



**HAL**  
open science

## A Concise Method for Kinetic Energy Quantisation

Yonggang Yang, Oliver Kühn

► **To cite this version:**

Yonggang Yang, Oliver Kühn. A Concise Method for Kinetic Energy Quantisation. *Molecular Physics*, 2008, 106 (21-23), pp.2445-2457. 10.1080/00268970802562117 . hal-00513233

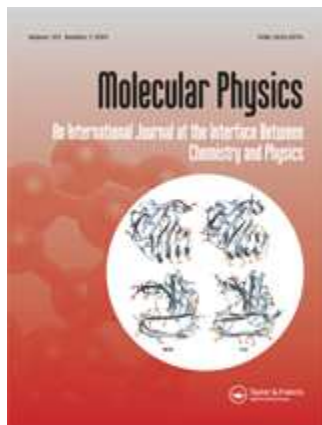
**HAL Id: hal-00513233**

**<https://hal.science/hal-00513233>**

Submitted on 1 Sep 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## A Concise Method for Kinetic Energy Quantisation

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2008-0246.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	15-Oct-2008
Complete List of Authors:	Yang, Yonggang; Freie Universität Berlin, Chemistry Kühn, Oliver; Rostock University, Physics
Keywords:	Vibrational Dynamics, Kinetic Energy Operator, Quantisation, Strong Hydrogen Bonds
<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>YangKuehnManuscriptRevised.tex</p>	



# A Concise Method for Kinetic Energy Quantisation

Yonggang Yang\* and Oliver Kühn†

*Institut für Chemie und Biochemie, Freie Universität Berlin,*

*Takustr. 3, D-14195 Berlin, Germany*

(Dated: October 15, 2008)

## Abstract

We present a straightforward method for obtaining exact classical and quantum molecular Hamiltonians in terms of arbitrary coordinates. As compared to other approaches the resulting expressions are rather compact, the physical meaning of each quantity is quite transparent, and in some cases the calculation effort will be greatly reduced. We also investigate systems with constraints to find the suggested method to be applicable in contrast to most conventional approaches to kinetic energy operators which cannot directly be applied to constrained systems. Two examples are discussed in detail, the monohydrated hydroxide anion and the protonated ammonia dimer.

Keywords: Vibrational Dynamics, Kinetic Energy Operator, Quantisation, Strong Hydrogen Bonds

---

\*Electronic address: [ygyang@chemie.fu-berlin.de](mailto:ygyang@chemie.fu-berlin.de)

†New Address: Institut für Physik, Universität Rostock, Universitätsplatz 3, D-18051 Rostock, Germany,

Tel. +493814986950, Fax: +493814986942; Electronic address: [oliver.kuehn@uni-rostock.de](mailto:oliver.kuehn@uni-rostock.de)

## I. INTRODUCTION

Theoretical modeling of molecular reaction dynamics requires to have at hand a Hamiltonian. For few-atom systems this may involve defining the potential energy surfaces (PES) explicitly in terms of properly chosen coordinates such as bond length and angles or distance vectors. In the latter case, for instance, it has been shown that PES in full-dimensionality including proper account of exchange symmetry can be generated for systems like the five-atomic  $\text{H}_3\text{O}_2^-$  [1] or the seven-atomic  $\text{H}_5\text{O}_2^+$  [2]. With increasing dimensionality this approach is no longer feasible due to the exponential scaling of the computational effort for explicit calculation of the PES on a numerical grid. Here, reaction surface concepts have been proven to be a versatile compromise, mapping out that PES region which is relevant for the considered reaction by combining suitable large amplitude reaction coordinates with orthogonal harmonic motions[3–7].

Besides the PES the kinetic energy operator (KEO) needs to be known in terms of the chosen coordinate system. In principle, kinetic energy quantisation had been discussed by Podolsky in terms of intricate tensor analysis right after the foundation of the Schrödinger equation had been laid [8]. Later studies are to some extent based on the same mathematical techniques [9, 10]. **Approximate KEOs using normal mode coordinates are widely adopted which go back to contributions by Eckart [11], Wilson [12], and Watson [13]. In particular, the Eckart equations [11] enable one to determine an orientation of molecule fixed axes suitable for using normal modes. The details of the derivation of a rovibrational Hamiltonian can be found in Ref. [12]. A significant simplification of this rovibrational Hamiltonian in terms of normal coordinates has been achieved by Watson [13, 14]. In fact the Watson Hamiltonian served as a starting point for many later investigations and is implemented, e.g., in the MULTIMODE program of Bowman, Carter, and coworkers [15]. In principle normal mode coordinates provide a very compact representation of the PES which is tailored, however, to the stationary point for which they have been defined. For large amplitude motions away from this stationary point the above mentioned reaction surface approach or the use of general curvilinear coordinates are more suitable. A detailed discussion of advantages and disadvantages of various coordinates for rovibrational Hamiltonians has been presented, e.g., in Ref. [16].**

In recent years Gatti and coworkers have developed a general scheme for obtaining a

1  
2  
3 KEO using vector parameterization, i.e., the non-trivial coordinates are expressed with  
4  $N - 1$  real vectors for system of  $N$  atoms [17–19]. This scheme is quite successful and  
5 convenient for a full dimensional description [20]. However, often one needs a reduced  
6 dimensional description leading to a problem with imposed constraints [21, 22]. Generally  
7 speaking in this case the coordinates can not be expressed as components of real vectors.  
8 Finally, we should point out that a numerical alternative to the analytical determination  
9 of the KEO has been suggested in Ref. [23].

10  
11  
12 In the present work we introduce a simple physical method of kinetic energy quanti-  
13 tation which directly quantises the classical Lagrange/Hamilton functions. The formal  
14 theory is presented in Section II. Here it is also shown that our method can be directly  
15 applied to constrained systems. In Section III the approach is applied to two molecular  
16 systems, that is,  $\text{H}_3\text{O}_2^-$  which is treated in full dimensionality and  $\text{N}_2\text{H}_7^+$  for which certain  
17 constraints are applied.

## 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

## II. GENERAL THEORY FOR OBTAINING A KEO

### A. Formal Development

In the following we focus on the most common cases where the kinetic energy includes purely quadratic terms and the potential energy does not depend on the velocity, although a generalisation would be straightforward. Further we adopt the laboratory reference frame (LRF). The classical Lagrange/Hamiltonian in terms of arbitrary variables can be written as

$$\begin{aligned}
 L(\mathbf{Q}, \dot{\mathbf{Q}}, t) &= T(\dot{\mathbf{Q}}) - V(\mathbf{Q}) = \frac{1}{2} \dot{\mathbf{Q}}^\dagger \mathbf{M} \dot{\mathbf{Q}} - V(\mathbf{Q}) \\
 H(\mathbf{Q}, \mathbf{P}) &= T(\mathbf{P}) + V(\mathbf{Q}) = \frac{1}{2} \mathbf{P}^\dagger \mathbf{M}^{-1} \mathbf{P} + V(\mathbf{Q}), \quad (1)
 \end{aligned}$$

where  $\mathbf{Q}$  and  $\mathbf{P}$  are single column vectors of the generalised coordinates and corresponding conjugate momenta, respectively. The generalised momentum vector is defined as  $\mathbf{P} = \partial L / \partial \dot{\mathbf{Q}} = \mathbf{M} \dot{\mathbf{Q}}$ . The generalised mass matrix,  $\mathbf{M}$ , in general is a function of the coordinates. We assume that it is defined such as to be Hermitian and “†” means Hermitian conjugate which is equivalent to the transpose in classical mechanics. In order to obtain the quantum mechanical Hamiltonian operator, the major task is to derive the quantum KEO in coordinate representation.

Since the choice of coordinates is quite arbitrary in Eq. (1), we start with Cartesian ones  $\{\mathbf{X}, \mathbf{P}_X\}$ ; in the following all the subscripts “ $X$ ” are associated with Cartesian coordinates.

The operator for each component of the momentum  $(\hat{\mathbf{P}}_X^\dagger)_j = (\hat{\mathbf{P}}_X)_j = -i\hbar\partial/\partial X_j$  is Hermitian. For non-Cartesian coordinates we define the momentum operator in the same way:

$$\hat{\mathbf{P}} = -i\hbar\frac{\partial}{\partial\mathbf{Q}}. \quad (2)$$

To obtain the quantum KEO in terms of non-Cartesian coordinates, we must exploit the coordinate transform relations,  $\mathbf{Q} = \mathbf{Q}(\mathbf{X})$ . The following relations can be derived easily

$$\begin{aligned} \dot{\mathbf{Q}} &= \frac{\partial\mathbf{Q}}{\partial\mathbf{X}}\dot{\mathbf{X}} \\ \hat{\mathbf{P}} &= \left(\frac{\partial\mathbf{X}}{\partial\mathbf{Q}}\right)^\dagger \hat{\mathbf{P}}_X \\ \frac{\partial\mathbf{Q}}{\partial\mathbf{X}} &= \left(\frac{\partial\mathbf{X}}{\partial\mathbf{Q}}\right)^{-1}, \end{aligned} \quad (3)$$

where the elements of the transformation matrices are defined as  $(\partial\mathbf{Q}/\partial\mathbf{X})_{ij} = \partial Q_i/\partial X_j$  and  $(\partial\mathbf{X}/\partial\mathbf{Q})_{ij} = \partial X_i/\partial Q_j$ . The quantum KEO in terms of non-Cartesian coordinates can be obtained by the simple coordinate transform from Cartesian coordinates

$$\begin{aligned} \hat{T} &= \frac{1}{2}\hat{\mathbf{P}}_X^\dagger \mathbf{M}_X^{-1} \hat{\mathbf{P}}_X \\ &= \frac{1}{2}\hat{\mathbf{P}}^\dagger \frac{\partial\mathbf{Q}}{\partial\mathbf{X}} \mathbf{M}_X^{-1} \left(\frac{\partial\mathbf{Q}}{\partial\mathbf{X}}\right)^\dagger \hat{\mathbf{P}}, \end{aligned} \quad (4)$$

where  $\mathbf{M}_X$  is the diagonal Cartesian mass matrix consisting of real mass associated with each Cartesian coordinate.

The momentum operator vector  $\hat{\mathbf{P}}$  can be replaced by the derivative operator  $\hat{\mathbf{P}} = -i\hbar\partial/\partial\mathbf{Q}$ . However, the expression for the Hermitian conjugate of momentum operator (HCMO) vector  $\hat{\mathbf{P}}^\dagger$  needs to be established yet. Since one has the relation between  $\hat{\mathbf{P}}$  and the Cartesian one  $\hat{\mathbf{P}}_X$  it is not difficult to directly apply the definition of Hermitian conjugation to Eq. (3)

$$\begin{aligned} (\hat{\mathbf{P}}^\dagger)_i &= \left( \left( \left( \frac{\partial\mathbf{X}}{\partial\mathbf{Q}} \right)^\dagger \hat{\mathbf{P}}_X \right)^\dagger \right)_i = \left( \hat{\mathbf{P}}_X^\dagger \frac{\partial\mathbf{X}}{\partial\mathbf{Q}} \right)_i \\ &= \sum_j (\hat{\mathbf{P}}_X)_j \left( \frac{\partial\mathbf{X}}{\partial\mathbf{Q}} \right)_{ji} \\ &= \sum_j \left( \frac{\partial\mathbf{X}}{\partial\mathbf{Q}} \right)_{ji} (\hat{\mathbf{P}}_X)_j + \sum_j \left[ (\hat{\mathbf{P}}_X)_j, \left( \frac{\partial\mathbf{X}}{\partial\mathbf{Q}} \right)_{ji} \right] \\ &= (\hat{\mathbf{P}})_i + \sum_j \left[ (\hat{\mathbf{P}}_X)_j, \left( \frac{\partial\mathbf{X}}{\partial\mathbf{Q}} \right)_{ji} \right], \end{aligned} \quad (5)$$

where the notation  $[\hat{A}, \hat{B}]$  means the commutator of two operators. Eq. (5) shows the non-Hermiticity of generalised momenta associated with non-Cartesian coordinates. Additional terms appear due to the non-commutability of the momenta and the transformation matrix. Using the basic commutator  $[\hat{X}_j, (\hat{P}_X)_k] = i\hbar\delta_{jk}$ , Eq. (5) can be simplified to (see also Ref. [24])

$$(\hat{P}^\dagger)_k = (\hat{P})_k - i\hbar \sum_j \left( \frac{\partial}{\partial X_j} \frac{\partial X_j}{\partial Q_k} \right)^\circ. \quad (6)$$

Here, the superscript  $^\circ$  means a differential operator inside the bracket can not operate on functions outside, in other words, the result is just normal function of coordinates.

Eq. (6) clearly shows the relation between a momentum operator and its Hermitian conjugate. Apparently, any set of functions of coordinates,  $\{f_j(Q_j)\}$ , can be multiplied from the left to the derivative operator in Eq. (2) yielding different schemes of momenta quantisation, i.e.,  $(\hat{P})_j = -i\hbar \cdot f_j(Q_j) \cdot \partial/\partial Q_j$  constitutes also an acceptable scheme. Since these momentum operators are in general non-Hermitian, we cannot simply set  $f_j(Q_j) = 1$ . For different schemes of momenta quantisation, the HCMOs will vary correspondingly to keep the KEO invariant. But, this enables us to optimise momenta quantisation schemes. In other words with proper functions one can obtain desired forms of momentum operators, e.g., symmetric forms.

With Eq. (4) and Eq. (5) we get the general scheme of constructing KEOs in terms of arbitrary coordinates. However, the final structure seems to be complicated and actually it can be simplified. To this end we compare Eq. (4) and Eq. (1) and take into account the invariance of the classical kinetic energy

$$\begin{aligned} T &= \frac{1}{2} \dot{\mathbf{Q}}^\dagger \mathbf{M} \dot{\mathbf{Q}} \\ &= \frac{1}{2} \dot{\mathbf{X}}^\dagger \mathbf{M}_X \dot{\mathbf{X}} \\ &= \frac{1}{2} \dot{\mathbf{Q}}^\dagger \left( \frac{\partial \mathbf{X}}{\partial \mathbf{Q}} \right)^\dagger \mathbf{M}_X \frac{\partial \mathbf{X}}{\partial \mathbf{Q}} \dot{\mathbf{Q}}. \end{aligned} \quad (7)$$

Since  $\dot{\mathbf{Q}}$  can be any vector we must have the relation  $\mathbf{M} = (\partial \mathbf{X} / \partial \mathbf{Q})^\dagger \mathbf{M}_X \partial \mathbf{X} / \partial \mathbf{Q}$ . Calculating the inverse of both sides we immediately see that the complicated central part  $(\partial \mathbf{Q} / \partial \mathbf{X}) \mathbf{M}_X^{-1} (\partial \mathbf{Q} / \partial \mathbf{X})^\dagger$  in Eq. (4) is exactly  $\mathbf{M}^{-1}$  in Eq. (1). The final KEO is therefore simplified as

$$\hat{T} = \frac{1}{2} \hat{\mathbf{P}}^\dagger \mathbf{M}^{-1} \hat{\mathbf{P}}. \quad (8)$$

This means we can directly exploit the result of Eq. (1) and quantise the generalised momenta without the knowledge of the Cartesian kinetic energy. All we need are the generalised mass matrix  $\mathbf{M}$  and the definition of coordinates which both appear in Eq. (1).

Therefore we can identify a concise and physically transparent scheme to construct the KEO:

1. Get the classical kinetic energy and make sure the mass matrix is symmetric, so that one has the same structure as Eq. (1),  $T(\dot{\mathbf{Q}}) = \frac{1}{2}\dot{\mathbf{Q}}^\dagger \mathbf{M} \dot{\mathbf{Q}}$ .
2. Exploit Eq. (5) or Eq. (6) to express HCMOs  $\hat{\mathbf{P}}^\dagger$  in terms of  $\hat{\mathbf{P}}$  and some functions of  $\mathbf{Q}$ .
3. Calculate the inverse matrix of  $\mathbf{M}$  hence the formal quantum KEO reads  $\hat{T} = \frac{1}{2}\hat{\mathbf{P}}^\dagger \mathbf{M}^{-1} \hat{\mathbf{P}}$ .
4. Replace  $\hat{\mathbf{P}}$  by  $-i\hbar\partial/\partial\mathbf{Q}$  for obtaining the coordinate representation.

The first step is quite familiar and one can choose arbitrary coordinates to get the classical kinetic energy. Actually we will introduce a useful partition method in Section II C which will significantly simplify this issue. The remaining three steps are quite straightforward to follow. Apparently, the major effort is in the second step, i.e. determining the HCMOs according to Eq. (6). However, for the familiar spherical coordinates the HCMOs are well-known which leads to a great simplification as shown in Section II D.

Apart from the KEO the volume element of integration is also of importance. Since we start from Cartesian coordinates and all that we have done is a coordinate transformation, the Euclidean normalisation remains correct:

$$d\tau = d\tau_X = \prod_i dX_i = |\text{Det} \left( \frac{\partial \mathbf{X}}{\partial \mathbf{Q}} \right)| \prod_i dQ_i. \quad (9)$$

## B. Systems with Constraints

Reduced dimensional descriptions are always necessary for large systems. In the following we will give the general description for systems with constraints. Considering a system with some active coordinates  $\mathbf{Q}_1$  and some frozen coordinates  $\mathbf{Q}_0$ , the full dimensional coordinates and corresponding conjugate momenta read

$$\mathbf{Q} = \begin{pmatrix} \mathbf{Q}_1 \\ \mathbf{Q}_0 \end{pmatrix} \quad \mathbf{P} = \begin{pmatrix} \mathbf{P}_1 \\ \mathbf{P}_0 \end{pmatrix}. \quad (10)$$



The constraining conditions are given by  $\dot{\mathbf{Q}}_0 = 0$ . Thus we can obtain the constrained classical kinetic energy

$$\begin{aligned}
 T &= \frac{1}{2} \dot{\mathbf{Q}}^\dagger \mathbf{M} \dot{\mathbf{Q}} \\
 &= \frac{1}{2} \begin{pmatrix} \dot{\mathbf{Q}}_1^\dagger & \dot{\mathbf{Q}}_0^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{M}_{11} & \mathbf{M}_{10} \\ \mathbf{M}_{01} & \mathbf{M}_{00} \end{pmatrix} \begin{pmatrix} \dot{\mathbf{Q}}_1 \\ \dot{\mathbf{Q}}_0 \end{pmatrix} \\
 &= \frac{1}{2} \dot{\mathbf{Q}}_1^\dagger \mathbf{M}_{11} \dot{\mathbf{Q}}_1,
 \end{aligned} \tag{11}$$

where  $\mathbf{M}_{ij}$  are corresponding sub-matrices.

To get the quantum KEO we have to rewrite the constraint conditions in terms of momenta. According to the definition of momenta it is not difficult to find the following relation

$$\begin{aligned}
 \begin{pmatrix} \dot{\mathbf{Q}}_1 \\ \dot{\mathbf{Q}}_0 \end{pmatrix} &= \begin{pmatrix} \mathbf{M}_{11} & \mathbf{M}_{10} \\ \mathbf{M}_{01} & \mathbf{M}_{00} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{P}_1 \\ \mathbf{P}_0 \end{pmatrix} \\
 &= \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} \begin{pmatrix} \mathbf{P}_1 \\ \mathbf{P}_0 \end{pmatrix},
 \end{aligned} \tag{12}$$

where  $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix}$  is the inverse of matrix  $\mathbf{M}$ . Thus one can rewrite the constraint conditions as  $\mathbf{C}\mathbf{P}_1 + \mathbf{D}\mathbf{P}_0 = 0$  or  $\mathbf{P}_0 = -\mathbf{D}^{-1}\mathbf{C}\mathbf{P}_1$ . After quantization we get the constraint relation for the corresponding quantum operators, i.e.,  $\hat{\mathbf{P}}_0 = -\mathbf{D}^{-1}\mathbf{C}\hat{\mathbf{P}}_1$ . Based on this observation we can obtain the quantum KEO

$$\begin{aligned}
 \hat{T} &= \frac{1}{2} \hat{\mathbf{P}}^\dagger \mathbf{M}^{-1} \hat{\mathbf{P}} \\
 &= \frac{1}{2} \begin{pmatrix} \hat{\mathbf{P}}_1^\dagger & \hat{\mathbf{P}}_0^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{M}_{11} & \mathbf{M}_{10} \\ \mathbf{M}_{01} & \mathbf{M}_{00} \end{pmatrix}^{-1} \begin{pmatrix} \hat{\mathbf{P}}_1 \\ \hat{\mathbf{P}}_0 \end{pmatrix} \\
 &= \frac{1}{2} \begin{pmatrix} \hat{\mathbf{P}}_1^\dagger & (-\mathbf{D}^{-1}\mathbf{C}\hat{\mathbf{P}}_1)^\dagger \end{pmatrix} \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} \begin{pmatrix} \hat{\mathbf{P}}_1 \\ -\mathbf{D}^{-1}\mathbf{C}\hat{\mathbf{P}}_1 \end{pmatrix} \\
 &= \frac{1}{2} \hat{\mathbf{P}}_1^\dagger (\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C}) \hat{\mathbf{P}}_1 \\
 &= \frac{1}{2} \hat{\mathbf{P}}_1^\dagger \mathbf{M}_{11}^{-1} \hat{\mathbf{P}}_1.
 \end{aligned} \tag{13}$$

The final result is quite compact. Comparing Eq. (11) with Eq. (13) we observe that the *same procedure* mentioned in the full dimensional case can be followed provided we only consider the active coordinates and completely ignore the frozen ones from the very

beginning when we generate the classical Lagrangian. This is an attractive point since when we need to deal with constrained systems the present scheme only requires the classical Lagrangian which can be obtained by traditional methods.

### C. A General Method for Partitioning the Classical Kinetic Energy

So far we have given the general theory of kinetic energy quantization starting from the classical Lagrangian. In the following we will introduce a method for obtaining the classical kinetic energy with a partitioning technique which will greatly simplify the problem in most cases. In general it is quite convenient to divide a large system into small subsystems especially when a subsystems has certain symmetry. If we arbitrarily divide a system into  $N$  parts the kinetic energy is a sum of the  $N$  subsystems. According to the König theorem,

$$T = \sum_{i=1}^N T_i^0 = T_{(C)}^0 + \sum_{i=1}^N T_i^{(C)}, \quad (14)$$

where  $T_A^B$  is the kinetic energy of the part  $A$  with respect to the reference frame defined by  $B$ . Here 0 is the laboratory reference frame and  $(C)$  is the centre of mass reference frame.

In the special case when  $N = 2$  the following relation can be obtained

$$\sum_{i=1}^N T_i^{(C)} = T_1^{(C)} + T_2^{(C)} = T_1^{(C_1)} + T_2^{(C_2)} + T_{(C_1)}^{(C_2)}, \quad (15)$$

where  $(C_i)$  is the centre of mass of the  $i$ th part and  $T_{(C_1)}^{(C_2)}$  is the kinetic energy of the centre of mass of the first part with respect to the centre of mass of the second part. If the two parts are both mass points Eq. (15) can be simplified as follows

$$T_1^{(C)} + T_2^{(C)} = T_{(C_1)}^{(C_2)} = T_{(C_2)}^{(C_1)}, \quad (16)$$

which is a familiar result from two-body mechanics. By exploiting Eq. (15) repeatedly we can easily express the total kinetic energy in terms of kinetic energies of subsystems which are much easier to obtain as will be seen in the following.

### D. Hermitian Conjugates of Momentum Operators

As mentioned in Section II A, the most tedious task for generating a KEO is to derive the expressions for the HCMOs. As an example let us consider a system described by the

3D spherical coordinates  $\{R, \theta, \varphi\}$ . The coordinate transformation between 3D spherical coordinates and 3D Cartesian ones  $\{x, y, z\}$  is defined as

$$\begin{aligned}x &= R \sin \theta \cos \varphi \\y &= R \sin \theta \sin \varphi \\z &= R \cos \theta.\end{aligned}\quad (17)$$

Here, we only give the corresponding HCMOs leading to the well-known KEO (for details, see Appendix V A)

$$\begin{aligned}\hat{P}_R^\dagger &= \hat{P}_R - \frac{2i\hbar}{R} = -i\hbar \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \\ \hat{P}_\theta^\dagger &= \hat{P}_\theta - i\hbar \cot \theta = -i\hbar \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \\ \hat{P}_\varphi^\dagger &= \hat{P}_\varphi = -i\hbar \frac{\partial}{\partial \varphi} \\ \hat{T} &= -\frac{\hbar^2}{2m} \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} - \frac{\hbar^2}{2m R^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{\hbar^2}{2m R^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}.\end{aligned}\quad (18)$$

So far our considerations have been concerned with the LRF. However, in order to describe a molecule in terms of its natural motions, e.g., bond lengths and bond angles, it is usually more convenient to use one or more molecular reference frames (MRFs). In the following we will discuss this point and derive results for HCMOs associated with MRF spherical coordinates. Consider the LRF and a MRF defined by sets of unit vectors  $\{\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z\}$  and  $\{\mathbf{e}_{x'}, \mathbf{e}_{y'}, \mathbf{e}_{z'}\}$ , respectively. The relation between the LRF and the MRF is just an orthogonal transformation characterised by the three Euler angles  $\{\vartheta, \phi, \chi\}$

$$\mathbf{e}_{\alpha'} = \mathbf{U}_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{e}_\alpha, \quad (19)$$

where  $\alpha = x, y, z$  and  $\mathbf{U}_\alpha$  is a rotation around  $\mathbf{e}_\alpha$ . (The expression for the rotational transformation matrix  $\mathbf{U}_\alpha$  and more details on the following derivations can be found in the Appendix V A.)

Now let us consider a vector  $\mathbf{R}_j$  characterised by three spherical coordinates  $\{R_j, \theta_j, \varphi_j\}$  in the MRF. According to Appendix V A, Eq. (46), we can express  $\mathbf{R}_j$  as

$$\mathbf{R}_j = R_j \mathbf{U}_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{U}_z(\varphi_j) \mathbf{U}_y(\theta_j) \mathbf{e}_z. \quad (20)$$

This is a vector equation and we can obtain the Cartesian coordinates of  $\mathbf{R}_j$  in LRF by projecting the equation onto each LRF axis. Based on Eq. (20) we can exploit Eq. (6) to derive the expressions for HCMOs associated with MRF coordinates. The final results

are quite concise and they actually have the same form as those associated with LRF spherical coordinates. That is to say, that for the momentum operators associated with  $\mathbf{R}_j$  ( $R_j, \theta_j, \varphi_j$ ) the following relations are valid

$$\begin{aligned}\hat{P}_{R_j}^\dagger &= \hat{P}_{R_j} - \frac{2i\hbar}{R_j} = -i\hbar \frac{1}{R_j^2} \frac{\partial}{\partial R_j} R_j^2 \\ \hat{P}_{\theta_j}^\dagger &= \hat{P}_{\theta_j} - i\hbar \cot \theta_j = -i\hbar \frac{1}{\sin \theta_j} \frac{\partial}{\partial \theta_j} \sin \theta_j \\ \hat{P}_{\varphi_j}^\dagger &= \hat{P}_{\varphi_j} = -i\hbar \frac{\partial}{\partial \varphi_j}.\end{aligned}\quad (21)$$

In Appendix V A we also confirm that the momentum operators associated with MRF Cartesian coordinates are Hermitian (cf. Eq. (63)). This result is quite important as it shows that one does not need to take the effort to derive the expressions for HCMOs provided that one uses spherical coordinates, Cartesian coordinates or combinations of both, no matter whether they are defined in the LRF or MRFs.

### E. Angular Momentum and Rotation

For a system with  $N$  atoms we have  $3N$  degrees of freedom (DOFs). They are normally divided into three translational DOFs, three rotational and  $3N - 6$  vibrational ones. The three translational DOFs can be separated while the remaining  $3N - 3$  DOFs are coupled. In general rotational excitation energies are quite small as compared with vibrational ones suggesting an approximate separation. For the following discussion it will be convenient to express the KEO as sum of rotational (three angles) and vibrational ( $3N - 6$  other coordinates) parts as well as their coupling. Specifically, we exploit the 3D vector  $\mathbf{Q}_{\text{rot}}$  defined as

$$\mathbf{Q}_{\text{rot}}^\dagger = (\vartheta \ \phi \ \chi) \quad (22)$$

containing the three Euler angles which connect the LRF and MRF according to Eq. (19). The kinetic energy and total angular momentum  $\mathbf{J}$  are defined as

$$\begin{aligned}2T &= \sum_{i=1}^N m_i \dot{\mathbf{R}}_i^\dagger \dot{\mathbf{R}}_i \\ \mathbf{J} &= \sum_{i=1}^N m_i \mathbf{R}_i \times \dot{\mathbf{R}}_i.\end{aligned}\quad (23)$$

With  $\dot{\mathbf{Q}}_{\text{rot}}$  being the angular velocity of MRF the velocities can be re-expressed as

$$\dot{\mathbf{R}}_i = \dot{\mathbf{Q}}_{\text{rot}} \times \mathbf{R}_i + \dot{\mathbf{R}}'_i, \quad (24)$$

where  $\dot{\mathbf{R}}'_i$  is the velocity of  $\mathbf{R}_i$  measured in the MRF. With the help of Eq. (24) and some vector algebra we can rewrite the kinetic energy and angular momentum as

$$\begin{aligned}
 2T &= \sum_{i=1}^N m_i \left( R_i^2 \dot{\mathbf{Q}}_{\text{rot}}^\dagger \dot{\mathbf{Q}}_{\text{rot}} - (\dot{\mathbf{Q}}_{\text{rot}}^\dagger \mathbf{R}_i)^2 + \dot{\mathbf{R}}'_i{}^\dagger \dot{\mathbf{R}}'_i + 2\dot{\mathbf{Q}}_{\text{rot}}^\dagger (\mathbf{R}_i \times \dot{\mathbf{R}}'_i) \right) \\
 \mathbf{J} &= \sum_{i=1}^N m_i \left( R_i^2 \dot{\mathbf{Q}}_{\text{rot}} - (\dot{\mathbf{Q}}_{\text{rot}}^\dagger \mathbf{R}_i) \mathbf{R}_i + (\mathbf{R}_i \times \dot{\mathbf{R}}'_i) \right).
 \end{aligned} \tag{25}$$

Using Eqs. (25) it is straightforward to derive the following relation

$$\mathbf{J} = \frac{\partial T}{\partial \dot{\mathbf{Q}}_{\text{rot}}}, \tag{26}$$

which is exactly the definition of the generalised momentum vector  $\mathbf{P}_{\text{rot}}$  associated with the three Euler angles.

Now we can draw the following important conclusion. If the set of coordinates contains the three Euler angles  $\{\vartheta, \phi, \chi\}$ , the total angular momentum vector is just the generalised momentum vector associated with the three Euler angles

$$\begin{aligned}
 J_\vartheta &= P_\vartheta = \frac{\partial T}{\partial \dot{\vartheta}} \\
 J_\phi &= P_\phi = \frac{\partial T}{\partial \dot{\phi}} \\
 J_\chi &= P_\chi = \frac{\partial T}{\partial \dot{\chi}} \\
 \mathbf{J} &= \mathbf{e}_\vartheta P_\vartheta + \mathbf{e}_\phi P_\phi + \mathbf{e}_\chi P_\chi.
 \end{aligned} \tag{27}$$

However, since the direction of angular velocities  $\{\mathbf{e}_\vartheta, \mathbf{e}_\phi, \mathbf{e}_\chi\}$  are complicated, it is better to transform the expressions to the Cartesian components in the LRF [12], i.e.

$$\begin{aligned}
 J_x &= \sin \chi P_\vartheta - \csc \vartheta \cos \chi P_\phi + \cot \vartheta \cos \chi P_\chi \\
 J_y &= \cos \chi P_\vartheta + \csc \vartheta \sin \chi P_\phi - \cot \vartheta \sin \chi P_\chi \\
 J_z &= P_\chi.
 \end{aligned} \tag{28}$$

Using Eq. (28) it is straightforward to express the KEO in terms of total angular momentum and generalised momenta associated with vibrational DOFs. In other words, starting from Eq. (25) the KEO can be readily expressed as contributions of rotational part, vibrational part and their coupling.

If the focus is on the vibrational spectrum, there are several arguments for neglecting rotational excitations. There is usually a clear time scale separation, that is, rotational excitation energies are much smaller than vibrational ones. If we are not aiming at high

1  
2  
3 resolution spectroscopy, rotational excitation will show up merely as a broadening of the  
4 vibrational bands and the band shifts of vibrational transitions due to the coupling can  
5 be considered as being much smaller than the accuracy achievable by the quantum chem-  
6 istry and quantum dynamics methods for obtaining the spectra. Therefore the following  
7 considerations will assume that rotational motion can be neglected, that is, we will set  
8  $\hat{\mathbf{J}} = 0$  or  $\hat{P}_\vartheta = \hat{P}_\phi = \hat{P}_\chi = 0$ .  
9  
10  
11  
12  
13  
14  
15

### 16 III. APPLICATIONS

17  
18  
19 In the following we will give two applications of the present approach. First, we  
20 will consider the full-dimensional KEO for  $\text{H}_3\text{O}_2^-$  employing polyspherical coordinates  
21 as introduced in more detail in Appendix V B. Second, we consider  $\text{N}_2\text{H}_7^+$  under the  
22 assumption of certain constraints and using bond length and angle coordinates.  
23  
24  
25  
26  
27

#### 28 A. Full Dimensional KEO for $\text{H}_3\text{O}_2^-$

29  
30  
31 In this section we will give the full dimensional KEO for the monohydrated hydroxide  
32 ion,  $\text{H}_3\text{O}_2^-$ , which had been used in the study of different isotopomers in Ref. [25]. The  
33 coordinates are defined in the MRF given by Eq. (19). The four Jacobi vectors shown in  
34 Fig. 1 are adopted. The three Euler angles are chosen in the same way as introduced in  
35 Section V B, i.e., the MRF spherical coordinates  $\mathbf{R}_4$  and  $\mathbf{R}_1$  are  $(R_4, 0, 0)$  and  $(R_1, \theta_1, 0)$ ,  
36 respectively. The other two vectors can be characterised by their spherical coordinates  
37 in the MRF  $(R_j, \theta_j, \varphi_j)$  ( $j = 2, 3$ ). We can calculate the  $\mathbf{G}$  matrix according to Eq. (76)  
38 and the required matrix elements are shown in Eq. (78). Therefore, we can directly write  
39 down the exact 9D KEO for total angular momentum  $\mathbf{J} = 0$  as  $2\hat{T}_{\text{vib}} = \hat{\mathbf{P}}_{\text{vib}}^\dagger \mathbf{G}_{\text{vib}} \hat{\mathbf{P}}_{\text{vib}}$   
40 with the HCMOs given in Section II D. However, this KEO will contain a large number  
41 of terms describing the angular momentum coupling between the shared Hydrogen and  
42 the  $(\text{OH})_2$  fragments. In order to simplify the KEO we will derive an approximate KEO  
43 which has the advantage that these couplings do not appear.  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53

54 The basic idea is to introduce a new MRF and express  $\mathbf{R}_3$  with Cartesian coordi-  
55 nates  $(x, y, z)$ . The remaining six coordinates are spherical coordinates in the old MRF  
56  $(R_1, R_2, \theta_1, \theta_2, R_4, \varphi = \varphi_2)$ . The new MRF is associated with the old MRF by a rotation  
57 of an angle  $\eta\varphi$  around the  $\mathbf{R}_4$  (the  $z$ -axis). The spherical coordinates for  $\mathbf{R}_3$  in the new  
58 MRF are  $(R_3, \theta_3, \tilde{\varphi}_3)$  with  $\tilde{\varphi}_3 = \varphi_3 - \eta\varphi$ , where  $\eta = \mu_1/(\mu_1 + \mu_2)$  is defined to minimise  
59  
60

the Coriolis type couplings involving the central Hydrogen. Here,  $\mu_1$  ( $\mu_2$ ) is the reduced mass associated with the Jacobi vector  $\mathbf{R}_1$  ( $\mathbf{R}_2$ ). After transforming the spherical coordinates  $(R_3, \theta_3, \tilde{\varphi}_3)$  to the Cartesian ones  $(x, y, z)$  we can obtain the KEO for the central Hydrogen

$$T_3 = -\frac{\hbar^2}{2\mu_3} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right), \quad (29)$$

where  $\mu_3$  is the reduced mass associated with the Jacobi vector  $\mathbf{R}_3$  and Coriolis type terms are ignored. Since the  $\mathbf{e}'_z$  is defined along the direction of  $\mathbf{R}_4$ , the  $z$  coordinate corresponds to the shared Hydrogen stretching vibration.

For the other 6 DOFs of the  $(\text{OH})_2$  fragment, the 6D KEO is written in terms of the  $\mathbf{G}_{\text{vib}}$  matrix elements Eq. (78). Here we take the angular momentum of the  $(\text{OH})_2$  fragment as total angular momentum since the angular momentum of the shared Hydrogen is negligible. Combining both parts we finally obtain the 9D KEO where we introduce the new coordinates  $u_i = \cos \theta_i$  ( $i = 1, 2$ ). For the simulation an additional normalisation transform was performed to reduce the numerical effort. This gives the following 9D KEO:

$$T = T_1 + T_2 + T_3 \quad (30)$$

with

$$T_1 = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial R_2^2} - \frac{\hbar^2}{2\mu_4} \frac{\partial^2}{\partial R_4^2} \quad (31)$$

$$\begin{aligned} T_2 = & -\sum_{i=1,2} \left( \frac{1}{2\mu_i R_i^2} + \frac{1}{2\mu_4 R_4^2} \right) \frac{\partial}{\partial u_i} (1 - u_i^2) \frac{\partial}{\partial u_i} \\ & - \sum_{i=1,2} \left( \frac{1}{2\mu_i R_i^2} \frac{1}{1 - u_i^2} + \frac{1}{2\mu_4 R_4^2} \frac{u_i^2}{1 - u_i^2} \right) \frac{\partial^2}{\partial \varphi^2} \\ & + \frac{1}{\mu_4 R_4^2} \frac{u_1}{\sqrt{1 - u_1^2}} \frac{u_2}{\sqrt{1 - u_2^2}} \frac{\partial}{\partial \varphi} \cos \varphi \frac{\partial}{\partial \varphi} \\ & - \frac{1}{2\mu_4 R_4^2} \left( \sqrt{1 - u_1^2} \frac{\partial}{\partial u_1} \frac{\partial}{\partial u_2} \sqrt{1 - u_2^2} + \frac{\partial}{\partial u_1} \sqrt{1 - u_1^2} \sqrt{1 - u_2^2} \frac{\partial}{\partial u_2} \right) \\ & - \frac{1}{2\mu_4 R_4^2} \frac{u_2}{\sqrt{1 - u_2^2}} \left( \frac{\partial}{\partial \varphi} \sin \varphi \sqrt{1 - u_1^2} \frac{\partial}{\partial u_1} + \frac{\partial}{\partial u_1} \sqrt{1 - u_1^2} \sin \varphi \frac{\partial}{\partial \varphi} \right) \\ & - \frac{1}{2\mu_4 R_4^2} \frac{u_1}{\sqrt{1 - u_1^2}} \left( \frac{\partial}{\partial \varphi} \sin \varphi \sqrt{1 - u_2^2} \frac{\partial}{\partial u_2} + \frac{\partial}{\partial u_2} \sqrt{1 - u_2^2} \sin \varphi \frac{\partial}{\partial \varphi} \right). \quad (32) \end{aligned}$$

The non-Euclidean normalisation according to the volume element is  $d_\tau = dR_1 dR_2 dR_4 dx dy dz du_1 du_2 d\varphi$ . The reduced masses for different isotopomers are defined as follows:  $\text{HOHOH}^- - \mu_1 = \mu_2 = m_{\text{H}} m_{\text{O}} / (m_{\text{H}} + m_{\text{O}})$ ,  $\mu_3 = 2m_{\text{H}}(m_{\text{H}} + m_{\text{O}}) / (3m_{\text{H}} + 2m_{\text{O}})$ ,  $\mu_4 = (m_{\text{H}} + m_{\text{O}}) / 2$ ;  $\text{HODOH}^- - \mu_3 = 2m_{\text{D}}(m_{\text{H}} + m_{\text{O}}) / (m_{\text{D}} + 2m_{\text{H}} + 2m_{\text{O}})$ ;  $\text{HOHOD}^- -$

1  
2  
3  
4  $\mu_1 = m_D m_O / (m_H + m_O)$  and  $\mu_3$  and  $\mu_4$  change correspondingly. For DODOD<sup>-</sup> the cor-  
5 responding masses of HOHOH<sup>-</sup> are modified by replacing  $m_H$  by  $m_D$ . In the same way  
6 we get the masses for DOHOD<sup>-</sup> by exchanging  $m_H$  and  $m_D$  in HODOH<sup>-</sup>, and similarly  
7 one can obtain DODOH<sup>-</sup> from DOHOH<sup>-</sup>.  
8  
9

## 10 11 12 **B. Reduced Dimensional KEO for N<sub>2</sub>H<sub>7</sub><sup>+</sup>**

13  
14  
15 In this section we give an example for a KEO for a system with constraints stressing  
16 again that our method is invariant for reduced dimensional descriptions. Specifically  
17 we focus on the protonated ammonia dimer, N<sub>2</sub>H<sub>7</sub><sup>+</sup>, whose IR spectrum in the range <  
18 1500 cm<sup>-1</sup> had been discussed in Ref. [26] on the basis of a 5D model including only  
19 the asymmetric stretching vibration of the shared proton. Subsequently, the model was  
20 extended to account for the two degenerate bendings as well in Ref. [27]. Here we will  
21 derive the 5D model and comment on its extension. A reasonable reduced description for  
22 the spectrum which is influenced by the shared proton motion should take into account  
23 the following two conditions: (i) experimental data suggest that the relevant energy range  
24 is presumably below 1000 cm<sup>-1</sup>, but might extend into the < 1500 cm<sup>-1</sup> range due to  
25 combination bands and (ii) symmetry selection rules dominate the anharmonic couplings  
26 especially in this low-energy range. Therefore, we first assume that the C<sub>3</sub> symmetry of  
27 the N<sub>2</sub>H<sub>6</sub> fragment, i.e., excluding the central proton, will not be broken. Second, the  
28 length of the N-H covalent bonds shall be fixed. Notice that this neglects the bending  
29 motion of the shared proton perpendicular to the line connecting the two nitrogen atoms.  
30 This is justified by the different symmetry and the lower anharmonicity of these two  
31 modes as compared to the proton motion along the N-N line. These constraints leave five  
32 internal coordinates to describe the system as shown in Fig. 2, i.e., the shared proton  
33 stretching with respect to the center of mass of the rest N<sub>2</sub>H<sub>6</sub> fragment,  $z$ , the relative  
34 motion of the centres of mass of the two ammonia,  $R$ , the umbrella type motion of the  
35 two ammonia,  $\theta_1$  and  $\theta_2$ , and the rotation (torsion) of the NH<sub>3</sub> fragments with respect to  
36 each other,  $\varphi$ .  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54

55 For these five active coordinates the classical kinetic energy with all other internal  
56  
57  
58  
59  
60



coordinates frozen can be obtained by exploiting Eq. (15) repeatedly

$$\begin{aligned}
 T &= T_{(\text{H})}^{(\text{N}_2\text{H}_6)} + T_{\text{N}_2\text{H}_6}^{(\text{N}_2\text{H}_6)} \\
 &= T_{(\text{H})}^{(\text{N}_2\text{H}_6)} + T_{\text{NH}_3}^{(\text{NH}_3)} + T_{\text{NH}_3'}^{(\text{NH}_3')} + T_{(\text{NH}_3)}^{(\text{NH}_3')} \\
 &= T_{(\text{H})}^{(\text{N}_2\text{H}_6)} + T_{(\text{NH}_3)}^{(\text{NH}_3')} + \left( T_{\text{H}_3}^{(\text{H}_3)} + T_{(\text{N})}^{(\text{H}_3)} \right) + \left( T_{\text{H}_3'}^{(\text{H}_3')} + T_{(\text{N}')}^{(\text{H}_3')} \right), \quad (33)
 \end{aligned}$$

where (AB) is the center of mass of AB. It is straightforward to obtain each term in above equation

$$\begin{aligned}
 T_{(\text{H})}^{(\text{N}_2\text{H}_6)} &= \frac{1}{2} \mu_p \dot{z}^2 \\
 T_{(\text{NH}_3)}^{(\text{NH}_3)} &= \frac{1}{2} \mu_R \dot{R}^2 \\
 T_{\text{H}_3}^{(\text{H}_3)} &= \frac{3}{2} m_{\text{H}} \left( \frac{d(R_0 \sin \theta_i)}{dt} \right)^2 + \frac{3}{2} m_{\text{H}} (R_0 \sin \theta_i)^2 \dot{\varphi}_i^2 \\
 T_{(\text{N})}^{(\text{H}_3)} &= \frac{1}{2} \mu_{(\text{N}-3\text{H})} \left( \frac{d(R_0 \cos \theta_i)}{dt} \right)^2, \quad (34)
 \end{aligned}$$

where  $\mu_p = 2m_{\text{H}}(3m_{\text{H}} + m_{\text{N}})/(7m_{\text{H}} + 2m_{\text{N}})$ ,  $\mu_R = \frac{1}{2}(3m_{\text{H}} + m_{\text{N}})$  and  $\mu_{(\text{N}-3\text{H})} = 3m_{\text{H}}m_{\text{N}}/(3m_{\text{H}} + m_{\text{N}})$ . The orientation angle of each individual ammonia is denoted by  $\varphi_{1,2}$  and only the difference between them is the torsion shown in Fig. 2 and  $R_0$  is the free N-H covalent bond length. Thus the final kinetic energy is

$$\begin{aligned}
 T &= \frac{1}{2} \mu_p \dot{z}^2 + \mu_R \dot{R}^2 + \frac{3m_{\text{H}}m_{\text{N}}}{2(3m_{\text{H}} + m_{\text{N}})} R_0^2 \left( \dot{\theta}_1^2 \sin^2 \theta_1 + \dot{\theta}_2^2 \sin^2 \theta_2 \right) \\
 &\quad + \frac{3}{2} m_{\text{H}} R_0^2 \sum_{i=1,2} \left( \dot{\theta}_i^2 \cos^2 \theta_i + \dot{\varphi}_i^2 \sin^2 \theta_i \right) \\
 &= \frac{1}{2} \mu_p \dot{z}^2 + \frac{1}{2} \mu_R \dot{R}^2 + \frac{1}{2} I_{\text{vib}}(\theta_1) \dot{\theta}_1^2 + \frac{1}{2} I_{\text{vib}}(\theta_2) \dot{\theta}_2^2 \\
 &\quad + \frac{1}{2} I_{\text{rot}}(\theta_1) \dot{\varphi}_1^2 + \frac{1}{2} I_{\text{rot}}(\theta_2) \dot{\varphi}_2^2, \quad (35)
 \end{aligned}$$

where  $I_{\text{vib}}(\theta) = I_0(\cos^2 \theta + m_{\text{N}} \sin^2 \theta)/(3m_{\text{H}} + m_{\text{N}})$ ,  $I_{\text{rot}}(\theta) = I_0 \sin^2 \theta$  and  $I_0 = 3m_{\text{H}} R_0^2$ . The last two terms in above equation can be rewritten and after separation of the global rotation we finally simplify the kinetic energy as

$$T = \frac{1}{2} \mu_p \dot{z}^2 + \frac{1}{2} \mu_R \dot{R}^2 + \sum_{i=1,2} \frac{1}{2} I_{\text{vib}}(\theta_i) \dot{\theta}_i^2 + \frac{1}{2} I_{\text{tor}}(\theta_1, \theta_2) \dot{\varphi}^2, \quad (36)$$

where the reduced moment of inertia for the torsion is  $I_{\text{tor}}(\theta_1, \theta_2) = I_{\text{rot}}(\theta_1) I_{\text{rot}}(\theta_2) / (I_{\text{rot}}(\theta_1) + I_{\text{rot}}(\theta_2))$ .

So far we did not consider the Coriolis type couplings with total angular velocity. However, due to the  $C_3$  symmetry, the total angular momentum equals to zero is equivalent

to total angular velocity equals to zero for this specific case since none of the adopted coordinates contributes to total angular momentum. Therefore the Coriolis type couplings are zero.

According to the general procedure detailed in Section II A we can obtain the following quantum KEO ( $\varphi = \varphi_2 - \varphi_1$ )

$$\begin{aligned} \hat{T} = & \frac{1}{2\mu_p} \hat{P}_z^\dagger \hat{P}_z + \frac{1}{2\mu_R} \hat{P}_R^\dagger \hat{P}_R + \frac{\hat{P}_\varphi^\dagger \hat{P}_\varphi}{2I_{\text{tor}}(\theta_1, \theta_2)} \\ & + \frac{1}{2} \hat{P}_{\theta_1}^\dagger I_{\text{vib}}^{-1}(\theta_1) \hat{P}_{\theta_1} + \frac{1}{2} \hat{P}_{\theta_2}^\dagger I_{\text{vib}}^{-1}(\theta_2) \hat{P}_{\theta_2}. \end{aligned} \quad (37)$$

Inspecting the adopted coordinates we notice that one of them is Cartesian and the other four are spherical coordinates defined in MRF. Therefore, according to Section II D the HCMOs are given by

$$\begin{aligned} \hat{P}_z^\dagger &= \hat{P}_z \\ \hat{P}_R^\dagger &= \hat{P}_R - \frac{2i\hbar}{R} \\ \hat{P}_{\theta_j}^\dagger &= \hat{P}_{\theta_j} - i\hbar \cot \theta_j, j = 1, 2 \\ \hat{P}_\varphi^\dagger &= \hat{P}_\varphi. \end{aligned} \quad (38)$$

Hence the final KEO and the Euclidean normalisation condition are given as follows

$$\begin{aligned} \hat{T} = & -\frac{\hbar^2}{2\mu_p} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2\mu_R} \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \\ & - \frac{\hbar^2}{2I_{\text{tor}}(\theta_1, \theta_2)} \frac{\partial^2}{\partial \varphi^2} - \frac{\hbar^2}{2} \sum_{i=1,2} \frac{1}{\sin \theta_i} \frac{\partial}{\partial \theta_i} \frac{\sin \theta_i}{I_{\text{vib}}(\theta_i)} \frac{\partial}{\partial \theta_i} \\ d\tau = & R^2 \sin \theta_1 \sin \theta_2 dz dR d\theta_1 d\theta_2 d\varphi. \end{aligned} \quad (39)$$

In Ref. [27] we have extended this model by including the shared proton bending coordinates  $x$  and  $y$  as shown in Fig. 2. In terms of the KEO this is straightforward since in Eq. (34) we simply have to set

$$T_{(\text{H})}^{(\text{N}_2\text{H}_6)} = \frac{1}{2}\mu_p(\dot{z}^2 + \dot{x}^2 + \dot{y}^2) \quad (40)$$

which is carried through the derivation to give a corresponding contribution to Eq. (39). Compared to the experiment this gives a rather good description of the bending fundamental transitions as well as an improvement concerning the shared proton fundamental stretching transition.

#### IV. SUMMARY

In summary we have presented a new method for obtaining kinetic energy operators which involves a straightforward quantisation of the classical Lagrange/Hamilton function. It is based on the notion of hermitian conjugate momentum operators whose derivation presents the major effort for practical applications. An important point of our approach is its validity for systems with constraints. This makes it particularly attractive for studying larger systems in reduced dimensionality.

We have applied our approach to the case of a general system described by polyspherical coordinates and showed the equivalence of the kinetic energy operator with that obtained by the method of Gatti and coworkers. Afterwards we discussed two specific applications to charged cluster systems having strong hydrogen bonds. The strong coupling between different coordinates as well their structural floppiness makes it necessary to perform high dimensional quantum dynamics simulations as done in Refs. [25–27] on the basis of the kinetic energy operators derived in Section III.

#### V. APPENDIX

##### A. Hermitian Conjugate Momentum Operators for Spherical Coordinates

The derivation of the expressions for the HCMOs in LRF is the most tedious part of the present method and it becomes even more involved if coordinates defined in MRFs are used. In this Appendix we will first summarise the relevant relations between the LRF and MRFs and subsequently turn to the derivation of HCMOs.

Consider the LRF defined by three orthogonal unit vectors  $\{\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z\}$  and a MRF defined by three orthogonal unit vectors  $\{\mathbf{e}_{x'}, \mathbf{e}_{y'}, \mathbf{e}_{z'}\}$ . The orientation angles of  $\mathbf{e}_{z'}$  in the LRF are  $(\vartheta, \phi)$ . To obtain the connection between the LRF and the MRF we first apply two excessive rotations  $\mathbf{U}_y(\vartheta)$  and  $\mathbf{U}_z(\phi)$  to the LRF, where  $\mathbf{U}_y(\theta)$  means rotating  $\vartheta$  around  $\mathbf{e}_y$  and  $\mathbf{U}_z(\phi)$  means rotating  $\phi$  around  $\mathbf{e}_z$ . The matrix representation of them

are

$$\begin{aligned}\mathbf{U}_y(\vartheta) &= \begin{pmatrix} \cos \vartheta & 0 & \sin \vartheta \\ 0 & 1 & 0 \\ -\sin \vartheta & 0 & \cos \vartheta \end{pmatrix} \\ \mathbf{U}_z(\phi) &= \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}.\end{aligned}\quad (41)$$

The new reference frame generated by applying  $\mathbf{U}_y(\vartheta)$  and  $\mathbf{U}_z(\phi)$  to the LRF has the same  $z$  axis as the MRF, i.e., the only difference between the two reference frames is just a rotation by  $\chi$  around  $\mathbf{e}_{z'}$ . Therefore, the MRF can be obtained by applying three successive rotations  $\mathbf{U}_y(\vartheta)$ ,  $\mathbf{U}_z(\phi)$  and  $\mathbf{U}_{z'}(\chi)$  to the LRF, namely

$$\mathbf{e}_{\alpha'} = \mathbf{U}_{z'}(\chi)\mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)\mathbf{e}_{\alpha}, \quad \alpha = x, y, z, \quad (42)$$

where  $\mathbf{U}_{z'}(\chi)$  means rotating  $\chi$  around  $\mathbf{e}_{z'}$ . The matrix representation for  $\mathbf{U}_{z'}(\chi)$  in the MRF is the same with  $\mathbf{U}_z(\chi)$  in the LRF. Since the third rotation  $\mathbf{U}_{z'}(\chi)$  in Eq. (42) has no effects on  $\mathbf{e}_{z'}$  we actually have  $\mathbf{e}_{z'} = \mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)\mathbf{e}_z$ . Exploiting the rules between vector and operator transformations we can obtain the expression for  $\mathbf{U}_{z'}(\chi)$  in the LRF

$$\mathbf{U}_{z'}(\chi) = [\mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)] \mathbf{U}_z(\chi) [\mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)]^{-1}. \quad (43)$$

Consequently Eq. (42) can be rewritten as

$$\mathbf{e}_{\alpha'} = \mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)\mathbf{U}_z(\chi)\mathbf{e}_{\alpha} \quad \alpha = x, y, z. \quad (44)$$

Eq. (44) tells us that an equivalent way to obtain the MRF is to apply three successive rotations  $\mathbf{U}_z(\chi)$ ,  $\mathbf{U}_y(\vartheta)$  and  $\mathbf{U}_z(\phi)$  to the LRF.

Now let us consider vectors  $\mathbf{R}_j$  characterised by spherical coordinates  $(R_j, \theta_j, \varphi_j)$  in the MRF ( $j = 1 - N$ ). With Eq. (44) and the rule between basis vectors and components transformations we can obtain the Cartesian components of these vectors in LRF

$$\begin{pmatrix} R_{jx} \\ R_{jy} \\ R_{jz} \end{pmatrix} = \mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)\mathbf{U}_z(\chi) \begin{pmatrix} R_{jx'} \\ R_{jy'} \\ R_{jz'} \end{pmatrix}, \quad (45)$$

where  $R_{j\alpha}$  and  $R_{j\alpha'}$  are Cartesian components of  $\mathbf{R}_j$  in the LRF and the MRF, respectively. We can rewrite Eq. (45) in more formally as

$$\mathbf{R}_j = R_j \mathbf{U}_z(\phi)\mathbf{U}_y(\vartheta)\mathbf{U}_z(\chi)\mathbf{U}_z(\varphi_j)\mathbf{U}_y(\theta_j)\mathbf{e}_z, \quad (46)$$

Eq. (46) is a vector equation therefore it is also valid for an arbitrary reference frame.

Now we turn to the main task, that is, deriving the Hermitian conjugate of momentum operators. This can be done step by step according to Eq. (6) with the help of the coordinate transformation Eq. (45). From Eq. (45) we can see that  $(\theta_j, \varphi_j)$  only appear in the Cartesian components of  $\mathbf{R}_j$ . This greatly simplifies the expression for the Hermitian conjugates of momentum operators as follows

$$\begin{aligned}\hat{P}_{R_j}^\dagger &= \hat{P}_{R_j} - i\hbar \sum_{\alpha=x,y,z} \left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial R_j} \right)^\circ \\ \hat{P}_{\theta_j}^\dagger &= \hat{P}_{\theta_j} - i\hbar \sum_{\alpha=x,y,z} \left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial \theta_j} \right)^\circ \\ \hat{P}_{\varphi_j}^\dagger &= \hat{P}_{\varphi_j} - i\hbar \sum_{\alpha=x,y,z} \left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial \varphi_j} \right)^\circ.\end{aligned}\quad (47)$$

Here the three Euler angles in Eq. (45) are purely parameters. To calculate the partial derivatives we first give some useful relations following from the orthogonality of the transformation Eq. (45)

$$\begin{aligned}R_{j\alpha} &= \sum_{\beta'} \frac{\partial R_{j\alpha}}{\partial R_{j\beta'}} R_{j\beta'}, & R_{j\beta'} &= \sum_{\alpha} \frac{\partial R_{j\beta'}}{\partial R_{j\alpha}} R_{j\alpha} \\ \sum_{\beta'} \left( \frac{\partial R_{j\alpha}}{\partial R_{j\beta'}} \right)^2 &= \sum_{\alpha} \left( \frac{\partial R_{j\alpha}}{\partial R_{j\alpha'}} \right)^2 = 1 \\ \frac{\partial R_{j\alpha}}{\partial R_{j\beta'}} &= \frac{\partial R_{j\beta'}}{\partial R_{j\alpha}}\end{aligned}\quad (48)$$

where  $\alpha = x, y, z$  and  $\beta' = x', y', z'$ . Note here all the derivatives  $\{\partial R_{j\beta'}/\partial R_{j\alpha}\}$  are parameters only depending on the three Euler angles.

Let us first derive the expression for  $\hat{P}_{R_j}^\dagger$ . It is straightforward to get the following derivatives of MRF Cartesian coordinates

$$\begin{aligned}\frac{\partial R_{jx'}}{\partial R_j} &= \sin \theta_j \cos \varphi_j = \frac{R_{jx'}}{R_j} \\ \frac{\partial R_{jy'}}{\partial R_j} &= \sin \theta_j \sin \varphi_j = \frac{R_{jy'}}{R_j} \\ \frac{\partial R_{jz'}}{\partial R_j} &= \cos \theta_j = \frac{R_{jz'}}{R_j}\end{aligned}\quad (49)$$

where  $R_j^2 = R_{jx}^2 + R_{jy}^2 + R_{jz}^2 = R_{jx'}^2 + R_{jy'}^2 + R_{jz'}^2$ . Based on Eq. (49) we can obtain the

derivatives of LRF Cartesian coordinates with respect to  $R_j$  and derive the final result

$$\begin{aligned}
\sum_{\alpha} \left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial R_j} \right)^{\circ} &= \sum_{\alpha} \left( \frac{\partial}{\partial R_{j\alpha}} \sum_{\alpha'} \frac{R_{j\beta'}}{R_j} \frac{\partial R_{j\alpha}}{\partial R_{j\beta'}} \right)^{\circ} \\
&= \sum_{\alpha, \beta'} \left( \frac{1}{R_j} \frac{\partial R_{j\beta'}}{\partial R_{j\alpha}} + R_{j\beta'} \frac{\partial (R_{jx}^2 + R_{jy}^2 + R_{jz}^2)^{-\frac{1}{2}}}{\partial R_{j\alpha}} \right) \frac{\partial R_{j\alpha}}{\partial R_{j\beta'}} \\
&= \sum_{\alpha, \beta'} \left( \frac{1}{R_j} \frac{\partial R_{j\beta'}}{\partial R_{j\alpha}} - \frac{R_{j\beta'} R_{j\alpha}}{R_j^3} \right) \frac{\partial R_{j\alpha}}{\partial R_{j\beta'}} \\
&= \sum_{\alpha} \left( \frac{1}{R_j} - \frac{R_{j\alpha}^2}{R_j^3} \right) \\
&= \frac{3}{R_j} - \frac{1}{R_j} = \frac{2}{R_j},
\end{aligned} \tag{50}$$

where Eq. (48) has been used in the fourth step. Finally we can get the HCMO associated with  $R_j$  as follows

$$\hat{P}_{R_j}^{\dagger} = \hat{P}_{R_j} - \frac{2i\hbar}{R_j} = -i\hbar \frac{1}{R_j^2} \frac{\partial}{\partial R_j} R_j^2. \tag{51}$$

Next we will derive the expression for  $\hat{P}_{\theta_j}^{\dagger}$  following the same procedure. The derivatives of MRF Cartesian coordinates read

$$\begin{aligned}
\frac{\partial R_{jx'}}{\partial \theta_j} &= R_j \cos \theta_j \cos \varphi_j = R_{jx'} \cot \theta_j \\
\frac{\partial R_{jy'}}{\partial \theta_j} &= R_j \cos \theta_j \sin \varphi_j = R_{jy'} \cot \theta_j \\
\frac{\partial R_{jz'}}{\partial \theta_j} &= -R_j \sin \theta_j = -\frac{R_{jz'}}{\cot \theta_j}.
\end{aligned} \tag{52}$$

Based on Eq. (52) we can obtain the derivatives of Cartesian coordinates in LRF with respect to  $\theta_j$

$$\frac{\partial R_{j\alpha}}{\partial \theta_j} = R_{jx'} \cot \theta_j \frac{\partial R_{j\alpha}}{\partial R_{jx'}} + R_{jy'} \cot \theta_j \frac{\partial R_{j\alpha}}{\partial R_{jy'}} - \frac{R_{jz'}}{\cot \theta_j} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \tag{53}$$

Furthermore, we obtain

$$\begin{aligned}
\left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial \theta_j} \right)^{\circ} &= \cot \theta_j \frac{\partial R_{j\alpha}}{\partial R_{jx'}} \frac{\partial R_{jx'}}{\partial R_{j\alpha}} + \cot \theta_j \frac{\partial R_{j\alpha}}{\partial R_{jy'}} \frac{\partial R_{jy'}}{\partial R_{j\alpha}} - \frac{1}{\cot \theta_j} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \frac{\partial R_{jz'}}{\partial R_{j\alpha}} \\
&\quad + \left( R_{jx'} \frac{\partial R_{j\alpha}}{\partial R_{jx'}} + R_{jy'} \frac{\partial R_{j\alpha}}{\partial R_{jy'}} + \frac{R_{jz'}}{\cot^2 \theta_j} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \right) \frac{\partial \cot \theta_j}{\partial R_{j\alpha}} \\
&= \cot \theta_j - \frac{1}{\sin \theta_j \cos \theta_j} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \frac{\partial R_{jz'}}{\partial R_{j\alpha}} \\
&\quad + \left( R_{j\alpha} + (\tan^2 \theta_j - 1) R_{jz'} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \right) \frac{\partial \cot \theta_j}{\partial R_{j\alpha}}.
\end{aligned} \tag{54}$$

Since  $\cot \theta_j = R_{jz'}/\sqrt{R_{jx'}^2 + R_{jy'}^2}$  we can get the following derivatives

$$\begin{aligned}\frac{\partial \cot \theta_j}{\partial R_{jx'}} &= -\frac{R_{jx'} R_{jz'}}{\sqrt{R_{jx'}^2 + R_{jy'}^2}^3} \\ \frac{\partial \cot \theta_j}{\partial R_{jy'}} &= -\frac{R_{jy'} R_{jz'}}{\sqrt{R_{jx'}^2 + R_{jy'}^2}^3} \\ \frac{\partial \cot \theta_j}{\partial R_{jz'}} &= \frac{1}{\sqrt{R_{jx'}^2 + R_{jy'}^2}}.\end{aligned}\quad (55)$$

Based on Eq. (55) we have

$$\begin{aligned}\frac{\partial \cot \theta_j}{\partial R_{j\alpha}} &= \frac{1}{\sqrt{R_{jx'}^2 + R_{jy'}^2}^3} \left( -R_{jx'} R_{jz'} \frac{\partial R_{jx'}}{\partial R_{j\alpha}} - R_{jy'} R_{jz'} \frac{\partial R_{jy'}}{\partial R_{j\alpha}} + (R_{jx'}^2 + R_{jy'}^2) \frac{\partial R_{jz'}}{\partial R_{j\alpha}} \right) \\ &= \frac{1}{\sqrt{R_{jx'}^2 + R_{jy'}^2}^3} \left( -R_{jz'} R_{j\alpha} + R_j^2 \frac{\partial R_{jz'}}{\partial R_{j\alpha}} \right).\end{aligned}\quad (56)$$

Combining Eq. (54) and Eq. (56) we can now derive

$$\begin{aligned}& \sum_{\alpha} \left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial \theta_j} \right)^{\circ} \\ &= \sum_{\alpha} \left( \cot \theta_j - \frac{1}{\sin \theta_j \cos \theta_j} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \frac{\partial R_{jz'}}{\partial R_{j\alpha}} \right) \\ &+ \sum_{\alpha} \frac{1}{\sqrt{R_{jx'}^2 + R_{jy'}^2}^3} \left( R_{j\alpha} + (\tan^2 \theta_j - 1) R_{jz'} \frac{\partial R_{j\alpha}}{\partial R_{jz'}} \right) \left( -R_{jz'} R_{j\alpha} + R_j^2 \frac{\partial R_{jz'}}{\partial R_{j\alpha}} \right) \\ &= 3 \cot \theta_j - \frac{1}{\sin \theta_j \cos \theta_j} \\ &+ \frac{1}{\sqrt{R_{jx'}^2 + R_{jy'}^2}^3} \left( -R_{jz'} R_j^2 + R_j^2 R_{jz'} + (\tan^2 \theta_j - 1) (-R_{jz'}^2 R_{jz'} + R_j^2 R_{jz'}) \right) \\ &= 3 \cot \theta_j - \frac{1}{\sin \theta_j \cos \theta_j} + (\tan^2 \theta_j - 1) \cot \theta_j \\ &= \cot \theta_j\end{aligned}\quad (57)$$

The Hermitian conjugate of each  $\hat{P}_{\theta_j}$  associated with the corresponding MRF polar angle  $\theta_j$  can be finally expressed as

$$\hat{P}_{\theta_j}^{\dagger} = \hat{P}_{\theta_j} - i\hbar \cot \theta_j = -\frac{i\hbar}{\sin \theta_j} \frac{\partial}{\partial \theta_j} \sin \theta_j.\quad (58)$$

Finally we come to  $\hat{P}_{\varphi_j}^{\dagger}$ . The procedure is the same, however, it is much simpler as

compared to  $\hat{P}_{\theta_j}^\dagger$ . Again we start with the derivatives of MRF Cartesian coordinates

$$\begin{aligned}\frac{\partial R_{jx'}}{\partial \varphi_j} &= -R_j \sin \theta_j \sin \varphi_j = -R_{jy'} \\ \frac{\partial R_{jy'}}{\partial \varphi_j} &= R_j \sin \theta_j \cos \varphi_j = R_{jx'} \\ \frac{\partial R_{jz'}}{\partial \varphi_j} &= 0\end{aligned}\quad (59)$$

to obtain the final

$$\begin{aligned}\left(\sum_{\alpha} \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial \varphi_j}\right)^\circ &= \left(\sum_{\alpha} \frac{\partial}{\partial R_{j\alpha}} \left(R_{jx'} \frac{\partial R_{j\alpha}}{\partial R_{jy'}} - R_{jy'} \frac{\partial R_{j\alpha}}{\partial R_{jx'}}\right)\right)^\circ \\ &= \sum_{\alpha} \left(\frac{\partial R_{jx'}}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial R_{jy'}} - \frac{\partial R_{jy'}}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial R_{jx'}}\right) = 0\end{aligned}\quad (60)$$

The momentum operator associated with each orientation angle  $\varphi_j$  is Hermitian according to Eq. (60), namely

$$\hat{P}_{\varphi_j}^\dagger = \hat{P}_{\varphi_j} = -i\hbar \frac{\partial}{\partial \varphi_j}.\quad (61)$$

Let us recall the above detailed procedure. The only condition we need is that the transformation matrix between Cartesian coordinates in the LRF and those in a MRF is orthogonal. First, if we set all the three Euler angles equal to zero we can obtain the HCMOs associated with spherical coordinates in the LRF. The final results are the same with Eq. (51), Eq. (58), and Eq. (61) since a unit matrix is also an orthogonal matrix. Second, we can use more rotations to define more MRFs and the HCMOs associated with the spherical coordinates in each different MRF obey Eq. (51), Eq. (58), and Eq. (61). As an important consequence the Hermitian conjugates of all the momentum operators associated with *real* bond lengths, bond angles and dihedral angles obey Eq. (51), Eq. (58), and Eq. (61), respectively, irrespective of how complicated the molecule might be. Similarly, the result holds for any reference frame provided there exists an orthogonal transformation to transform it to the LRF. Based on the above conclusions we can see the HCMOs associated with the three Euler angles obey the same relations

$$\begin{aligned}\hat{P}_{\vartheta}^\dagger &= \hat{P}_{\vartheta} - i\hbar \cot \vartheta = -\frac{i\hbar}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \sin \vartheta \\ \hat{P}_{\phi}^\dagger &= \hat{P}_{\phi} = -i\hbar \frac{\partial}{\partial \phi} \\ \hat{P}_{\chi}^\dagger &= \hat{P}_{\chi} = -i\hbar \frac{\partial}{\partial \chi}.\end{aligned}\quad (62)$$

Finally, we can obtain the HCMOs  $\hat{P}_{j\alpha'}^\dagger$  associated with MRF Cartesian coordinates following the same procedure. Since  $\partial R_{j\alpha}/\partial R_{j\alpha'}$  is just a parameter which does not



depends on  $R_{jx}$ ,  $R_{jy}$  or  $R_{jz}$  we can easily get

$$\hat{P}_{j\alpha'}^\dagger = \hat{P}_{j\alpha'} - i\hbar \sum_{\alpha} \left( \frac{\partial}{\partial R_{j\alpha}} \frac{\partial R_{j\alpha}}{\partial R_{j\alpha'}} \right)^\circ = \hat{P}_{j\alpha'}, \quad (63)$$

where  $\alpha' = x', y', z'$ . Apparently, the momenta associated with MRF Cartesian coordinates are Hermitian.

### B. KEO in Terms of Polyspherical Coordinates

In order to connect our approach to existing one we consider the KEO in terms of so called polyspherical coordinates defined in the LRF and a MRF. This will lead us to expression which have been reported in Ref. [17]. Consider a molecular system composed of  $N + 1$  atoms. After separating the total centre of mass motion we can describe it with  $N$  vectors  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$ . The three Euler angles  $(\vartheta, \phi, \chi)$  are chosen in such a way that the spherical coordinates of  $\mathbf{R}_N$  in the LRF are  $(R_N, \vartheta, \phi)$  and the spherical coordinates of  $\mathbf{R}_1$  in the MRF are  $(R_1, \theta_1, \varphi_1 = 0)$ . That is to say the  $\mathbf{e}_{z'}$  axis of the MRF is defined to be along the direction of  $\mathbf{R}_N$ . The rest  $N - 2$  vectors are characterised by spherical coordinates  $\{R_j, \theta_j, \varphi_j\}$  in the MRF ( $j = 2, \dots, N - 1$ ).

Using Eq. (20) with  $j = 1, \dots, N$  and  $\theta_N = \varphi_N = \varphi_1 = 0$ , we can derive the LRF components of the  $N$  velocity vectors

$$\begin{aligned} \dot{\mathbf{R}}_j = & R_j \dot{\vartheta} \mathbf{U}_z(\phi) \mathbf{U}'_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{U}_z(\varphi_j) \mathbf{U}_y(\theta_j) \mathbf{e}_z \\ & + R_j \dot{\phi} \mathbf{U}'_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{U}_z(\varphi_j) \mathbf{U}_y(\theta_j) \mathbf{e}_z \\ & + R_j \dot{\chi} \mathbf{U}_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}'_z(\chi) \mathbf{U}_z(\varphi_j) \mathbf{U}_y(\theta_j) \mathbf{e}_z \\ & + \dot{R}_j \mathbf{U}_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{U}_z(\varphi_j) \mathbf{U}_y(\theta_j) \mathbf{e}_z \\ & + R_j \dot{\theta}_j \mathbf{U}_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{U}_z(\varphi_j) \mathbf{U}'_y(\theta_j) \mathbf{e}_z \\ & + R_j \dot{\varphi}_j \mathbf{U}_z(\phi) \mathbf{U}_y(\vartheta) \mathbf{U}_z(\chi) \mathbf{U}'_z(\varphi_j) \mathbf{U}_y(\theta_j) \mathbf{e}_z, \end{aligned} \quad (64)$$

where  $\mathbf{U}'$  is the first order derivative of the corresponding rotational transformation matrix. The above equations are still vector equations, however, they are only valid in the LRF since we have used the relation  $\dot{\mathbf{e}}_z = 0$ . To make them valid in an arbitrary reference frame we only need to add the corresponding terms containing  $\dot{\mathbf{e}}_z$  to the right hand side.

Before proceeding we will discuss the orthogonality of the terms appearing in Eq. (64). The last three terms in Eq. (64) are just the spherical velocity components measured in the MRF while the first three terms are components of the velocity caused by the

non-inertial MRF. Each term in Eq. (64) can be expressed in a formally simple way in terms of angular velocity vectors

$$\begin{aligned}\dot{\mathbf{R}}_j &= \dot{\vartheta} \mathbf{e}_{\dot{\vartheta}} \times \mathbf{R}_j + \dot{\phi} \mathbf{e}_{\dot{\phi}} \times \mathbf{R}_j + \dot{\chi} \mathbf{e}_{\dot{\chi}} \times \mathbf{R}_j \\ &+ \dot{R}_j \mathbf{R}_j / R_j + \dot{\theta}_j \mathbf{e}_{\dot{\theta}_j} \times \mathbf{R}_j + \dot{\varphi}_j \mathbf{e}_{\dot{\varphi}_j} \times \mathbf{R}_j,\end{aligned}\quad (65)$$

where  $\mathbf{e}_{\dot{\vartheta}}$  is the direction of the angular velocity  $\dot{\vartheta}$ , and similar for  $\mathbf{e}_{\dot{\phi}}$ ,  $\mathbf{e}_{\dot{\chi}}$ ,  $\mathbf{e}_{\dot{\theta}_j}$ , and  $\mathbf{e}_{\dot{\varphi}_j}$ . With the help of Eq. (65) one can immediately see that the fourth term is parallel to  $\mathbf{R}_j$  while the other terms are perpendicular to  $\mathbf{R}_j$ . Recalling the velocity in spherical coordinates we know that the last three terms are orthogonal to each other. Therefore, in Eq. (64) (or Eq. (65)), the fourth term (namely the  $\dot{R}_j$  term) is orthogonal to the other terms and the last three terms are orthogonal to each other.

Having at hand all the velocities it is quite straightforward to write the classical kinetic energy [28] according to

$$T = \frac{1}{2} \sum_{i,j=1}^N \mu_{ij} \dot{\mathbf{R}}_i^\dagger \dot{\mathbf{R}}_j, \quad (66)$$

where the matrix  $\{\mu_{jk}\}$  combines the reduced masses and the transformation matrix between adopted and Jacobi vectors [28]. The final results in LRF can be written in a symmetric form as in Eq. (1)

$$T = \frac{1}{2} \dot{\mathbf{Q}}^\dagger \mathbf{M} \dot{\mathbf{Q}}, \quad \mathbf{Q} = \begin{pmatrix} \mathbf{Q}_{\text{rot}} \\ \mathbf{Q}_{\text{vib}} \end{pmatrix}, \quad (67)$$

where the coordinates are separated as rotational, Eq. (22), and vibrational DOFs

$$\mathbf{Q}_{\text{vib}}^\dagger = \left( R_1 \cdots R_N \theta_1 \cdots \theta_{N-1} \varphi_2 \cdots \varphi_{N-1} \right). \quad (68)$$

The next step is to calculate the inverse matrix of  $\mathbf{M}$  to generate the quantum KEO. Aiming at a separation of the rotational and vibrational DOFs, we divide the matrix  $\mathbf{M}$  into the following four blocks

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}_{\text{rot}} & \mathbf{M}_{\text{Cor}} \\ \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{M}_{\text{vib}} \end{pmatrix}, \quad (69)$$

where the subscripts “rot”, “Cor”, and “vib” correspond to rotational, Coriolis, and vibrational terms, respectively. Therefore,  $\mathbf{M}_{\text{rot}}$ ,  $\mathbf{M}_{\text{Cor}}$ , and  $\mathbf{M}_{\text{vib}}$  are  $3 \times 3$ ,  $3 \times (3N - 3)$  and  $(3N - 3) \times (3N - 3)$  dimensional matrices, respectively. Suppose the inverse matrix of  $\mathbf{M}$  is divided in the same spirit as

$$\mathbf{M}^{-1} = \begin{pmatrix} \mathbf{G}_{\text{rot}} & \mathbf{G}_{\text{Cor}} \\ \mathbf{G}_{\text{Cor}}^\dagger & \mathbf{G}_{\text{vib}} \end{pmatrix}, \quad (70)$$

we can express the quantum KEO as a sum of rotational, vibrational, and Coriolis terms

$$\begin{aligned}\hat{T} &= \hat{T}_{\text{rot}} + \hat{T}_{\text{vib}} + \hat{T}_{\text{Cor}} \\ &= \frac{1}{2} \hat{\mathbf{P}}_{\text{rot}}^\dagger \mathbf{G}_{\text{rot}} \hat{\mathbf{P}}_{\text{rot}} + \frac{1}{2} \hat{\mathbf{P}}_{\text{vib}}^\dagger \mathbf{G}_{\text{vib}} \hat{\mathbf{P}}_{\text{vib}} + \frac{1}{2} \left( \hat{\mathbf{P}}_{\text{rot}}^\dagger \mathbf{G}_{\text{Cor}} \hat{\mathbf{P}}_{\text{vib}} + \text{h.c.} \right).\end{aligned}\quad (71)$$

According to Section II E, the generalised momentum vector  $\hat{\mathbf{P}}_{\text{rot}}$  associated with the rotational DOFs is just the total angular momentum vector  $\mathbf{J}$ . If we are interested in the rotational DOFs only, we obtain upon setting the vibrational momenta equal to zero:

$$\hat{T}_{\text{rot}} = \frac{1}{2} \hat{\mathbf{P}}_{\text{rot}}^\dagger \mathbf{G}_{\text{rot}} \hat{\mathbf{P}}_{\text{rot}} = \frac{1}{2} \hat{\mathbf{J}}^\dagger \mathbf{G}_{\text{rot}} \hat{\mathbf{J}},\quad (72)$$

where the components of  $\mathbf{J}$  should be along the directions of  $\mathbf{e}_{\dot{\theta}}$ ,  $\mathbf{e}_{\dot{\phi}}$  and  $\mathbf{e}_{\dot{\chi}}$  according to Eq. (27). In passing we note that one can also transform the components to Cartesian ones according to Eq. (28). On the other hand, if we are interested in the vibrational DOFs, the KEO for the total angular momentum  $\mathbf{J} = 0$  reads

$$\hat{T}_{\text{vib}} = \frac{1}{2} \hat{\mathbf{P}}_{\text{vib}}^\dagger \mathbf{G}_{\text{vib}} \hat{\mathbf{P}}_{\text{vib}}.\quad (73)$$

Finally, we give the details on how to calculate the different blocks of the inverse matrix of  $\mathbf{M}$ . One can see that the matrix  $\mathbf{M}$  can be congruently block-diagonalised in the following way

$$\begin{aligned}& \begin{pmatrix} \mathbf{1} & -\mathbf{M}_{\text{Cor}} \mathbf{M}_{\text{vib}}^{-1} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{M}_{\text{rot}} & \mathbf{M}_{\text{Cor}} \\ \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{M}_{\text{vib}} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ -\mathbf{M}_{\text{vib}}^{-1} \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{1} \end{pmatrix} \\ &= \begin{pmatrix} \mathbf{M}_{\text{rot}} - \mathbf{M}_{\text{Cor}} \mathbf{M}_{\text{vib}}^{-1} \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{0} \\ \mathbf{0} & \mathbf{M}_{\text{vib}} \end{pmatrix}.\end{aligned}\quad (74)$$

Calculating the inverse of both sides of Eq. (74) leads to

$$\begin{aligned}\mathbf{M}^{-1} &= \begin{pmatrix} \mathbf{G}_{\text{rot}} & \mathbf{G}_{\text{Cor}} \\ \mathbf{G}_{\text{Cor}}^\dagger & \mathbf{G}_{\text{vib}} \end{pmatrix} = \begin{pmatrix} \mathbf{M}_{\text{rot}} & \mathbf{M}_{\text{Cor}} \\ \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{M}_{\text{vib}} \end{pmatrix}^{-1} \\ &= \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ -\mathbf{M}_{\text{vib}}^{-1} \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{M}_{\text{rot}} - \mathbf{M}_{\text{Cor}} \mathbf{M}_{\text{vib}}^{-1} \mathbf{M}_{\text{Cor}}^\dagger & \mathbf{0} \\ \mathbf{0} & \mathbf{M}_{\text{vib}} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{1} & -\mathbf{M}_{\text{Cor}} \mathbf{M}_{\text{vib}}^{-1} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}.\end{aligned}\quad (75)$$

Calculating the matrix product in above equation leads to the final results

$$\begin{aligned}\mathbf{G}_{\text{rot}} &= \left( \mathbf{M}_{\text{rot}} - \mathbf{M}_{\text{Cor}} \mathbf{M}_{\text{vib}}^{-1} \mathbf{M}_{\text{Cor}}^\dagger \right)^{-1} \\ \mathbf{G}_{\text{Cor}} &= -\mathbf{G}_{\text{rot}} \mathbf{M}_{\text{Cor}} \mathbf{M}_{\text{vib}}^{-1} \\ \mathbf{G}_{\text{vib}} &= \mathbf{M}_{\text{vib}}^{-1} + \mathbf{M}_{\text{vib}}^{-1} \mathbf{M}_{\text{Cor}}^\dagger \mathbf{G}_{\text{rot}}.\end{aligned}\quad (76)$$

The matrix  $\mathbf{G}$  is essentially the same as the one reported in Ref. [17]. There, however, the essential point has been to express the MRF Cartesian components of the angular momentum associated with each vector  $\{\mathbf{R}_i\}$  in terms of  $\mathbf{J}$  and  $\{P_{\theta_i}, P_{\varphi_i}\}$ .

For the special case of Jacobi vectors,  $\mathbf{M}_{\text{vib}}$  is diagonal which greatly simplifies the calculation of Eq. (76). It is straightforward to obtain the diagonal elements according to Eq. (64)

$$\begin{aligned} (\mathbf{M}_{\text{vib}})_{R_j R_j} &= \mu_j \\ (\mathbf{M}_{\text{vib}})_{\theta_j \theta_j} &= \mu_j R_j^2 \\ (\mathbf{M}_{\text{vib}})_{\varphi_j \varphi_j} &= \mu_j R_j^2 \sin^2 \theta_j. \end{aligned} \quad (77)$$

The inverse matrix of  $\mathbf{M}_{\text{vib}}$  can be obtained quite easily. We only need to calculate the inverse of a matrix of dimension  $3 \times 3$  as well as some matrix products to get the final results. Here we give the matrix elements for  $\mathbf{G}_{\text{vib}}$  (Hermitian) which will be used in Section III:

$$\begin{aligned} G_{R_i R_j} &= \frac{\delta_{ij}}{\mu_j}, & G_{R_i \theta_j} &= 0, & G_{R_i \varphi_j} &= 0, \\ G_{\theta_i \theta_j} &= \frac{\delta_{ij}}{\mu_j R_j^2} + \frac{\cos(\varphi_i - \varphi_j)}{\mu_N R_N^2}, \\ G_{\theta_i \varphi_j} &= \frac{\cot \theta_j \sin(\varphi_i - \varphi_j) - \cot \theta_1 \sin \varphi_i}{\mu_N R_N^2}, \\ G_{\varphi_i \varphi_j} &= \frac{\delta_{ij}}{\mu_j R_j^2 \sin^2 \theta_j} + \frac{1}{\mu_1 R_1^2 \sin^2 \theta_1} \\ &+ \frac{\cot \theta_i \cot \theta_j \cos(\varphi_i - \varphi_j) + \cot^2 \theta_1 - \cot \theta_1 (\cos \varphi_i \cot \theta_i + \cos \varphi_j \cot \theta_j)}{\mu_N R_N^2}. \end{aligned} \quad (78)$$

### Acknowledgments

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft through the GK 788.

- 
- 1  
2  
3  
4  
5  
6  
7 [1] X. Huang, B. J. Braams, S. Carter, and J. M. Bowman, *J. Am. Chem. Soc.* **126**, 5042  
8 (2004).  
9  
10 [2] X. Huang, B. J. Braams, and J. M. Bowman, *J. Chem. Phys.* **122**, 044308 (2005).  
11  
12 [3] W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.* **72**, 99 (1980).  
13  
14 [4] T. Carrington and W. H. Miller, *J. Chem. Phys.* **81**, 3942 (1984).  
15  
16 [5] N. Shida, P. F. Barbara, and J. E. Almlöf, *J. Chem. Phys.* **91**, 4061 (1989).  
17  
18 [6] D. P. Tew, N. C. Handy, and S. Carter, *Phys. Chem. Chem. Phys.* **3**, 1958 (2001).  
19  
20 [7] K. Giese and O. Kühn, *J. Chem. Phys.* **123**, 054315 (2005).  
21  
22 [8] B. Podolsky, *Phys. Rev.* **32**, 812 (1928).  
23  
24 [9] P. R. Bunker, *Molecular symmetry and spectroscopy* (Academic, New York, 1979).  
25  
26 [10] R. Mecke, *Z. Phys.* **101**, 405 (1936).  
27  
28 [11] C. Eckart, *Phys. Rev.* **47**, 552 (1935).  
29  
30 [12] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (Dover, New York, 1955).  
31  
32 [13] J. K. G. Watson, *Mol. Phys.* **15**, 479 (1968).  
33  
34 [14] J. K. G. Watson, *Mol. Phys.* **29**, 465 (1970).  
35  
36 [15] J. M. Bowman, S. Carter, and X. Huang, *Int. Rev. Phys. Chem.* **22**, 533 (2003).  
37  
38 [16] M. J. Bramley, W. H. Green, Jr., and N. C. Handy, *Mol. Phys.* **73**, 1183, (1991).  
39  
40 [17] F. Gatti, C. Munoz, and C. Iung, *J. Chem. Phys.* **114**, 8275 (2001).  
41  
42 [18] F. Gatti and C. Iung, *J. Theor. Comp. Chem.* **2**, 507 (2003).  
43  
44 [19] C. Iung and F. Gatti, *Int. J. Quant. Chem.* **106**, 130 (2006).  
45  
46 [20] O. Vendrell, F. Gatti, D. Lauvergnat, and H.-D. Meyer, *J. Chem. Phys.* **127**, 184302 (2007).  
47  
48 [21] F. Gatti, Y. Justum, M. Menou, A. Nauts, and X. Chapuisat, *J. Mol. Spectr.* **181**, 403  
49 (1997).  
50  
51 [22] A. Nauts and X. Chapuisat, *Chem. Phys. Lett.* **136**, 164 (1987).  
52  
53 [23] D. Lauvergnat and A. Nauts, *J. Chem. Phys.* **116**, 8560 (2002).  
54  
55 [24] W. S. l'Yi, *Phys. Rev. A* **53**, 1251 (1996).  
56  
57 [25] Y. Yang and O. Kühn, *Z. Phys. Chem.* **222**, 1375 (2008).  
58  
59 [26] K. R. Asmis, Y. Yang, G. Santambrogio, M. Brümmer, J. R. Roscioli, L. R. McCunn, M. A.  
60 Johnson, and O. Kühn, *Angew. Chem. Int. Ed.* **46**, 8691 (2007).  
[27] Y. Yang, O. Kühn, G. Santambrogio, D. J. Goebbert, and K. R. Asmis, submitted.  
[28] C. Iung, F. Gatti, A. Viel, and X. Chapuisat, *Phys. Chem. Chem. Phys.* **1**, 3377 (1999).

1  
2  
3 **Figure Captions**  
4  
5  
6

7  
8 FIG. 1: The four Jacobi vectors of the  $\text{H}_3\text{O}_2^-$  anion which are used to define the 9D KEO.  
9

10  
11  
12 FIG. 2: Definition of active coordinates of the reduced  $\text{N}_2\text{H}_7^+$  model.  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

For Peer Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

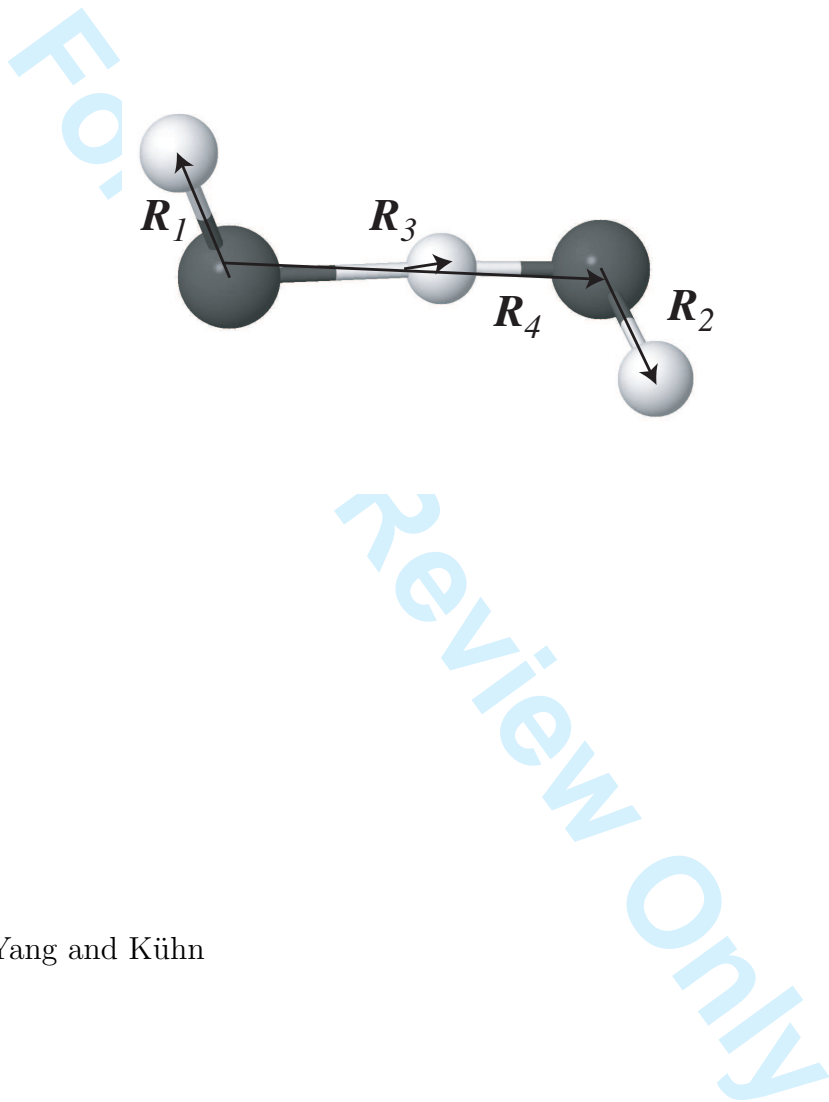


Figure 1, Yang and Kühn

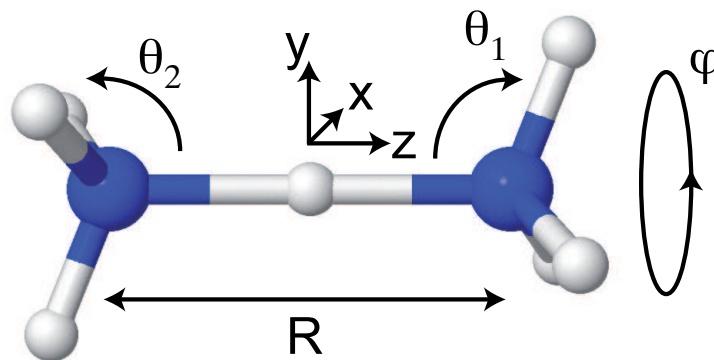
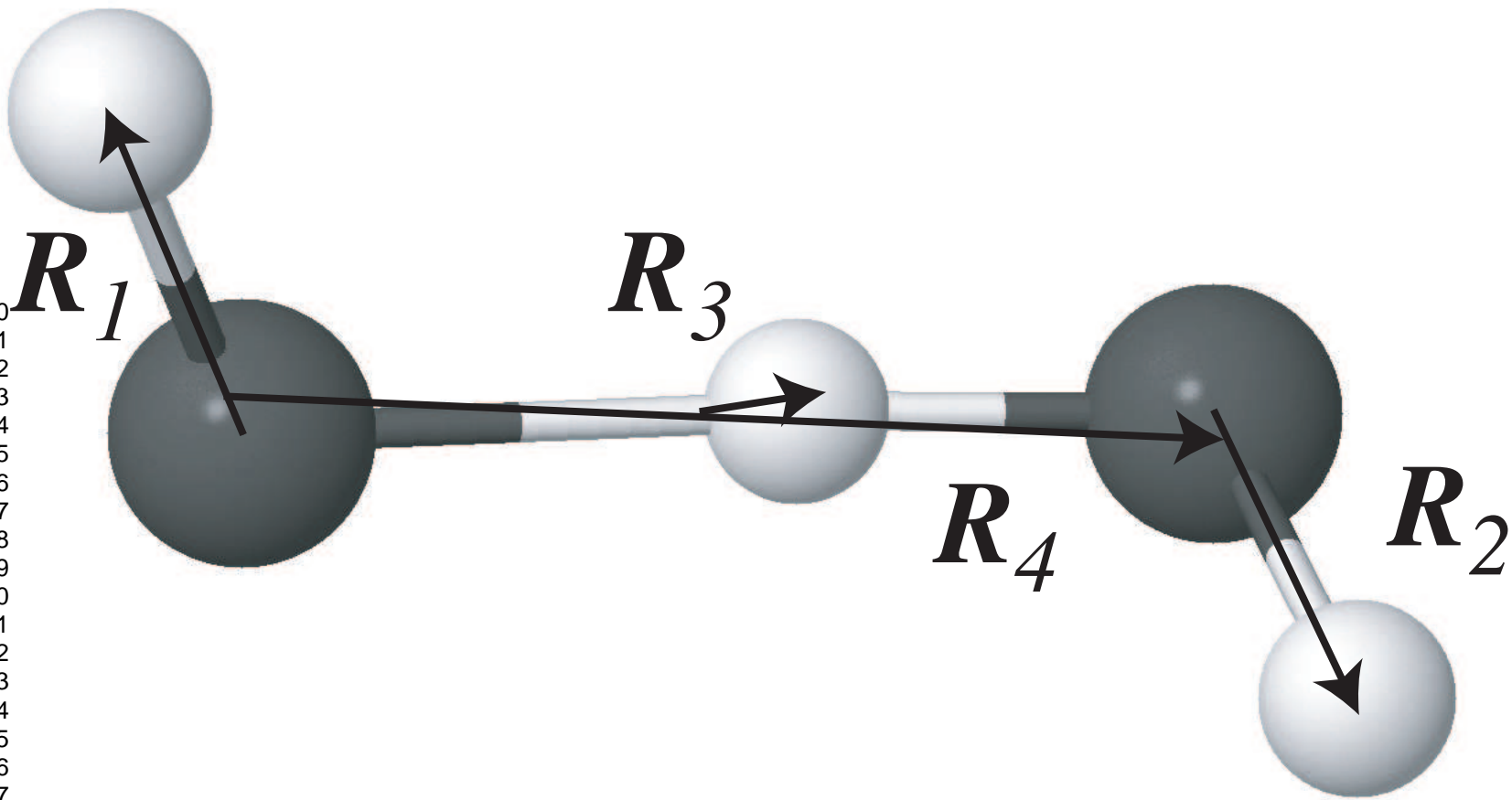
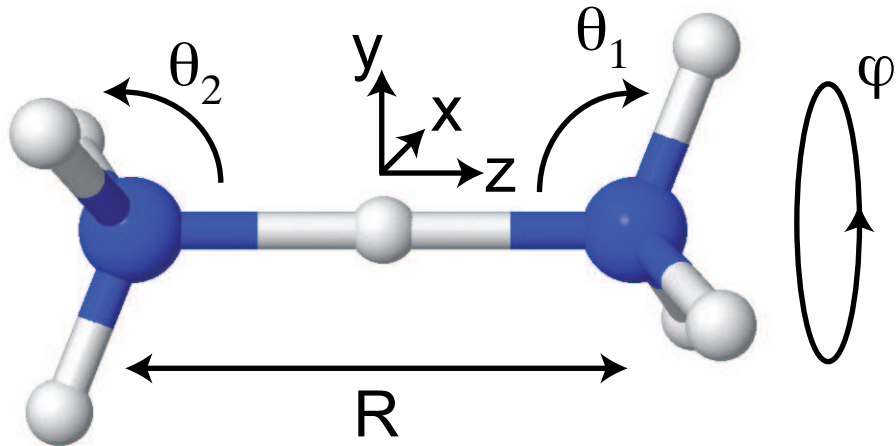


Figure 2, Yang and Kühn



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34





URL: <http://mc.manuscriptcentral.com/tandf/tmlph>

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19