermitian part. [31] The classical Lagrangian cannot be transformed to a correct quantum mechanical kinetic energy operator by replacing the generalized velocity $\dot{q}_i$ [the Poisson bracket (q_i, H)] by the commutator bracket $-\frac{i}{\hbar}[q_i, H]$, no matter what ordering is chosen for the generalized velocities and elements of the covariant metric tensor. [32]

On the other hand, the representation of the kinetic energy operator for an N-atomic molecule

$$\hat{T}^{(\text{nucl})} = -\frac{\hbar^2}{2} \sum_{\alpha}^{N} \frac{1}{m_\alpha} \nabla_\alpha^2 \qquad (76)$$

can be obtained (at least in principle) by expressing the gradient operators ∇_α directly in terms of the generalized coordinates (or the components of the quasi-momentum operators such as the angular momentum operator). This is the approach followed in my work.

4.1 Coordinate representation

The shape of the molecule can be described by a set of $3N - 6$ translationally and rotationally invariant internal coordinates q_i. The rotation of the molecule as a whole can be parametrized by three translationally invariant Euler angles ϕ, θ, χ, which relate the orientation of an orthonormal molecule-fixed axis system $\{\mathbf{u}_1', \mathbf{u}_2', \mathbf{u}_3'\}$ to some standard orthonormal space-fixed frame $\{\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3\}$ as

$$\mathbf{u}_i' = R^\dagger \mathbf{u}_i R \qquad (77)$$

where the rotor R is parametrized by

$$R = e^{i\chi\mathbf{u}_3/2} e^{i\theta\mathbf{u}_1/2} e^{i\phi\mathbf{u}_3/2} = e^{i\chi\mathbf{u}_3'/2} e^{i\theta\mathbf{u}_1'/2} e^{i\phi\mathbf{u}_3'/2} = e^{i\phi\mathbf{u}_3/2} e^{i\theta\mathbf{n}_2/2} e^{i\chi\mathbf{u}_3'/2} \qquad (78)$$

$(\mathbf{n}_2 = \mathbf{u}_3 \times \mathbf{u}_3' / |\mathbf{u}_3 \times \mathbf{u}_3'|)$. The location of the molecule can be parametrized by three Cartesian coordinates $X_i = \mathbf{u}_i \cdot \mathbf{X}$ $(i = 1, 2, 3)$ of the center-of-mass

$$\mathbf{X} = \sum_{\alpha=1}^{N} \frac{m_\alpha \mathbf{x}_\alpha}{M} \tag{79}$$

of the molecule $(M = \sum_\alpha^N m_\alpha$ is the mass of the molecule). By the chain rule, the vector derivative operator ∇_α can be represented as

$$\nabla_\alpha = \sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} \frac{\partial}{\partial q_i} \tag{80}$$

where it is understood that $q_{3N-5} = \phi$, $q_{3N-4} = \theta$, $q_{3N-3} = \chi$, $q_{3N-2} = X_1$, $q_{3N-1} = X_2$, and $q_{3N} = X_3$. The quantity

$$\mathbf{e}_\alpha^{(q_i)} = \nabla_\alpha q_i \tag{81}$$

is the measuring vector associated to the coordinate q_i, and to the αth nucleus of the molecule. The name "measuring vector" originates from the property that the vector $\mathbf{e}_\alpha^{(q_i)}$ gives the measure of the rate of change in the coordinate $q_i\,(\mathbf{x}_\alpha)$ for any given rate of the change $\frac{d\mathbf{x}_\alpha}{dt}$ of the nuclear position $\mathbf{x}_\alpha$ as [4]

$$\frac{dq_i}{dt} = \sum_\alpha^N \mathbf{e}_\alpha^{(q_i)} \cdot \frac{d\mathbf{x}_\alpha}{dt} \tag{82}$$

Geometric algebra can be used to define internal coordinates in terms of the position vectors of the nuclei. Their gradients can then be obtained algebraicly by manipulating the atomic position vectors themselves in the manner presented in Section 2.4. The effort required in part of the reader to master the basics of the geometric algebra is more than compensated by the simplifications in the gradient calculations. This is demonstrated explicitly in Papers 1 and 2 and applied (in good success) to the symmetric vibrations of ammonia in Paper 3.

Example 5 *We define a new ammonia inversion coordinate S_2 in Paper 3 as*

$$S_2(A_2'') = \pm \frac{1}{3^{1/4}} \left(2\pi - \theta_{23} - \theta_{13} - \theta_{12} \right)^{1/2} \tag{83}$$

where θ_{ij} is the angle between the bond vectors $\mathbf{x}_{H_i} - \mathbf{x}_N$ and $\mathbf{x}_{H_j} - \mathbf{x}_N$, and the "+" sign is for the right-handed and the "−" sign for the left-handed configuration

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(the other symmetric displacement coordinates $S_1(A_1')$, $S_{3a}(E')$, $S_{3b}(E')$, $S_{4a}(E')$, and $S_{4b}(E')$ are defined as linear combinations of the bond stretching and valence angle displacements in the usual way. The symmetry labels refer to the D_{3h} point group). It is unnecessary to express the sign factor explicitly, because the coordinate gradients can be calculated from the square

$$S_2^2 = \frac{2\pi - (\theta_{23} + \theta_{13} + \theta_{12})}{3^{1/2}} \tag{84}$$

of the inversion coordinate with the chain rule of Eq. (60). As a simple example, the vector derivative of S_2 with respect to the position $\mathbf{x}_{H_1}$ of the proton H_1 can be solved from

$$S_2 \nabla_{H_1} S_2 = -\frac{\nabla_{H_1}\theta_{13} + \nabla_{H_1}\theta_{12}}{3^{1/2}} \tag{85}$$

by substituting the known vector derivatives $\nabla_{H_1}\theta_{12}$ and $\nabla_{H_1}\theta_{13}$ [1]. The result can be expressed in terms of the symmetry coordinates by using the inverse coordinate relations, such as

$$\theta_{13} - \frac{2\pi}{3} = -\frac{1}{\sqrt{3}}S_2^2 - \frac{1}{\sqrt{6}}S_{4a} + \frac{1}{\sqrt{2}}S_{4b} \tag{86}$$

When the coordinate representation in Eq. (80) is substituted to Eq. (76), the kinetic energy operator reads as

$$\hat{T} = -\frac{\hbar^2}{2}\sum_{\alpha}^{N}\sum_{j}^{3N}\frac{1}{m_\alpha}\nabla_\alpha \cdot \mathbf{e}_\alpha^{(q_j)}\frac{\partial}{\partial q_j} \tag{87}$$

The above expression can be written in many ways. By introducing the "contravariant metric tensor"

$$g^{(q_i q_j)} = \sum_{\alpha}^{N}\frac{1}{m_\alpha}\mathbf{e}_\alpha^{(q_i)} \cdot \mathbf{e}_\alpha^{(q_j)} \tag{88}$$

one can use the formal results of the classical tensor analysis [33] to show that

$$\sum_{\alpha}^{N}\frac{1}{m_\alpha}\nabla_\alpha \cdot \mathbf{e}_\alpha^{(q_j)}\frac{\partial}{\partial q_j} = \frac{1}{g^{-1/2}}\sum_{i}\frac{\partial}{\partial q_i}g^{-1/2}g^{(q_i q_j)}\frac{\partial}{\partial q_j} \tag{89}$$

where $g = \det g^{(q_i q_j)}$ is the determinant of the contravariant metric tensor and the kinetic energy operator reads as

$$\hat{T}^{(\text{nucl})} = -\frac{\hbar^2}{2}\sum_{ij}^{3N}\left(\frac{\partial}{\partial q_i} + \frac{1}{g^{-1/2}}\frac{\partial g^{-1/2}}{\partial q_i}\right)g^{(q_i q_j)}\frac{\partial}{\partial q_j} \tag{90}$$

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It should be emphasized that now all integrations are performed using the volume-element $d\tau = J dq_1 dq_2 \ldots$, where $J = g^{-1/2}$ is the Jacobian. If one wishes to integrate using the volume-element $d\tau_w = w dq_1 dq_2 \ldots$ instead of the volume-element $d\tau = J dq_1 dq_2 \ldots$, the corresponding kinetic energy operator $\widehat{T}_w$ is given as [34]

$$\hat{T}_w^{(\text{nucl})} = J^{1/2} w^{-1/2} \hat{T}^{(\text{nucl})} w^{1/2} J^{-1/2} \tag{91}$$

in terms of the kinetic energy operator $\hat{T}^{(\text{nucl})}$ of Eq. (90).

The translation is completely separated from the vibrational and rotational degrees of freedom, i.e. the matrix $[\mathsf{G}]$ with elements $[\mathsf{G}]_{ij} = g^{(q_i q_j)}$ is partitioned into an internal block of the size $(3N - 3) \times (3N - 3)$ and to a translational block of the size 3×3 as

$$[\mathsf{G}] = \begin{bmatrix} \mathsf{G}^{(\text{int})} & \mathsf{0} \\ \mathsf{0}^{\mathrm{T}} & \mathsf{G}^{(\text{transl})} \end{bmatrix} \tag{92}$$

where $\mathsf{0}$ represents a $(3N - 3) \times 3$ block of zeros, and $\mathsf{0}^{\mathrm{T}}$ represents a $3 \times (3N - 3)$ block of zeros. This is seen straightforwardly when the measuring vectors for the Cartesian coordinates of the center of the mass

$$\mathbf{e}_\alpha^{(X_i)} = \nabla_\alpha X_i = \sum_{\beta=1}^{N} \nabla_\alpha \frac{m_\beta \mathbf{u}_i \cdot \mathbf{x}_\beta}{M} = \frac{m_\alpha}{M} \mathbf{u}_i \tag{93}$$

are substituted to Eq. (90), and the translational invariance of the shape and rotational coordinates (denoted now for short as $B_1 = \phi$, $B_2 = \theta$, and $B_3 = \chi$),

$$\sum_\alpha \nabla_\alpha q_i = 0 \tag{94}$$

$$\sum_\alpha \nabla_\alpha B_i = 0 \tag{95}$$

is taken into account. Thus, the kinetic energy operator can be written as the sum

$$\hat{T}^{(\text{nucl})} = \hat{T}^{(\text{int})} + \hat{T}^{(\text{transl})} \tag{96}$$

of the internal part

$$\hat{T}^{(\text{int})} = -\frac{\hbar^2}{2} \sum_{ij}^{3N-3} \left(\frac{\partial}{\partial q_i} + \frac{1}{g^{-1/2}} \frac{\partial g^{-1/2}}{\partial q_i} \right) g^{(q_i q_j)} \frac{\partial}{\partial q_j} \tag{97}$$

and the translational part

$$\hat{T}^{(\text{transl})} = -\frac{\hbar^2}{2M} \sum_{i=1}^{3} \frac{\partial^2}{\partial X_i^2} \tag{98}$$

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where the partitioning of $[\mathsf{G}]$ follows.

Instead of representing the rotational part of each gradient operator in terms of the partial derivative operators $\partial/\partial B_i$, it is customary to represent it in terms of the body-fixed components $\hat{l}_i = \mathbf{u}'_i \cdot \hat{\mathbf{l}}$ of the angular momentum operator $\hat{\mathbf{l}}$. One of the main results of Paper 4 is the relation

$$(\nabla_\alpha \phi)\frac{\partial}{\partial \phi} + (\nabla_\alpha \theta)\frac{\partial}{\partial \theta} + (\nabla_\alpha \chi)\frac{\partial}{\partial \chi} = \sum_i^3 \mathbf{e}_\alpha^{(L_i)}\hat{l}_i \tag{99}$$

The measuring vectors $\mathbf{e}_\alpha^{(L_k)}$ associated to the nucleus α and kth component of the angular momentum operator $\hat{\mathbf{l}}$ are obtained as

$$\mathbf{e}_\alpha^{(L_k)} = \nabla_\mathbf{a}\left[(\mathbf{a}\cdot\nabla_\alpha\mathbf{u}'_i)\cdot\mathbf{u}'_j\right] \tag{100}$$

The target of differentiation is implied by the parenthesis and the indices i, j, and k are in cyclic order. The internal part of the kinetic energy operator can be written compactly as

$$\hat{T}^{(\text{int})} = -\frac{\hbar^2}{2}\sum_{ij}^{3N-3}\hat{\pi}_i^\dagger g^{(ij)}\hat{\pi}_j \tag{101}$$

where $\hat{\pi}_i$ in Eq. (101) is the body-frame component $\hat{l}_i/\hbar$ of the total angular momentum operator for the rotational degrees of freedom ($i = 1, 2, 3$) and the shape coordinate partial derivative operator $\partial/\partial q_{i-3}$ for the vibrational degrees of freedom ($i = 4, 5, ..., 3N-3$). The "adjoint" $\hat{\pi}_i^\dagger$ is the same as $\hat{\pi}_i$ for the rotational degrees of freedom and it is $\partial/\partial q_{i-3} + g'^{1/2}\partial g'^{-1/2}/\partial q_{i-3}$ for the shape coordinates ($i = 4, 5, ..., 3N-3$). The quantity $g' = \det g^{(ij)}$ is the determinant of the contravariant metric tensor $g^{(ij)}$ with vibrational elements

$$g^{(ij)} = \sum_\alpha^N \frac{1}{m_\alpha}\mathbf{e}_\alpha^{(q_{i-3})}\cdot\mathbf{e}_\alpha^{(q_{j-3})} \text{ for } i,j = 4, 5, ..., 3N-3 \tag{102}$$

Coriolis elements

$$g^{(ij)} = \sum_\alpha^N \frac{1}{m_\alpha}\mathbf{e}_\alpha^{(q_{i-3})}\cdot\mathbf{e}_\alpha^{(L_j)} \text{ for } i = 4, 5, ..., 3N-3 \text{ and } j = 1, 2, 3 \tag{103}$$

and the rotational elements

$$g^{(ij)} = \sum_\alpha^N \frac{1}{m_\alpha}\mathbf{e}_\alpha^{(L_i)}\cdot\mathbf{e}_\alpha^{(L_j)} \text{ for } i,j = 1, 2, 3 \tag{104}$$

The gradients of the Euler angles (again denoted as $B_1 = \phi$, $B_2 = \theta$ and $B_3 = \chi$) are related to the rotational measuring vectors $\mathbf{e}_\alpha^{(L_i)}$ as

$$\nabla_\alpha B_j = \mathbf{e}_\alpha^{(B_j)} = \sum_i^3 \mathbf{e}_\alpha^{(L_i)} \Omega_{ij}^{-1} \tag{105}$$

where $\Omega_{ij}^{-1} = [\Omega]_{ij}^{-1}$ is the element of the inverse of the matrix $[\Omega]_{ij} = \mathbf{n}_i \cdot \mathbf{u}_j'$ ($\mathbf{n}_1 = \mathbf{u}_3$, $\mathbf{n}_2 = \mathbf{u}_3 \times \mathbf{u}_3' / |\mathbf{u}_3 \times \mathbf{u}_3'| = \mathbf{u}_3 \times \mathbf{u}_3' / \sin\theta$, and $\mathbf{n}_3 = \mathbf{u}_3'$ are the nodal line vectors). Explicitly, the matrix $[\Omega]^{-1}$ is given as

$$[\Omega]^{-1} = \begin{bmatrix} \sin\theta\sin\chi & \sin\theta\cos\chi & \cos\theta \\ \cos\chi & -\sin\chi & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} \frac{\sin\chi}{\sin\theta} & \cos\chi & -\frac{\cos\theta\sin\chi}{\sin\theta} \\ \frac{\cos\chi}{\sin\theta} & -\sin\chi & -\frac{\cos\theta\cos\chi}{\sin\theta} \\ 0 & 0 & 1 \end{bmatrix} \tag{106}$$

Thus, one can write

$$g^{(B_j B_l)} = \sum_\alpha^N \frac{1}{m_\alpha} \mathbf{e}_\alpha^{(B_j)} \cdot \mathbf{e}_\alpha^{(B_l)} = \sum_{ik}^3 \sum_\alpha^N \frac{1}{m_\alpha} \mathbf{e}_\alpha^{(L_i)} \cdot \mathbf{e}_\alpha^{(L_k)} \Omega_{ij}^{-1} \Omega_{kl}^{-1} = \sum_{ik}^3 g^{(L_i L_k)} \Omega_{ij}^{-1} \Omega_{kl}^{-1} \tag{107}$$

and

$$g^{(B_j q_l)} = \sum_\alpha^N \frac{1}{m_\alpha} \mathbf{e}_\alpha^{(B_j)} \cdot \mathbf{e}_\alpha^{(q_l)} = \sum_i^3 \sum_\alpha^N \frac{1}{m_\alpha} \mathbf{e}_\alpha^{(L_i)} \cdot \mathbf{e}_\alpha^{(q_l)} \Omega_{ij}^{-1} = \sum_i^3 g^{(L_i q_l)} \Omega_{ij}^{-1} \tag{108}$$

where q_l is a shape coordinate. Because the determinant of $[\Omega]^{-1}$ is $\det[\Omega]^{-1} = -1/\sin\theta$, the determinants of the two contravariant metric tensors $g = \det g^{(q_i q_j)}$ (where q_{3N-5}, q_{3N-4}, and q_{3N-3} refer to the Euler angles, and q_{3N-2}, q_{3N-1}, and q_{3N} refer to the coordinates of the center-of-mass) and $g' = \det g^{(ij)}$ are related as

$$g' = \sin^2\theta g \tag{109}$$

The determinant g' depends only on the shape coordinates. The evaluation of g' by any conventional means is rather tedious, because the elements of the metric tensor can be complicated functions of the shape coordinates. Luckily, as shown in Paper 5 by geometric algebra, it is possible to represent the volume-element of integration $d\tau = |d^3\mathbf{x}_1| |d^3\mathbf{x}_2| \ldots |d^3\mathbf{x}_N| = J dq_1 dq_2 \ldots dq_{3N-6} d\phi d\theta d\chi dX_1 dX_2 dX_3$ as a product of N volume-elements, each associated to a set of three coordinates. To be more precise, the volume-element is obtained as a product

$$d\tau = \frac{|d^3\mathbf{z}_1| |d^3\mathbf{z}_2| \ldots |d^3\mathbf{z}_N|}{|\det[\mathsf{c}]|^3} \tag{110}$$

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where $\mathbf{z}_\alpha = \sum_\beta^N c_\alpha^{(\beta)} \mathbf{x}_\beta$ ($\alpha = 1, 2, ..., N-1$) are some translationally invariant linear combinations of the nuclear position vectors, $\mathbf{z}_N$ is the position vector of the center-of-mass, and $[\mathsf{c}]$ is the $N \times N$ matrix with elements $[\mathsf{c}]_{ij} = c_i^{(j)}$, which are independent of nuclear positions. In the case of ordinary shape coordinates, such as bond lengths and valence angles, the bond vectors $\mathbf{r}_{\alpha\beta} = \mathbf{x}_\beta - \mathbf{x}_\alpha$ are suitable candidates for the translationally invariant z-vectors. Explicitly, in terms of the Euler angles, shape coordinates, and Cartesian center-of-mass coordinates the volume-elements $|d^3\mathbf{z}_\alpha|$ are given by

$$
\begin{align}
\left|d^3\mathbf{z}_1\right| &= \frac{d\phi d\theta dq_1}{|(\nabla_{\mathbf{z}_1}\phi) \wedge (\nabla_{\mathbf{z}_1}\theta) \wedge (\nabla_{\mathbf{z}_1}q_1)|} = \frac{z_1^3 \sin\theta d\phi d\theta dq_1}{|\mathbf{z}_1 \cdot (\nabla_{\mathbf{z}_1}q_1)|} \tag{111} \\
\left|d^3\mathbf{z}_2\right| &= \frac{d\chi dq_2 dq_3}{|(\nabla_{\mathbf{z}_2}\chi) \wedge (\nabla_{\mathbf{z}_2}q_2) \wedge (\nabla_{\mathbf{z}_2}q_3)|} \\
&= \frac{z_2 \sin^2\theta_{12} d\chi dq_2 dq_3}{|(\mathbf{u}_{\mathbf{z}_1} \times \mathbf{u}_{\mathbf{z}_2}) \wedge (\nabla_{\mathbf{z}_2}q_2) \wedge (\nabla_{\mathbf{z}_2}q_3)|} \tag{112} \\
\left|d^3\mathbf{z}_\alpha\right| &= \frac{dq_i dq_j dq_k}{|(\nabla_{\mathbf{z}_\alpha}q_i) \wedge (\nabla_{\mathbf{z}_\alpha}q_j) \wedge (\nabla_{\mathbf{z}_\alpha}q_k)|} \text{ for } \alpha = 2, 3, ..., N-1 \tag{113} \\
\left|d^3\mathbf{z}_N\right| &= dX_1 dX_2 dX_3 \tag{114}
\end{align}
$$

where $\mathbf{u_a} = \mathbf{a}/a$. Unlike any other approach, this method applies to an *arbitrary* choice of the shape coordinates q_i. The inverse of the square root of the determinant of the contravariant metric tensor is then obtained from the Jacobian J as

$$
g'^{-1/2} = \frac{J}{\sin\theta} \prod_\alpha^N m_\alpha^{3/2} \tag{115}
$$

4.2   Body-frames

Each body-fixed position vector $\mathbf{y}'_\alpha$ can be rotated to the space-fixed position vector $\mathbf{y}_\alpha = \mathbf{x}_\alpha - \mathbf{X}$ by

$$
\mathbf{y}_\alpha = R^\dagger \mathbf{y}'_\alpha R \tag{116}
$$

As seen from Eq. (78), the parametrization of the rotor R depends on the body-axes. Each choice of the body-axes specifies a reference orientation, in which the body-frame coincides with the space-fixed frame. For a given shape, the change in the orientation of the molecule is identical to the change in the orientation of the body-axes, but it is independent of any particular choice of the body-frame. However, if the molecule deforms (i.e. the initial and final shape differs), it makes

no sense to ask "how much has the molecule rotated", because the answer would depend on the choice of the body-axes. [35]

The body-axes can be written as

$$\mathbf{u}'_3 \;=\; \frac{\mathbf{r}}{|\mathbf{r}|} \tag{117}$$

$$\mathbf{u}'_2 \;=\; \frac{\mathbf{r} \times \mathbf{s}}{|\mathbf{r} \times \mathbf{s}|} \tag{118}$$

$$\mathbf{u}'_1 \;=\; \mathbf{u}'_2 \times \mathbf{u}'_3 \tag{119}$$

where $\mathbf{r}$ and $\mathbf{s}$ are two directions which are defined by

$$\mathbf{r} \;=\; \sum_{\alpha} c_{\alpha}\mathbf{x}_{\alpha} \tag{120}$$

$$\mathbf{s} \;=\; \sum_{\alpha} d_{\alpha}\mathbf{x}_{\alpha} \tag{121}$$

The coefficients c_{α} and d_{α} may depend on the internal coordinates,

$$\mathbf{r} \times \mathbf{s} \neq 0 \tag{122}$$

to assure that these vectors are not collinear, and

$$\sum_{\alpha} c_{\alpha} \;=\; 0 \tag{123}$$

$$\sum_{\alpha} d_{\alpha} \;=\; 0 \tag{124}$$

to guarantee the translational invariance of these vectors. The rotational measuring vectors were shown in Paper 4 to be

$$\mathbf{e}_{\alpha}^{(L_1)} \;=\; -\frac{c_{\alpha}\mathbf{u}'_2 + \sum_{\beta}\mathbf{x}_{\beta} \cdot \mathbf{u}'_2 \nabla_{\alpha}c_{\beta}}{r} \tag{125}$$

$$\mathbf{e}_{\alpha}^{(L_2)} \;=\; \frac{c_{\alpha}\mathbf{u}'_1 + \sum_{\beta}\mathbf{x}_{\beta} \cdot \mathbf{u}'_1 \nabla_{\alpha}c_{\beta}}{r} \tag{126}$$

$$\mathbf{e}_{\alpha}^{(L_3)} \;=\; -\frac{1}{|\mathbf{r} \times \mathbf{s}|}[\mathbf{s} \cdot \mathbf{u}'_3(c_{\alpha}\mathbf{u}'_2 + \sum_{\beta}\mathbf{x}_{\beta} \cdot \mathbf{u}'_2 \nabla_{\alpha}c_{\beta})$$
$$-r(d_{\alpha}\mathbf{u}'_2 + \sum_{\beta}\mathbf{x}_{\beta} \cdot \mathbf{u}'_2 \nabla_{\alpha}d_{\beta})] \tag{127}$$

Because the above formulas apply to *arbitrary* choices of the $\mathbf{r}$ and $\mathbf{s}$, it is simple to obtain the rotational measuring vectors by the present approach once the body-axes (or the directions $\mathbf{r}$ and $\mathbf{s}$) have been defined. Thus, it seems that the present

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approach offers an effective tool for finding the vibration-rotation kinetic energy operator in the case where it is desirable to minimize some rotation-vibration coupling terms in the Hamiltonian.

4.3 Covariant measuring vectors and Lagrangian formulation

For conservative systems (subjected to time-independent constraints, or no constraints at all), the kinetic energy part of the classical Lagrangian $L = T - V$ is given in terms of the generalized velocities $\dot{q}_i$ as

$$T = \frac{1}{2} \sum_{ij}^{P} \dot{q}_i g_{q_i q_j} \dot{q}_j \tag{128}$$

(Ref. [4], pages 350-354), where P is the number of active coordinates,

$$g_{q_i q_j} = \sum_{\alpha}^{N} m_\alpha \mathbf{e}_{q_i}^{(\alpha)} \cdot \mathbf{e}_{q_j}^{(\alpha)} \tag{129}$$

is the covariant metric tensor, and the covariant measuring vectors are defined as

$$\mathbf{e}_{q_i}^{(\alpha)} = \frac{\partial \mathbf{x}_\alpha}{\partial q_i} \tag{130}$$

It is worth the trouble to relate the properties of the covariant measuring vectors to those of the contravariant measuring vectors. In what follows, I shall consider only the unconstrained case, where the number of active coordinates is $P = 3N$. First, if one sets $t = q_j$ in Eq. (82), the result is

$$\frac{\partial q_i}{\partial q_j} = \sum_{\alpha}^{N} \frac{\partial \mathbf{x}_\alpha}{\partial q_j} \cdot \nabla_\alpha q_i = \delta_{ij} \tag{131}$$

where δ_{ij} equals one if $i = j$ and zero otherwise. Thus, one obtains the reciprocality condition between the covariant and contravariant measuring vectors as

$$\sum_{\alpha}^{N} \mathbf{e}_{q_i}^{(\alpha)} \cdot \mathbf{e}_\alpha^{(q_j)} = \delta_{ij} \tag{132}$$

Second, by using the representation of ∇_α in Eq. (80), it follows that

$$\nabla_\alpha \left(A_{\bar{r}} \mathbf{x}_\beta \right) = \delta_{\alpha\beta} \sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} A_{\bar{r}} \frac{\partial \mathbf{x}_\beta}{\partial q_i} = \delta_{\alpha\beta} \sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} A_{\bar{r}} \mathbf{e}_{q_i}^{(\beta)} \tag{133}$$

where $A_{\bar{r}}$ is an r-blade independent of $\mathbf{x}_\alpha$, and $r = 0, 1, 2, 3$. But because

$$A_{\bar{r}}\mathbf{x}_\beta = A_{\bar{r}} \cdot \mathbf{x}_\beta + A_{\bar{r}} \wedge \mathbf{x}_\beta = (-1)^{r+1}\,\mathbf{x}_\beta \cdot A_{\bar{r}} + (-1)^r\,\mathbf{x}_\beta \wedge A_{\bar{r}} \tag{134}$$

and

$$\nabla_\alpha \mathbf{x}_\beta \cdot A_{\bar{r}} = \delta_{\alpha\beta} r A_{\bar{r}} \tag{135}$$

$$\nabla_\alpha \mathbf{x}_\beta \wedge A_{\bar{r}} = \delta_{\alpha\beta}\left(3 - r\right) A_{\bar{r}} \tag{136}$$

it follows that

$$\sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} A_{\bar{r}} \mathbf{e}_{q_i}^{(\beta)} = \delta_{\alpha\beta}\left(-1\right)^r \left(3 - 2r\right) A_{\bar{r}} \tag{137}$$

where many special cases can be read off. For example, by setting $A_{\bar{r}} = 1$ (so $r = 0$), the identity

$$\sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} \mathbf{e}_{q_i}^{(\beta)} = 3\delta_{\alpha\beta} \tag{138}$$

follows. By decomposing this into a sum of inner and outer products,

$$\sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} \cdot \mathbf{e}_{q_i}^{(\beta)} = 3\delta_{\alpha\beta} \tag{139}$$

and

$$\sum_i^{3N} \mathbf{e}_\alpha^{(q_i)} \times \mathbf{e}_{q_i}^{(\beta)} = 0 \tag{140}$$

follow. Also, if the inner products are expressed in terms of the geometric products, and Eq. (137) used, it is easy to prove that

$$\sum_k^{3N} g^{(q_i q_k)} g_{q_k q_j} = \delta_{ij} \tag{141}$$

Should the reader be interested in the approach of obtaining the contravariant vibration-rotation metric tensor by inverting the covariant one, it is advised to read Refs. [34, 35]. However, as shown in the present work, it is considerably easier to obtain the contravariant metric tensor directly.

5 Outlines for future research

There are several possibilities to further apply geometric algebra to theoretical chemistry. Some promising yet challenging tasks are listed below:

1. Decompose the vector derivative operators $\nabla_1, \nabla_2, ..., \nabla_N$ in translational, vibrational and rotational parts *without the intervention of scalar coordinates.*

2. Obtain kinetic energy operators for polyatomic molecules subjected to constraints by using tangential vector derivative operators ∂_α (or related operators) in the place of ∇_α. This belongs under the subject of differentiation in vector manifolds (Refs. [5, 8]).

3. Use the generalized integral calculus to evaluate multicenter molecular integrals over Slater and Gaussian type of orbitals.

The first task in the list belongs solely to the realms of geometric algebra, and it has not been studied in any length. Thus, it could be a promising starting point for new research.

On the other hand, the quantization of the (coordinate representations of the) constrained systems has been a subject of intense research for the past fifty years or so. There exist many different approaches and applications (see e.g. Refs. [36]-[39]), but not all the proposed solutions agree with each others. I believe that geometric algebra can be used not only to reformulate the problem but also to gain practical advantages in finding the constrained kinetic energy operators. It should also offer an answer to the question when and why some other approaches succeed or fail in solving the problem.

There exists some literature on the subject of analytical evaluation of multicenter molecular integrals (see e.g. [40]). But no doubt, geometric algebra can be used to still improve the existing approaches, and to find new ones. From the practical point of view, this is an important area because multicenter integrals are encountered in electronic structure calculations.

Errata

Paper 1

1. *The sentence in the parenthesis after Eq. (27), page 3123, should read*
   see especially Chap. 2.6 of Ref. 19

2. *The sentence before Eq. (48), page 3124, should read*
   The vibrational displacements are rotationally invariant, so

3. *Eq. (A2), page 3132, should read*

$$\mathbf{a} \cdot (\mathbf{b}_1 \wedge \ldots \wedge \mathbf{b}_p) = \sum_{k=1}^{p} (-1)^{k+1} \mathbf{a} \cdot \mathbf{b}_k \left(\mathbf{b}_1 \wedge \ldots \wedge \overset{\vee}{\mathbf{b}}_k \wedge \ldots \wedge \mathbf{b}_p \right)$$

Paper 4

1. *The sentence before Appendix B1, page 10606, should read*
   In terms of the directions $\mathbf{r}$ of Eq. (18) and $\mathbf{s}$ of Eq. (20), this can done by choosing $\mathbf{r}$ and the cross-product $\mathbf{r} \times \mathbf{s}$ to depend on all of the nuclear positions, which results in $c_\alpha d_\beta - c_\beta d_\alpha \neq 0$ for $\alpha < \beta = 2, 3, \ldots, N$.

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