Vibration-rotation kinetic energy operators and geometric algebra

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Outline

Molecular energy levels

- In 1920's it was observed that molecular energy levels are quantized
- IR spectrum shows band structure

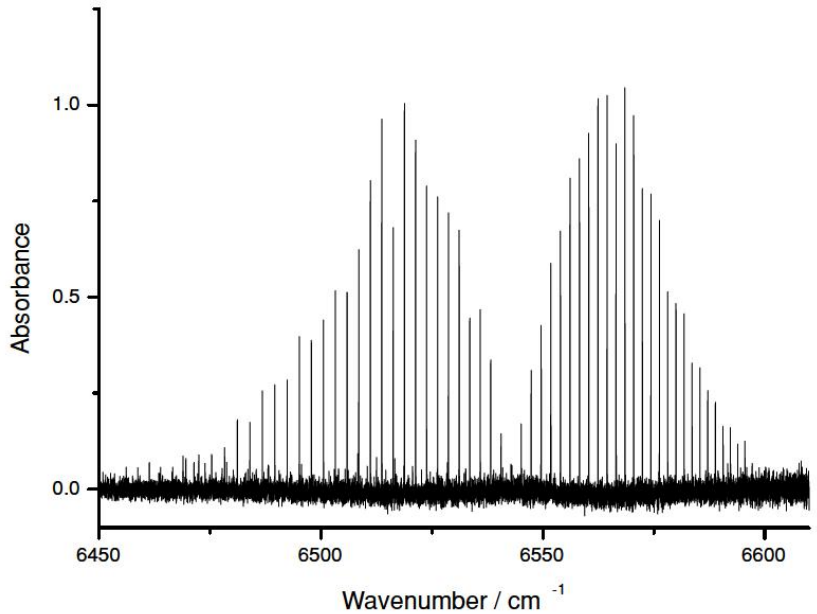


Figure: A part of absorption spectrum of $^{12}CH^{13}CH$, recorded in the Laboratory of physical chemistry, University of Helsinki.

Molecular energy levels (cntnd.)

- To explain observed spectras (or to predict energy level structure), we need to solve the Schrödinger equation

$$H\Psi = E\Psi \tag{1}$$

- Eigenfunction Ψ and the eigenvalue E are unknown.
- Hamiltonian $H = T + V$ is known

Vibration-rotation SY

- Born-Oppenheimer approximation assumed!
  - Molecule in an electronic eigenstate.
  - Potential V obtained by fitting the electronic energies for given values of nuclear coordinates.
- Only nuclear coordinates included.

Vibration-rotation KEO

- Vibration-rotation Kinetic energy operator (KEO) given by

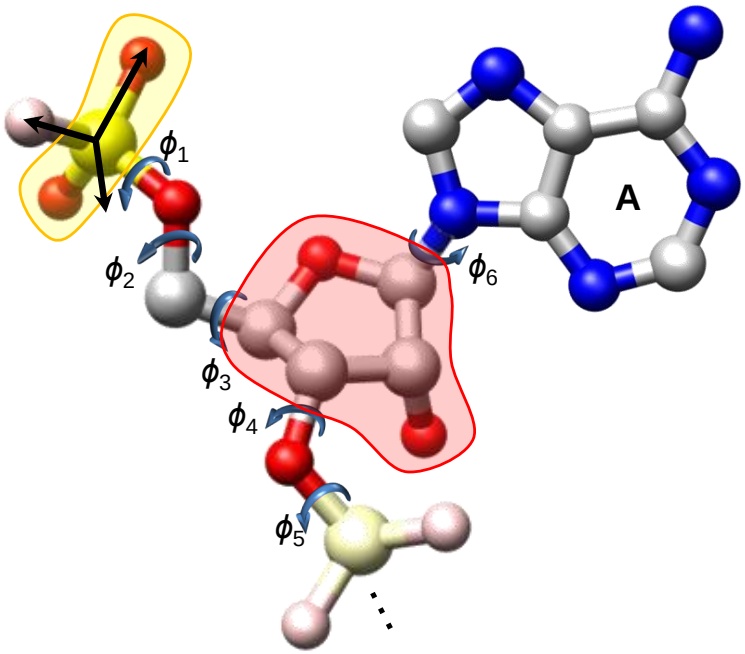
$$T = -\frac{\hbar^2}{2} \sum_{\alpha}^{N} \nabla^2_{\mathbf{x}_\alpha} \tag{2}$$

- The Laplacian $\nabla^2_{\mathbf{x}_\alpha} = \nabla_{\mathbf{x}_\alpha} \cdot \nabla_{\mathbf{x}_\alpha}$ is the square of the gradient operator $\nabla_{\mathbf{x}_\alpha}$, which operates on the position vector $\mathbf{x}_\alpha$ of the atom α.

Vibration-rotation KEO (cntd.)

- The degrees of freedom that a polyatomic molecule possess are classified into three different types:
  - Position (of the center-of mass) – 3 cartesian coordinates.
    - Translation.
  - Orientation (of the body-frame w.r.t. constant lab-frame) – 3 Euler angles.
    - Rotation.
  - Shape – N_s ($\leq 3N-6$) internal coordinates.
    - Deformation, vibration.

Vibration-rotation KEO (cntd.)



Vibration-rotation KEO (cntd.)

- In internal coordinates, the vibration-rotation part of KEO reads as

$$T = \frac{1}{2}\sum_{ij}^{3N-6} p_i^{\dagger} g^{(s_i s_j)} p_j + \frac{1}{2}\sum_{i}^{3N-6}\sum_{j}^{3}\left(p_i^{\dagger} g^{(s_i l_j)} l_j + l_j g^{(s_i l_j)} p_i\right) + \frac{1}{2}\sum_{ij}^{3} l_i^{\dagger} g^{(l_i l_j)} l_j \quad (3)$$

Vibration-rotation KEO (cntd.)

- $p_i = -\imath\hbar\partial/\partial s_i$ and $p_i^\dagger = -\imath\hbar[\partial/\partial s_i + (\partial J/\partial s_i)/J]$
  - J is the Jacobian.
- Angular momentum operator is self-adjoint, i.e., $I_i^\dagger = I_i$.
- $g^{(s_i s_j)}$ is the vibrational, $g^{(s_i I_j)}$ is the Coriolis, and $g^{(I_i I_j)}$ is the rotational element of the contravariant metric tensor.
  - Functions of the shape coordinates only.
  - Euler angles do not appear in metric tensor elements!

Vibration-rotation KEO (cntd.)

- Q: How to obtain KEO and related quantities?
- A: By Geometric algebra (= Real Clifford algebra with geometric interpretation).

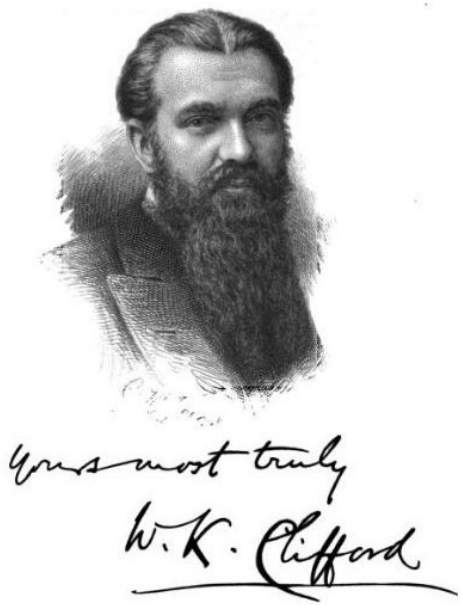


Figure: William Kingdon Clifford (1845-1879)

Geometric (Clifford) algebra

- Algebra of Euclidean displacements (vectors)
  - $\mathbf{a}(\mathbf{bc}) = (\mathbf{ab})\mathbf{c} = \mathbf{abc}$
  - $\mathbf{a}(\mathbf{b}+\mathbf{c}) = \mathbf{ab}+\mathbf{ac}$
  - $(\mathbf{b}+\mathbf{c})\mathbf{a} = \mathbf{ba}+\mathbf{ca}$
- Reflects directly the geometric properties:
  - $\mathbf{a} \parallel \mathbf{b} \Leftrightarrow \mathbf{ab} \in \mathbb{R}$ (especially, $\mathbf{a}^2 \equiv |\mathbf{a}|^2$).
  - $\mathbf{a} \perp \mathbf{b} \Leftrightarrow \mathbf{ab} = -\mathbf{ba}$

Geometric (Clifford) algebra (cntnd.)

- Vectors used in calculations, not their components!

Example

For example,

$$\mathbf{a} \to \mathbf{a}' = -\mathbf{uau}$$

is the reflection of $\mathbf{a}$ along the (unit) vector $\mathbf{u}$ (it reverses the part of $\mathbf{a}$, which is perpendicular to $\mathbf{u}$ and does nothing to the parallel part). As a consequence,

$$\mathbf{a} \to \mathbf{a}'' = \mathbf{vuauv}$$

is the rotation of $\mathbf{a}$ in the plane $\mathbf{u} \wedge \mathbf{v}$ the through twice the angle between $\mathbf{u}$ and $\mathbf{v}$.

Vibrational part of metric tensor

- The vibrational metric tensor elements is obtained as

$$g^{(s_i s_j)} = \sum_{\alpha=1}^{N} \frac{(\nabla_{\mathbf{x}_\alpha} s_i) \cdot (\nabla_{\mathbf{x}_\alpha} s_j)}{m_\alpha} \tag{4}$$

- By utilizing geometric algebra, it is easy to evaluate the gradients $\nabla_{\mathbf{x}_\alpha} s_i$.

Shape coordinate gradients

Example

Gradient $\nabla_{\mathbf{x}_\beta} r_{\alpha\beta}$ of bond length $r_{\alpha\beta} = |\mathbf{r}_{\alpha\beta}| = (\mathbf{r}_{\alpha\beta} \cdot \mathbf{r}_{\alpha\beta})^{1/2}$ (now $\mathbf{r}_{\alpha\beta} = \mathbf{x}_\beta - \mathbf{x}_\alpha$). Start from

$$r_{\alpha\beta}^2 = \mathbf{r}_{\alpha\beta} \cdot \mathbf{r}_{\alpha\beta}$$

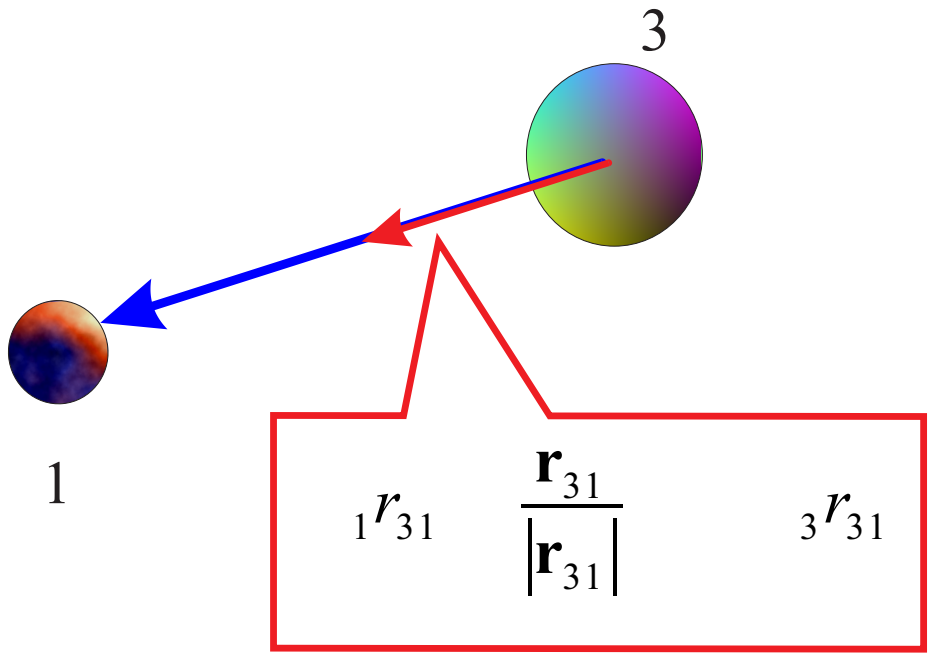
Take the vectorial derivative of both sides as

$$2 r_{\alpha\beta} \nabla_{\mathbf{x}_\beta} r_{\alpha\beta} = 2 \mathbf{r}_{\alpha\beta}$$

to get

$$\nabla_{\mathbf{x}_\beta} r_{\alpha\beta} = \frac{\mathbf{r}_{\alpha\beta}}{r_{\alpha\beta}} = -\nabla_{\mathbf{x}_\alpha} r_{\alpha\beta}$$

Shape coordinate gradients (cntd.)



Rotational and Coriolis parts of metric tensor

- Rotational and Coriolis parts of the metric tensor elements are given by

$$g^{(l'_i l'_j)} = \sum_{\alpha=1}^{N} \frac{\mathbf{e}_\alpha^{(l'_i)} \cdot \mathbf{e}_\alpha^{(l'_j)}}{m_\alpha} \tag{5}$$

$$g^{(l'_i s_j)} = \sum_{\alpha=1}^{N} \frac{\mathbf{e}_\alpha^{(l'_i)} \cdot (\nabla_{\mathbf{x}_\alpha} s_j)}{m_\alpha} \tag{6}$$

- $\mathbf{e}_\alpha^{(l'_k)}$ is the measuring vector associated to nucleus α and kth body-frame component of the angular momentum operator.

Rotational measuring vectors

- Generally

$$(\nabla_{\mathbf{x}_\alpha}\theta)\,p_\theta + (\nabla_{\mathbf{x}_\alpha}\chi)\,p_\chi + (\nabla_{\mathbf{x}_\alpha}\phi)\,p_\phi = \sum_k^3 \mathbf{e}_\alpha^{(l'_k)}\, l'_k \tag{7}$$

- However,

$$\mathbf{e}_\alpha^{(l'_i)} \neq \nabla_{\mathbf{x}_\alpha}\theta, \nabla_{\mathbf{x}_\alpha}\chi, \nabla_{\mathbf{x}_\alpha}\phi \tag{8}$$

  i.e. components of angular momentum are not conjugated to any rotational coordinates.

- By a short calculation (omitted here), it turns out that

$$\mathbf{e}_\alpha^{(l'_i)} = \nabla_{\mathbf{a}}\left[\left(\mathbf{a}\cdot\nabla_{\mathbf{x}_\alpha}\mathbf{u}'_j\right)\cdot\mathbf{u}'_k\right] \tag{9}$$

  where i, j, k are in cyclic order.

Rotational measuring vectors (cntnd.)

Example

Let us choose

$$\mathbf{u}_3' = \hat{\mathbf{r}}_{12}$$

Then

$$\mathbf{a} \cdot \nabla_{\mathbf{x}_2} \mathbf{u}_3' = \mathbf{a} \cdot \nabla_{\mathbf{x}_2} \hat{\mathbf{r}}_{12} = \frac{\mathbf{a} - \mathbf{a} \cdot \hat{\mathbf{r}}_{12} \hat{\mathbf{r}}_{12}}{|\mathbf{r}_{12}|}$$

Hence,

$$\mathbf{e}_2^{(I_2')} = \nabla_{\mathbf{a}} \left[\left(\mathbf{a} \cdot \nabla_{\mathbf{x}_2} \mathbf{u}_3' \right) \cdot \mathbf{u}_1' \right] = \nabla_{\mathbf{a}} \frac{\mathbf{a} \cdot \mathbf{u}_1'}{|\mathbf{r}_{12}|} = \frac{\mathbf{u}_1'}{|\mathbf{r}_{12}|}$$

Jacobian

- Conventionally the Jacobian J is evaluated as $J = (\det g)^{-1/2}$. In practice, way too complicated!
- Better, $J = J_1 J_2 J_3 \ldots$, where

$$
\begin{aligned}
J_1 &= \frac{\sin\theta}{\left|\mathbf{e}_1^{(l_1')} \wedge \mathbf{e}_1^{(l_2')} \wedge (\nabla_{\mathbf{x}_1} s_1)\right|} \\
J_2 &= \frac{1}{\left|\mathbf{e}_2^{(l_3')} \wedge (\nabla_{\mathbf{x}_2} s_2) \wedge (\nabla_{\mathbf{x}_2} s_3)\right|} \\
J_\alpha &= \frac{1}{|(\nabla_{\mathbf{x}_\alpha} s_i) \wedge (\nabla_{\mathbf{x}_\alpha} s_j) \wedge (\nabla_{\mathbf{x}_\alpha} s_k)|} \quad \text{for } \alpha = 3, 4, \ldots, N-1
\end{aligned}
$$

Jacobian (cntnd.)

Example

Consider polyspherical coordinates. The jacobian reads as

$$J = \sin\theta \prod_{i=1}^{N-1} r_i^2 \prod_{j=1}^{N-2} \sin\theta_j \tag{10}$$

where the bond lengths have been denoted as r_i, the bond-angles as θ_j, and the torsional (dihedral) angles as ϕ_k.

Recent advances

- GA approach produces KEOs also when the implicitly defined Eckart body-frames are used.
  - Eckart frames occupy very important role in the developement of vibration-rotation theory.
- Constraints in shape do not cause problems.
  - A correction term is added to ecah active measuring vectors.
  - Riemannian quantization.

Conclusions

- Geometric algebra is an ideal tool for obtaining vibration-rotation KEOs
  - Applies for abitrary coordinates and body-frames.
  - Based on measuring vectors.

Further Reading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