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# **Vector parametrization of the N-atom problem in quantum mechanics with Non-Orthogonal Coordinates**

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## Abstract

This article aims at presenting a general method that enables one to build kinetic energy matrices in getting rid, for the angular coordinates (internal and Eulerian), of the heaviness of differential calculus (for expressing kinetic energy operators) and numerical integration (for calculating matrix elements). Therefore, instead of  $3N-3$  coordinates, only  $N-1$  radial distances are to be treated as coordinates. In the present formulation, the system is described by any set of  $n$  vectors  $\{\vec{R}_i, i = 1, \dots, n\}$  and the kinetic energy operator is expressed in term of  $(n-1)$  angular momenta  $\{\vec{L}_i, i = 1, \dots, n-1\}$  and the total angular momentum  $\vec{J}$ . The formalism proposed is general and gives a remarkably compact expression of the kinetic energy in terms of the angular momenta. This expression allows one to circumvent the seeming angular singularities.

## I. INTRODUCTION

In previous articles [1–3], hereafter called Ref[1], Ref[2] and Ref[3], the continuous geometrical representation of a deformable N-atom molecular system and the variational determination of its dynamical states, by diagonalization of the Hamiltonian matrix in an appropriate basis, have been studied for a triatomic molecule (Ref[2]) or a molecule parametrized by Jacobi vectors (Ref[1]). This approach avoids the differential calculus steps usually required for expressing quantum mechanical kinetic energy operators in terms of curvilinear internal coordinates. Indeed, many sets of internal coordinates can be considered [3–20] and the larger the molecule, the more diversified the coordinate sets that all include 3N-6 internal coordinates. Moreover, the rotation of the Body-Fixed frame (BF) (whose axes rotate in a conventional manner when the atoms move), is measured by three Euler angles in the Space-Fixed frame (SF) [21]. In Ref[1], a set of n Jacobi vectors ( $\vec{R}_i, i = 1, \dots, n$ ) has been used to describe the molecule ( $n = N - 1$ ). Vector  $\vec{R}_n$  has been taken parallel to the  $Gz^{BF}$  axis whereas  $\vec{R}_{n-1}$  is parallel to the  $(xz)^{BF}$  plane. The (n-2) other vectors has been viewed as totally free in BF. It is worth noticing that  $\vec{R}_n$  and  $\vec{R}_{n-1}$  played a specific role, being linked either totally ( $\vec{R}_n$ ) or partially ( $\vec{R}_{n-1}$ ) to the definition of the orientation of BF. Consequently, the BF components of the angular momenta associated with  $\vec{R}_n$  and  $\vec{R}_{n-1}$  do not satisfy the usual properties of angular momenta (commutation relations and hermiticity) and do not commute with the other angular momenta associated to the vectors  $\vec{R}_i$  ( $i=1, \dots, (n-2)$ ) and the total angular momentum  $\vec{J}$ . This crucial point will be referred to several times in this work.

In the present article, we generalize the results obtained in Ref[1] by using a set of n vectors *which are not Jacobi vectors* and thus could be parametrized by non-orthogonal coordinates, such as e.g. valence vectors. Our aim is to present a general method that enables, *for all angular coordinates (internal and Eulerian)*, the construction of kinetic energy matrices without resorting to (i) differential calculus for expressing kinetic energy operators and (ii) numerical integration to calculate angular matrix element for any selected vectors  $\{\vec{R}_i; i = 1, \dots, n\}$ . Consequently, only n radial distances must be treated numerically as coordinates instead of 3n coordinates when the angles are explicitly treated.

This work is based on the concept introduced in 1992 in Ref[3], where a general expression

of the kinetic energy has been given in terms of the BF-components of the angular momenta associated with the vectors  $\{\vec{R}_i; i = 1, \dots, n - 1\}$  used to describe the system. But the non-hermiticity of the BF-components of the angular momenta associated with  $\vec{R}_n$  and  $\vec{R}_{n-1}$  and the non commutation of them with the other angular momenta has not been fully appreciated in Ref[3]. Fortunately, we demonstrate in this article that most terms generated by non-hermiticity and non-commutation cancel each other. Therefore, the quantization of the kinetic energy for N atoms adds only very few specific terms, compared with the classical expression of the kinetic energy.

This article also constitutes a generalization of Ref[2] which has been dedicated to a vector parametrization of three-atom systems by valence coordinates. In the latter work, the quantum expression of the kinetic energy has been established in terms of the angular momenta associated with two valence vectors only. The quantization has led to one single specific quantum term, i.e. which has no counterpart in the classical expression of the kinetic energy. In section 2, we present the quantum mechanical background used to express the kinetic energy operator in terms of the momentum vectors  $\{\vec{P}_i; i = 1, \dots, n\}$  conjugated to the n vectors  $\{\vec{R}_i; i = 1, \dots, n\}$ . In Section 3, the expressions of the projections in BF of vectors  $\{\vec{P}_i; i = 1, \dots, n\}$  are given, along with their adjoints, in terms of the BF components of the angular momenta  $\{\vec{L}_i; i = 1, \dots, n - 1\}$  of the (n-1) rotating vectors  $\{\vec{R}_i; i = 1, \dots, n - 1\}$  and the total angular momentum  $\vec{J}$ . In Section 4, the results of Sections 2 and 3 are used for deriving a compact expression of the kinetic energy operator in terms of  $\{\vec{L}_i; i = 1, \dots, n - 1\}$  and  $\vec{J}$ . This expression is compared with its classical counterpart; the main difference arises from the fact that the frame axes depend on  $\vec{R}_n$  and  $\vec{R}_{n-1}$ . In Section 5, we propose a particular basis set which results in an analytical angular representation of the kinetic energy operator. Finally, in Section 6, the formalism is applied to the hexa-atomic system (AB)CD(EF) which has been recently tackled in the litterature[20]. We compare our method with that initiated by Handy[22] and used by Remple and Watts[20] in order to give a developed expression of the kinetic energy of (AB)CD(EF) described by valence coordinates. Some general conclusions and prospective views are also drawn in Section 6.

## II. QUANTUM MECHANICAL BACKGROUND

Let  $\vec{R}_1, \vec{R}_2, \dots, \vec{R}_n$  be the set of vectors chosen for the description of the molecular system. It is possible to connect these vectors to a set of Jacobi vectors  $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n$  (i.e. vectors pointing from one atomic group center of mass to another) that describe the system uniquely. The relation between the two sets is :

$$\begin{pmatrix} \vec{R}_1 \\ \vec{R}_2 \\ \dots \\ \vec{R}_n \end{pmatrix} = \mathbf{A} \begin{pmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \dots \\ \vec{r}_n \end{pmatrix} \quad (1)$$

where  $\mathbf{A}$  is a non singular constant matrix [3].

The quantum expression of the kinetic energy operator,  $\hat{\mathbf{T}}$ , in terms of Jacobi coordinates is given by [1, 23, 24] :

$$2\hat{\mathbf{T}} = \sum_{i=1}^n \frac{\hat{p}_i^\dagger \hat{p}_i}{\mu_i} = \left( \hat{p}_1^\dagger, \hat{p}_2^\dagger, \dots, \hat{p}_n^\dagger \right) \mu^{-1} \left( \hat{p}_1, \hat{p}_2, \dots, \hat{p}_n \right)^t \quad (2)$$

where the  $\mu$  matrix is the diagonal matrix of the reduced masses associated with the Jacobi vectors and  $\vec{p}_i$  is the conjugate momentum vector associated with  $\vec{r}_i$ . Using (Eq.3) that relates the conjugate vector  $\vec{P}_i$  associated with  $\vec{R}_i$  to the  $\vec{p}_i$  vectors :

$$\begin{pmatrix} \vec{p}_1 \\ \vec{p}_2 \\ \dots \\ \vec{p}_n \end{pmatrix} = \mathbf{A}^t \begin{pmatrix} \vec{P}_1 \\ \vec{P}_2 \\ \dots \\ \vec{P}_n \end{pmatrix} \quad (3)$$

Eq.2 can be rewritten in terms of the conjugate momentum vectors  $\vec{P}_i$  ( $i=1, \dots, n$ ) :

$$2\hat{\mathbf{T}} = \sum_{i,j=1}^n \hat{P}_i^\dagger M_{i,j} \hat{P}_j = \left( \hat{P}_1^\dagger, \hat{P}_2^\dagger, \dots, \hat{P}_n^\dagger \right) \mathbf{M} \left( \hat{P}_1, \hat{P}_2, \dots, \hat{P}_n \right)^t \quad (4)$$

where the symmetric mass-dependent constant matrix  $\mathbf{M}$  is given by :

$$\mathbf{M} = \mathbf{A} \mu^{-1} \mathbf{A}^t \quad (5)$$

In Section 6, we will illustrate how the  $\mathbf{A}$  and  $\mathbf{M}$  matrices can be easily obtained for a given system. In Section 3, we will express the kinetic energy operator in terms of the total

angular momentum  $\vec{J}$  and the angular momenta  $\vec{L}_i$  ( $i=1, \dots, n-1$ ) associated with  $\vec{R}_i$  ( $i=1, \dots, n-1$ ) and given by :

$$\vec{J} = \sum_{i=1}^n \vec{L}_i = \sum_{i=1}^n \vec{R}_i \times \vec{P}_i \quad (6)$$

The conjugate momentum  $\vec{P}_i$  can be expressed in terms of the angular momentum  $\vec{L}_i$  :

$$\vec{P}_i = P_i^r \vec{e}_i - \frac{\vec{e}_i \times \vec{L}_i}{R_i} \quad (7)$$

where  $\vec{e}_i$  denotes the unit vector along  $\vec{R}_i$ .

### III. CONJUGATE MOMENTUM VECTOR IN THE BODY FIXED FRAME

First of all, the  $Gz^{BF}$  axis chosen corresponds either to a symmetry axis of the system or to an axis that plays a specific role in the modelization of the system. Vector  $\vec{R}_n$  is, by definition, parallel to this axis. Consequently, the orientation of  $\vec{R}_n$  is crucial and directly related to the physical property of the molecule. For instance, in the study of  $NH_3$  treated in Ref. [25],  $\vec{R}_{n=3}$  links the nitrogen atom to the barycenter of the three hydrogen atoms. Such a choice is adapted to the symmetry of the equilibrium geometry and minimizes the effect of the Coriolis couplings.  $\vec{R}_n$  is characterized by its spherical coordinates  $(R_n, \theta_n^{SF}, \phi_n^{SF})$  in SF. Consequently, the two first Euler rotations  $D_z(\alpha)$  and  $D_y(\beta)$  used to define the  $Gz^{BF}$  axis correspond to  $D_y(\theta_n^{SF})$  and  $D_z(\phi_n^{SF})$ . The frame obtained after these two rotations is called  $E_2$ . A last rotation  $D_z(\gamma)$  around  $Gz^{E_2}$  is defined such that  $\vec{R}_{n-1}$  lies parallel to the  $(x^{BF}Gz^{BF}, x^{BF} > 0)$  half plane. This last rotation has no intrinsic physical meaning.

The aim of this paper is to express the kinetic energy operator in terms of the BF components of  $n$  angular momenta, namely the total angular momentum  $\vec{J}$  and the  $(n-1)$  angular momenta  $\vec{L}_i$  ( $i = 1, \dots, n-1$ ) associated to the freely rotating vectors  $\vec{R}_i$  ( $i=1, \dots, n-2$ ) and to  $\vec{R}_{n-1}$ , which is partially linked to BF frame. Consequently, the last angular momentum  $\vec{L}_n$  is redundant and  $\vec{J} - \sum_{i=1}^{n-1} \vec{L}_i$  substituted for it. It is worth mentioning that  $L_{nz}^{BF}$  is equal to zero because  $\vec{R}_n$  lies parallel to the  $Gz^{BF}$  axis.

Because of their different properties or expressions, one should distinguish three types of angular momenta :

- The total angular momentum  $\hat{J}$   
The BF components of  $\hat{J}$  are self-adjoint and satisfy the abnormal commutation relations. Their expressions are given elsewhere (for instance, Refs.26 and 27 or Eqs.19-20 of Ref[1]).
- The angular momenta  $\hat{L}_i$  ( $i=1, \dots, n-2$ ) associated to the freely rotating vectors  $\vec{R}_i$  ( $i=1, \dots, n-2$ ).  
These vectors are independent of the definition of either SF, E2 or BF. Consequently, they are characterized by the usual formulae given in Ref[1] for instance (Eq. 34-36).



Their SF, E2 and BF components obey the normal commutation relations[28].

- The angular momentum  $\hat{\vec{L}}_{n-1}$  associated to  $\vec{R}_{n-1}$

The y-BF component of  $\hat{\vec{L}}_{n-1}$  is not hermitian because BF depends on the orientation of  $\vec{R}_{n-1}$ . We have established in Ref.[1] that :

$$\hat{L}_{(n-1)\pm BF} = \hat{L}_{(n-1)x BF} \pm i\hat{L}_{(n-1)y BF} = -\cot \theta_{n-1} [\hat{J}_{z BF} - \sum_{i=1}^{n-2} \hat{L}_{iz BF}] \pm \hbar \partial_{\theta_{n-1}} \quad (8)$$

$$\hat{L}_{(n-1)z BF} = \hat{J}_{z BF} - \sum_{i=1}^{n-2} \hat{L}_{iz BF} \quad (9)$$

$$(\hat{L}_{(n-1)\pm BF})^\dagger = \hat{L}_{(n-1)\pm BF} \pm \hbar \cot \theta_{n-1} ; (\hat{L}_{(n-1)z BF})^\dagger = \hat{L}_{(n-1)z BF} \quad (10)$$

Using these equations, the BF components of  $\vec{L}_n^\dagger$  can be expressed as:

$$(\vec{L}_n)^\dagger = \vec{L}_n + \begin{pmatrix} 0 \\ i\hbar \cot \theta_{n-1} \\ 0 \end{pmatrix} \quad (11)$$

From now on, we are going to express the operators  $\hat{P}_i^\dagger$  et  $\hat{P}_i$  in terms of the angular momenta  $\hat{L}_i$  ( $i=1, \dots, n-1$ ) and their projections  $\hat{P}_i^r$  (Eq.7). This formula will be necessary to establish in Section 4 the kinetic energy in terms of the BF components of the angular momenta  $\hat{L}_i$  ( $i=1, \dots, n-1$ ) and  $\hat{J}$ .

It is worth mentioning that a Euclidian normalization is used [24, 29], i.e. the elementary volume is :

$$d\tau = R_n^2 \sin \beta dR_n d\alpha d\beta R_{n-1}^2 \sin \theta_{n-1}^{BF} dR_{n-1} d\gamma d\theta_{n-1}^{BF} \prod_{i=1}^{n-2} R_i^2 \sin \theta_i^{BF} dR_i d\phi_i^{BF} d\theta_i^{BF} \quad (12)$$

In that case, the operators  $(\hat{P}_i^r)^\dagger$  and  $\hat{P}_i^r$  are given by  $\hat{P}_i^r = -i\hbar \partial_{R_i}$  and :

$$(\hat{P}_i^r)^\dagger = \hat{P}_i^r - \frac{2i\hbar}{R_i} \quad (13)$$

Using Eq.7, the BF components of the self-adjoint operators  $\hat{P}_i$  ( $i=1, \dots, n-2$ ) and the operator  $\hat{P}_{n-1}$  are given by :

$$\hat{P}_i = (\hat{P}_i)^\dagger = \begin{pmatrix} \hat{P}_i^r \sin \theta_i^{BF} \cos \phi_i^{BF} + \frac{1}{R_i} \left( -\sin \theta_i^{BF} \sin \phi_i^{BF} \hat{L}_{iz BF} + \cos \theta_i^{BF} \hat{L}_{iy BF} \right) \\ \hat{P}_i^r \sin \theta_i^{BF} \sin \phi_i^{BF} + \frac{1}{R_i} \left( -\cos \theta_i^{BF} \hat{L}_{ix BF} + \sin \theta_i^{BF} \cos \phi_i^{BF} \hat{L}_{iz BF} \right) \\ \hat{P}_i^r \cos \theta_i^{BF} + \frac{1}{R_i} \left( -\sin \theta_i^{BF} \cos \phi_i^{BF} \hat{L}_{iy BF} + \sin \theta_i^{BF} \sin \phi_i^{BF} \hat{L}_{ix BF} \right) \end{pmatrix} \quad (14)$$

Because of the non-hermiticity of the y-BF component of  $\hat{\vec{L}}_{n-1}$  (Eq. 10), all the BF components of  $\hat{\vec{P}}_{n-1}$  are not self-adjoint.

$$(\hat{\vec{P}}_{n-1})^\dagger = \vec{e}_{n-1} \hat{P}_{n-1}^r + \frac{\hat{\vec{L}}_{n-1}^\dagger \times \vec{e}_{n-1}}{R_{n-1}} \quad (15)$$

A straightforward calculation provides the expression of  $(\hat{\vec{P}}_{n-1})^\dagger$  in terms of  $\hat{\vec{P}}_{n-1}$  :

$$(\hat{\vec{P}}_{n-1})^\dagger = \hat{\vec{P}}_{n-1} + \begin{pmatrix} \frac{-i\hbar}{R_{n-1} \sin \theta_{n-1}^{BF}} \\ 0 \\ 0 \end{pmatrix} \quad (16)$$

just in making use of the following commutators :

$$[\hat{L}_{(n-1)x^{BF}}, \cos \theta_{n-1}^{BF}] = 0 ; [\hat{L}_{(n-1)x^{BF}}, \sin \theta_{n-1}^{BF}] = 0 \quad (17)$$

$$[\hat{L}_{(n-1)y^{BF}}, \cos \theta_{n-1}^{BF}] = i\hbar \sin \theta_{n-1}^{BF} ; [\hat{L}_{(n-1)y^{BF}}, \sin \theta_{n-1}^{BF}] = -i\hbar \cos \theta_{n-1}^{BF} \quad (18)$$

$$[\hat{L}_{(n-1)z^{BF}}, \cos \theta_{n-1}^{BF}] = 0 ; [\hat{L}_{(n-1)z^{BF}}, \sin \theta_{n-1}^{BF}] = 0 \quad (19)$$

Finally, the  $\hat{\vec{P}}_n$  vector is obtained by substituting  $\hat{\vec{L}}_n$  by its expression in terms of the other angular momenta :

$$\hat{\vec{P}}_n = \begin{pmatrix} \frac{1}{R_n} (\hat{J}_y^{BF} - \sum_{i=1}^{n-1} \hat{L}_{iy}^{BF}) \\ \frac{1}{R_n} (-\hat{J}_x^{BF} + \sum_{i=1}^{n-1} \hat{L}_{ix}^{BF}) \\ \hat{P}_n^r \end{pmatrix} \quad (20)$$

This equation, along with Eq(8-10), leads to the expression of the BF-components of  $\hat{\vec{P}}_n^\dagger$

:

$$\hat{\vec{P}}_n^\dagger = \hat{\vec{P}}_n + \begin{pmatrix} \frac{i\hbar \cot \theta_{n-1}^{BF}}{R_n} \\ 0 \\ \frac{-2i\hbar}{R_n} \end{pmatrix} \quad (21)$$

Therefore, all the expressions of the BF-components of  $\hat{\vec{P}}_i$  and  $\hat{\vec{P}}_i^\dagger$  ( $i=1, \dots, n$ ) are available. We are now able to propose a compact expression of the kinetic energy operator in terms of the BF components of  $\hat{\vec{J}}$  and  $\hat{\vec{L}}_i$  ( $i=1, \dots, n-1$ ).

#### IV. QUANTUM EXPRESSION OF THE KINETIC ENERGY IN TERMS OF ANGULAR MOMENTA

First of all, the  $\hat{P}_i^\dagger$  vectors are substituted in the expression of the kinetic energy operator (Eq.4) by their expressions (Eqs.14,16,21) which leads to:

$$2\hat{\mathbf{T}} = \sum_{i,j=1}^n M_{i,j} \hat{P}_i \cdot \hat{P}_j \quad (22)$$

$$+ \sum_{i=1}^n \left( -M_{i,n-1} \frac{i\hbar \hat{P}_{ix}^{BF}}{R_{n-1} \sin \theta_{n-1}^{BF}} + M_{i,n} \left( \frac{i\hbar \cot \theta_{n-1}^{BF} \hat{P}_{ix}^{BF}}{R_n} - \frac{2i\hbar \hat{P}_{iz}^{BF}}{R_n} \right) \right) \quad (23)$$

The first term (Eq.22) can be indentified with the expression of the kinetic energy in classical mechanics (which will be called the "classical" kinetic energy), *except for the BF components of  $\hat{P}_{n-1}$  and  $\hat{P}_n$  which do not commute with the BF components of vectors  $\hat{P}_i$* . Consequently, the commutators  $[\hat{P}_i, \hat{P}_j] = \hat{P}_i \cdot \hat{P}_j - \hat{P}_j \cdot \hat{P}_i$  must be taken into account when deriving the kinetic energy. The result is :

$$2\hat{\mathbf{T}} = \sum_{i=1}^n M_{i,i} (\hat{P}_i)^2 - \frac{i\hbar M_{n-1,n-1}}{R_{n-1} \sin \theta_{n-1}^{BF}} \hat{P}_{(n-1)x}^{BF} + \frac{i\hbar M_{n,n}}{R_n} (\cot \theta_{n-1}^{BF} \hat{P}_{nx}^{BF} - 2\hat{P}_{nz}^{BF}) \quad (24)$$

$$+ 2 \sum_{i=1}^{n-1} \sum_{j>i,j=1}^{n-1} M_{i,j} \hat{P}_i \cdot \hat{P}_j + 2 \sum_{i=1}^{n-2} M_{i,n} \hat{P}_i \cdot \hat{P}_n + 2M_{n,n-1} \hat{P}_n \cdot \hat{P}_{n-1} \quad (25)$$

$$+ \sum_{i=1}^{n-2} M_{i,n-1} \left( -\frac{i\hbar \hat{P}_{ix}^{BF}}{R_{n-1} \sin \theta_{n-1}^{BF}} + [\hat{P}_{n-1}, \hat{P}_i] \right) \quad (26)$$

$$+ \sum_{i=1}^{n-2} M_{i,n} \left( \frac{i\hbar \cot \theta_{n-1}^{BF} \hat{P}_{ix}^{BF}}{R_n} - \frac{2i\hbar \hat{P}_{iz}^{BF}}{R_n} + [\hat{P}_n, \hat{P}_i] \right) \quad (27)$$

$$+ M_{n-1,n} \left( \frac{i\hbar \cot \theta_{n-1}^{BF} \hat{P}_{(n-1)x}^{BF}}{R_n} - \frac{2i\hbar \hat{P}_{(n-1)z}^{BF}}{R_n} - \frac{i\hbar \hat{P}_{nx}^{BF}}{R_{n-1} \sin \theta_{n-1}^{BF}} + [\hat{P}_{n-1}, \hat{P}_n] \right) \quad (28)$$

Therefore, the fact that the operators  $\hat{P}_{(n-1)y}^{BF}$  and  $\hat{P}_{ny}^{BF}$  are non hermitian and that some commutators  $[\hat{P}_i, \hat{P}_j]$  are not equal to zero, generate the last two terms in Eq.24 and Eqs.25-28. We shall not examine Eq.24 because it has been explicitly treated in Ref[1], dedicated to the description of a molecule by Jacobi vectors. We have established that Eq.24 can be rewritten in the following form :

$$\begin{aligned}
& \sum_{i=1}^n M_{i,i} (\hat{\vec{P}}_i)^2 - \frac{i\hbar M_{n-1,n-1}}{R_{n-1} \sin \theta_{n-1}^{BF}} \hat{P}_{(n-1)x^{BF}} + \frac{i\hbar M_{n,n}}{R_n} (\cot \theta_{n-1}^{BF} \hat{P}_{nx^{BF}} - 2\hat{P}_{nz^{BF}}) = \\
& \sum_{i=1}^n M_{i,i} \left( (\hat{P}_i^r)^2 - \frac{2i\hbar \hat{P}_i^r}{R_i} \right) + \sum_{i=1}^{n-1} \left( \frac{M_{n,n}}{R_n^2} + \frac{M_{i,i}}{R_i^2} \right) \hat{L}_i^\dagger \cdot \hat{L}_i \\
& + \sum_{i=1}^{n-2} \sum_{j>i, j=1}^{n-1} \left( \frac{M_{n,n} \hat{L}_i \cdot \hat{L}_j}{R_n^2} \right) + \frac{M_{n,n} \left( \hat{J} \cdot \hat{J} - 2 \sum_{i=1}^{n-1} \hat{J} \cdot \hat{L}_i \right)}{R_n^2} \tag{29}
\end{aligned}$$

We have shown that the order of the operators in the products that contain  $\hat{L}_{n-1}$  is not immaterial: placing the BF components of  $\hat{L}_{n-1}$  on the right hand side of all products is particularly useful for simplifying the expression of the kinetic energy operator and its representation in the angular basis set. Therefore, it is worth noticing that the substitution of the  $(\hat{\vec{P}}_i)^2$  by their expression (Eq.7) in the classical formula  $\sum_{i=1}^n M_{i,i} (\hat{\vec{P}}_i)^2$  leads exactly to the quantum expression Eq(29), except for  $\hat{L}_i^\dagger \cdot \hat{L}_i$  which must be substituted for  $(\hat{L}_i)^2$ . This is no longer true for  $i = n - 1$  and  $n$ .

Next, the quantization of the terms generated by the off-diagonal masses is undertaken. Consequently, terms 25 to 28 have to be calculated. The results are summarized below :

(i) Term 25 corresponds to the classical expression of the kinetic energy generated by the off-diagonal masses. Vector  $\hat{\vec{P}}_{n-1}$  must be placed on the right of all scalar products where it appears.

(ii) Term 26 comes from the non-hermitian character of  $\hat{\vec{P}}_{n-1}$  and the non-commutation of  $\hat{\vec{P}}_i$  with  $\hat{\vec{P}}_{n-1}$ . By means of the commutators given in Appendix 1, it can be shown that this term is equal to zero, which implies that :

$$\hat{\vec{P}}_i^\dagger \hat{\vec{P}}_{n-1} + \hat{\vec{P}}_{n-1}^\dagger \hat{\vec{P}}_i = 2\hat{\vec{P}}_i \cdot \hat{\vec{P}}_{n-1} \tag{30}$$

Here again, the order of the operators in the scalar product is strictly fixed.

(iii) Term 27 comes from the non-hermitian character of  $\hat{\vec{P}}_n$  and the non-commutation of  $\hat{\vec{P}}_i$  with  $\hat{\vec{P}}_n$ . With the help of the commutators given in Appendix 1, it can similarly be shown that this term is equal to zero, i.e. :

$$\hat{\vec{P}}_i^\dagger \hat{\vec{P}}_n + \hat{\vec{P}}_n^\dagger \hat{\vec{P}}_i = 2\hat{\vec{P}}_i \cdot \hat{\vec{P}}_n \tag{31}$$

(iv) Term 28 comes from the non-hermitian character of  $\hat{\vec{P}}_n$  and  $\hat{\vec{P}}_{n-1}$ , and the non-commutation of  $\hat{\vec{P}}_{n-1}$  with  $\hat{\vec{P}}_n$ . Using Appendix 1, it can be shown that :

$$(28) = \frac{2i\hbar M_{n-1,n}}{R_n} \left\{ -\hat{P}_{n-1}^r \cos \theta_{n-1}^{BF} + \frac{(1 + \sin^2(\theta_{n-1}^{BF})) \hat{L}_{(n-1)y}^{BF}}{\sin \theta_{n-1}^{BF}} \right\} \quad (32)$$

The fact that Term 28 is not equal to zero means that non-hermiticity and non-commutation of the two operators generates purely quantum terms.

*It should be emphasized that the calculations leading to results in Eqs.(30,31,32) are long and tedious and that the order of the operators in the scalar product is strictly fixed, i.e. is not immaterial.*

The following equation establishes the relationship between the "classical" expression of the kinetic energy and its "quantum" counterpart :

$$2\hat{\mathbf{T}}_{\text{quant}} = 2\hat{\mathbf{T}}_{\text{class}} + \frac{i\hbar M_{n-1,n-1}}{R_{n-1} \sin \theta_{n-1}} \hat{P}_{(n-1)x}^{BF} + \frac{i\hbar M_{n,n}}{R_n} (\cot \theta_{n-1} \hat{P}_{nx}^{BF} - 2\hat{P}_{nz}^{BF}) \quad (33)$$

$$+ \frac{2i\hbar M_{n-1,n}}{R_n} \left\{ -\hat{P}_{n-1}^r \cos \theta_{n-1}^{BF} + \frac{(1 + \sin^2(\theta_{n-1}^{BF})) \hat{L}_{(n-1)y}^{BF}}{\sin \theta_{n-1}^{BF} R_{n-1}} \right\} \quad (34)$$

$$2\hat{\mathbf{T}}_{\text{class}} = \sum_{i=1}^n M_{i,i} (\hat{\vec{P}}_i)^2 + 2 \sum_{i=1}^{n-1} \sum_{j>i,j=1}^n M_{i,j} \hat{\vec{P}}_i \cdot \hat{\vec{P}}_j + 2 \sum_{i=1}^{n-2} M_{i,n} \hat{\vec{P}}_i \cdot \hat{\vec{P}}_n + 2M_{n-1,n} \hat{\vec{P}}_n \cdot \hat{\vec{P}}_{n-1} \quad (35)$$

Consequently, the quantum expression contains only two additional terms generated by the diagonal masses ( $M_{n,n}$  et  $M_{n-1,n-1}$ ) and two other terms coming from the off-diagonal  $M_{n,n-1}$  mass.

Another long and tedious calculation that takes into account the non-commutation of the operators, leads to the following expression of the kinetic energy for an N-atom molecule in terms of BF components of angular momenta and the BF-angles  $\theta_i^{BF}$  and  $\phi_i^{BF}$  noted  $\theta_i$  and  $\phi_i$  ( $\phi_{n-1}^{BF} = 0, \theta_n^{BF} = 0$ ):

$$\hat{\mathbf{T}}^{\mathbf{J}} = \sum_{i=1}^n M_{i,i} \left( \frac{(\hat{P}_i^r)^2}{2} - \frac{i\hbar \hat{P}_i^r}{R_i} \right)$$

$$\begin{aligned}
& + \sum_{i,j=1;i < j}^n M_{i,j} \left\{ \sin(\theta_i) \sin(\theta_j) \cos(\phi_i - \phi_j) + \cos(\theta_i) \cos(\theta_j) \right\} \hat{P}_i^r \hat{P}_j^r \\
& + \sum_{i,j=1;i \neq j}^{n-1} M_{i,j} \sin(\theta_i) \sin(\theta_j) \sin(\phi_i - \phi_j) \left( \frac{\hat{P}_i^r \hat{L}_{jz}}{R_j} \right) \\
& + \sum_{i,j=1;i \neq j}^{n-1} \hat{P}_i^r \sin(\theta_i) \left( \frac{M_{i,j} \cos(\theta_j)}{R_j} - \frac{M_{i,n}}{R_n} \right) \left( \frac{e^{-i\phi_i} \hat{L}_j^+ - e^{i\phi_i} \hat{L}_j^-}{2i} \right) \\
& - \sum_{i=1}^{n-1} \frac{M_{i,n}}{R_n} \hat{P}_i^r \sin(\theta_i) \left( \frac{e^{-i\phi_i} \hat{L}_i^+ - e^{i\phi_i} \hat{L}_i^-}{2i} \right) \\
& - \sum_{i,j=1;i \neq j}^n \frac{M_{i,j}}{R_i} \hat{P}_j^r \cos(\theta_j) \sin(\theta_i) \left( \frac{e^{-i\phi_i} \hat{L}_i^+ - e^{i\phi_i} \hat{L}_i^-}{2i} \right) \\
& + \sum_{i,j=1;i < j}^{n-1} \left\{ \frac{M_{i,j}}{R_i R_j} \left( \cos(\theta_i) \cos(\theta_j) + \frac{1}{2} e^{-i\phi_i} \sin(\theta_i) e^{i\phi_j} \sin(\theta_j) \right) \right. \\
& \left. - \frac{M_{i,n}}{R_i R_n} \cos(\theta_i) - \frac{M_{j,n}}{R_j R_n} \cos(\theta_j) + \frac{M_{n,n}}{2R_n^2} \right\} \left( \frac{\hat{L}_i^+ \hat{L}_j^-}{2} \right) \\
& + \sum_{i,j=1;i < j}^{n-1} \left\{ \frac{M_{i,j}}{R_i R_j} \left( \cos(\theta_i) \cos(\theta_j) + \frac{1}{2} e^{i\phi_i} \sin(\theta_i) e^{-i\phi_j} \sin(\theta_j) \right) \right. \\
& \left. - \frac{M_{i,n}}{R_i R_n} \cos(\theta_i) - \frac{M_{j,n}}{R_j R_n} \cos(\theta_j) + \frac{M_{n,n}}{2R_n^2} \right\} \left( \frac{\hat{L}_i^- \hat{L}_j^+}{2} \right) \\
& - \sum_{i,j=1;i < j}^{n-1} \frac{M_{i,j}}{4R_i R_j} \sin(\theta_i) \sin(\theta_j) \left( e^{-i(\phi_i+\phi_j)} \hat{L}_i^+ \hat{L}_j^+ + e^{i(\phi_i+\phi_j)} \hat{L}_i^- \hat{L}_j^- \right) \\
& + \sum_{i=1}^{n-1} \left\{ \frac{M_{n,n}}{2R_n^2} + \frac{M_{i,i}}{2R_i^2} - \frac{M_{i,n} \cos(\theta_i)}{R_i R_n} \right\} \hat{L}_i^+ \hat{L}_i^- \\
& + \sum_{i,j=1;i < j}^{n-1} \left\{ \frac{M_{i,j}}{R_i R_j} \sin(\theta_i) \sin(\theta_j) \cos(\phi_i - \phi_j) + \frac{M_{n,n}}{2R_n^2} \right\} \hat{L}_{iz} \hat{L}_{jz} \\
& + \sum_{i,j=1;i < j}^{n-1} \sin(\theta_j) \left( -\frac{M_{i,j}}{R_i R_j} \cos(\theta_i) + \frac{M_{j,n}}{R_j R_n} \right) \left( \frac{e^{-i\phi_j} \hat{L}_i^+ + e^{i\phi_j} \hat{L}_i^-}{2} \right) \hat{L}_{jz} \\
& + \sum_{i,j=1;i < j}^{n-1} \sin(\theta_i) \left( -\frac{M_{i,j}}{R_i R_j} \cos(\theta_j) + \frac{M_{i,n}}{R_i R_n} \right) \left( \frac{e^{-i\phi_i} \hat{L}_{iz} \hat{L}_j^+ + e^{i\phi_i} \hat{L}_{iz} \hat{L}_j^-}{2} \right) \\
& + \sum_{i=1}^{n-1} \frac{M_{i,n}}{R_n} P_i^r \sin(\theta_i) \left( \frac{e^{-i\phi_i} \hat{J}^+ - e^{i\phi_i} \hat{J}^-}{2i} \right) \\
& + \sum_{i=1}^{n-1} \frac{-M_{i,n}}{R_i R_n} \sin(\theta_i) \left( \frac{e^{-i\phi_i} \hat{J}^+ + e^{i\phi_i} \hat{J}^-}{2} \right) \hat{L}_{iz} \\
& + \left\{ \frac{M_{i,n} \cos(\theta_i)}{R_i R_n} - \frac{M_{n,n}}{R_n^2} \right\} \left( \frac{\hat{J}^+ \hat{L}_i^- + \hat{J}^- \hat{L}_i^+}{2} \right)
\end{aligned}$$

$$-\sum_{i=1}^{n-1} \left( \frac{M_{n,n} \hat{J}_z \hat{L}_{iz}}{R_n^2} \right) + \frac{M_{n,n} \hat{J}^2}{2R_n^2} + \sum_{i=1}^{n-1} \frac{\hbar M_{i,n}}{R_i R_n} \sin(\theta_i) \left( \frac{e^{-i\phi_i} \hat{L}_i^+ - e^{i\phi_i} \hat{L}_i^-}{2} \right) \quad (36)$$

The advantage of this equation compared to some developed expression previously proposed by other authors in the case of polyatomics is to be as compact and general as possible. This later point will be discussed in Section 6. The physical meaning of each terms is clear because of the presence of the angular momenta. Therefore, if we compare this equation to those obtained by substituting, in the classical expression  $\hat{\mathbf{T}} = \frac{1}{2} \sum_{i,j=1}^n \hat{P}_i M_{i,j} \hat{P}_j$ , vectors  $\hat{P}_i$  for their expression (Eq.7), there is only one purely quantum term, namely  $\sum_{i=1}^{n-1} \frac{\hbar M_{i,n}}{R_i R_n} \sin(\theta_i^{BF}) \left( \frac{e^{-i\phi_i} \hat{L}_i^+ - e^{i\phi_i} \hat{L}_i^-}{2} \right)$ , under the condition that the BF-components of  $\hat{L}_{n-1}$  are appropriately placed on the right of each product.

In a previous work dedicated to triatomic molecules [2], the quantization of the classical expression of the kinetic energy provided an additional term,  $\frac{i\hbar M_{1,2}}{R_1 R_2} \sin(\theta_1^{BF}) \hat{L}_{1y}$ , which corresponds to the extra-term obtained in the general formula if  $n=2$  ( $\phi_2^{BF} = 0$ ).  $M_{1,2}$ ,  $R_1$ ,  $R_2$  and  $\theta_1^{BF}$  were noted in this article M, r, R and  $\alpha$ , respectively. Therefore, the quantum and classical expressions are very similar only if the non-commutating operators are placed in the different products in a prescribed order.

## V. ANGULAR BASIS FUNCTIONS : INTEGRATION OVER ANGULAR COORDINATES, MATRIX REPRESENTATION

We now focus our attention on the action of the kinetic operator on an angular basis set that describes the various rotations of the molecule, parametrized by three Euler angles ( $\alpha = \theta_n^{SF}$ ,  $\beta = \phi_n^{SF}$ ,  $\gamma = \phi_{n-1}^{E2}$ ) and the spherical angles of the vectors  $\vec{R}_i$  ( $i = 1, \dots, n-1$ ) viewed in BF ( $\theta_i^{BF}, \phi_i^{BF}$ ).

Moreover, in the absence of external field, SF is isotropic, i.e. the orientation of  $z^{SF}$  is arbitrary, so that any observable must be  $\alpha$ -independent [30]. The overall rotation of the molecule can thus be described by the following basis set [31–33]:

$$\langle (\alpha), \beta, \gamma \mid J, 0, \Omega \rangle = Y_J^\Omega(\beta, \gamma)(-1)^\Omega \quad (37)$$

The current element of the working angular function basis for the BF spherical angles of vectors  $\vec{R}_i$  ( $i = 1, \dots, n-1$ ) is given by :

$$\begin{aligned} & \langle (\alpha), \beta, \gamma, \theta_{n-1}^{BF}, \phi_1^{BF}, \theta_1^{BF}, \dots, \phi_{n-2}^{BF}, \theta_{n-2}^{BF} \mid \Omega, \ell_{n-1}, \ell_1, \Omega_1, \dots, \ell_{n-2}, \Omega_{n-2} \rangle_{J=} \\ & Y_J^\Omega(\beta, \gamma)(-1)^\Omega \mathcal{P}_{\ell_{n-1}}^{\Omega - \Omega_1 - \dots - \Omega_{n-2}}(\cos(\theta_{n-1}^{BF})) Y_{\ell_1}^{\Omega_1}(\theta_1^{BF}, \phi_1^{BF}) \dots Y_{\ell_{n-2}}^{\Omega_{n-2}}(\theta_{n-2}^{BF}, \phi_{n-2}^{BF}) \end{aligned} \quad (38)$$

where  $\mathcal{P}_\ell^\Omega(\cos(\theta))$  is a normalized associated Legendre function times  $(-1)^\Omega$  and  $Y_\ell^\Omega(\theta, \phi)$  is a spherical harmonics  $Y_\ell^\Omega(\theta, \phi) = \mathcal{P}_\ell^\Omega(\cos(\theta)) \frac{1}{\sqrt{2\pi}} \exp(i\Omega\phi)$ .

The current element of this working angular basis set is, hereafter, denoted by  $\{\langle \text{angles} \mid \dots \rangle_J\}$ .

The action of the kinetic energy operator on the angular basis functions requires the use of the basic formulae given in Appendix 2 for the angular momenta  $\vec{L}_i$  ( $i = 1, \dots, n-2$ ) as well as the specific formula established in Ref[1] (Eq. 73.a), given below for  $\hat{L}_{(n-1)\pm BF}$ ,  $\hat{L}_{(n-1)zBF}$  :

$$\hat{L}_{(n-1)\pm BF} \{\langle \text{angles} \mid \dots \rangle_J\} = \hbar c_\pm(\ell_{n-1}, \Omega_{n-1}) \langle (\alpha), \beta, \gamma \mid J, 0, \Omega \rangle \mathcal{P}_{\ell_{n-1}}^{\Omega - (\sum_{i=1}^{n-2} \Omega_i) \pm 1}(\cos(\theta_{n-1}^{BF})) \langle \phi_1^{BF}, \theta_1^{BF}, \dots, \phi_{n-2}^{BF}, \theta_{n-2}^{BF} \mid \ell_1, \Omega_1, \dots, \ell_{n-2}, \Omega_{n-2} \rangle \quad (39)$$

$$\hat{L}_{(n-1)zBF} \{\langle \text{angles} \mid \dots \rangle_J\} = i\hbar(\Omega - \sum_{i=1}^{n-2} \Omega_i) \{\langle \text{angles} \mid \dots \rangle_J\} \quad (40)$$



Actually, no real difficulties are generated by the fact that the operators  $\hat{L}_{n-1}$  and  $\hat{L}_i$  ( $i = 1, \dots, n-2$ ) do not satisfy similar relationships. In order to illustrate this important point, the following calculation shows how one of the more complicated terms of the kinetic energy,  $\left(\frac{M_{i,n-1}}{4R_i R_{n-1}} \sin(\theta_i^{BF}) \sin(\theta_{n-1}^{BF}) e^{-i\phi_i} \hat{L}_i^+ \hat{L}_{n-1}^+\right)$  ( $i=1, \dots, n-2$ ) acts upon the angular basis function:

$$\begin{aligned}
& \sin(\theta_i^{BF}) \sin(\theta_{n-1}^{BF}) e^{-i\phi_i} \hat{L}_i^+ \hat{L}_{n-1}^+ \{ \langle \text{angles} \mid \dots \rangle_J \} \\
&= c_+(\ell_{n-1}, \Omega_{n-1}) \sin(\theta_i^{BF}) \sin(\theta_{n-1}^{BF}) e^{-i\phi_i} \hat{L}_i^+ \langle (\alpha), \beta, \gamma \mid J, 0, \Omega \rangle \\
& \quad \mathcal{P}_{\ell_{(n-1)}}^{\Omega - (\sum_{i=1}^{n-2} \Omega_i) + 1} (\cos(\theta_{n-1}^{BF})) \langle \phi_1^{BF}, \theta_1^{BF}, \dots, \phi_{n-2}^{BF}, \theta_{n-2}^{BF} \mid \ell_1, \Omega_1, \dots, \ell_{n-2}, \Omega_{n-2} \rangle \\
&= c_+(\ell_{n-1}, \Omega_{n-1}) c_+(\ell_i, \Omega_i) \sin(\theta_i^{BF}) \sin(\theta_{n-1}^{BF}) e^{-i\phi_i} \langle (\alpha), \beta, \gamma \mid J, 0, \Omega \rangle \\
& \quad \mathcal{P}_{\ell_{(n-1)}}^{\Omega - (\sum_{i=1}^{n-2} \Omega_i) + 1} (\cos(\theta_{n-1}^{BF})) \langle \phi_1^{BF}, \theta_1^{BF}, \dots, \phi_{n-2}^{BF}, \theta_{n-2}^{BF} \mid \ell_1, \Omega_1, \dots, \ell_i, \Omega_i + 1, \dots \rangle \\
&= c_+(\ell_{n-1}, \Omega_{n-1}) c_+(\ell_i, \Omega_i) \langle (\alpha), \beta, \gamma \mid J, 0, \Omega \rangle \sin(\theta_{n-1}^{BF}) \mathcal{P}_{\ell_{(n-1)}}^{\Omega - (\sum_{i=1}^{n-2} \Omega_i) + 1} (\cos(\theta_{n-1}^{BF})) \\
& \quad \left\{ B_+^-(\ell_i, \Omega_i + 1) \langle \phi_1^{BF}, \theta_1^{BF}, \dots, \phi_{n-2}^{BF}, \theta_{n-2}^{BF} \mid \ell_1, \Omega_1, \dots, \ell_i + 1, \Omega_i, \dots \rangle \right. \\
& \quad \left. + B_-^-(\ell_i, \Omega_i + 1) \langle \phi_1^{BF}, \theta_1^{BF}, \dots, \phi_{n-2}^{BF}, \theta_{n-2}^{BF} \mid \ell_1, \Omega_1, \dots, \ell_i - 1, \Omega_i, \dots \rangle \right\} \\
&= c_+(\ell_{n-1}, \Omega_{n-1}) c_+(\ell_i, \Omega_i) \\
& \quad \left\{ B_+^-(\ell_i, \Omega_i + 1) B_+^-(\ell_{n-1}, \Omega_{n-1} + 1) \langle \dots \mid \dots, \ell_{n-1} + 1, \Omega_{n-1}, \dots, \ell_i + 1, \Omega_i, \dots \rangle_J \right. \\
& \quad + B_+^-(\ell_i, \Omega_i + 1) B_-^-(\ell_{n-1}, \Omega_{n-1} + 1) \langle \dots \mid \dots, \ell_{n-1} - 1, \Omega_{n-1}, \dots, \ell_i + 1, \Omega_i, \dots \rangle_J \\
& \quad + B_-^-(\ell_i, \Omega_i + 1) B_+^+(\ell_{n-1}, \Omega_{n-1} + 1) \langle \dots \mid \dots, \ell_{n-1} + 1, \Omega_{n-1}, \dots, \ell_i - 1, \Omega_i, \dots \rangle_J \\
& \quad \left. + B_-^-(\ell_i, \Omega_i + 1) B_-^+(\ell_{n-1}, \Omega_{n-1} + 1) \langle \dots \mid \dots, \ell_{n-1} - 1, \Omega_{n-1}, \dots, \ell_i - 1, \Omega_i, \dots \rangle_J \right\} \quad (41)
\end{aligned}$$

In the latter expressions, the notation introduced in Appendix 2 has been used.

We now calculate  $\hat{\mathbf{T}}^J$ , the matrix representing the kinetic energy operator in the angular basis set  $\{ \langle \text{angles} \mid \dots \rangle_J \}$ . The integration is over the angles only, (i.e. the matrix elements are expressed in terms of  $J, \Omega, M, \ell_i, \Omega_i$  ( $i = 1, \dots, n-2$ )), and  $\ell_{n-1}$  on the one hand,  $R_i$  and  $\hat{P}_i^r$  ( $i = 1, \dots, n$ ) on the other hand.  $J$  and  $M=0$  are fixed, i.e.  $\hat{\mathbf{T}}^J$  is a diagonal block of  $\hat{\mathbf{T}}$  at constant  $J$ . In the basis  $\{ \langle \text{angles} \mid \dots \rangle_J \}$ , using an approach similar to that used for Eq.(52), it is rather easy but long to establish the matrix elements  $\langle \dots \Omega'_i, \ell'_i, \dots, \Omega'_j, \ell'_j \dots \mid \hat{\mathbf{T}}^J \mid \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle$  which are non zero. Inspection of equation (36) reveals that the non-zero matrix elements fulfil the following conditions:

- $\Delta\Omega = \Omega - \Omega' = 0, \pm 1$
- $\Delta\Omega_i = \Omega_i - \Omega'_i = 0, \pm 1$  ( $\forall i = 1, 2, \dots, n-2$ )
- $\Delta\Omega = \Delta\Omega_i + \Delta\Omega_j$  ( $\forall i \neq j = 1, 2, \dots, n-2$ )
- $\Delta\ell_i = \ell_i - \ell'_i = 0, \pm 1$  ( $\forall i = 1, 2, \dots, n-1$ )

Consequently, the non-zero matrix elements  $\langle \dots \Omega'_i, \ell'_i, \dots, \Omega'_j, \ell'_j \dots | \hat{\mathbf{T}}^J | \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle$  with  $i < j$  are given by the following formulae in which only the modified quantum numbers are mentioned. Therefore,  $\epsilon_i$  represents either + or -,  $c_+(J, \Omega) = \hbar^2 \sqrt{J(J+1) - \Omega(\Omega+1)}$  and  $c_-(J, \Omega) = \hbar^2 \sqrt{J(J+1) - \Omega(\Omega-1)}$ :

(i): Diagonal Terms of  $\hat{\mathbf{T}}^J$

$$\begin{aligned}
& \langle \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots | \hat{\mathbf{T}}^J | \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle = \\
& \sum_{i=1}^n M_{i,i} \left( \frac{(\hat{P}_i^r)^2}{2} - \frac{i\hbar \hat{P}_i^r}{R_i} \right) \\
& + \sum_{i=1}^{n-1} \hbar^2 \ell_i (\ell_i + 1) \left( \frac{M_{n,n}}{2R_n^2} + \frac{M_{i,i}}{2R_i^2} \right) + \sum_{i,j=1; i < j}^{n-1} \frac{M_{n,n} \hbar^2 \Omega_i \Omega_j}{2R_n^2} \\
& - \sum_{i=1}^{n-1} \frac{M_{n,n} \hbar^2 \Omega \Omega_i}{R_n^2} + \frac{M_{n,n} \hbar^2 J(J+1)}{2R_n^2} \\
& \text{Let us note that } \Omega_{n-1} = \Omega - \sum_{i=1}^{n-2} \Omega_i
\end{aligned} \tag{42}$$

(ii): Non diagonal terms for  $\Delta\Omega = 0, \Delta\Omega_i = 0; \Delta\ell_i = \pm 1$

$$\begin{aligned}
& \langle \dots \Omega_i, \ell_i + (\epsilon_i 1) \dots | \hat{\mathbf{T}}^J | \dots \Omega_i, \ell_i, \dots \rangle = \\
& \left\{ -\frac{M_{i,n} \hat{P}_n^r}{2iR_i} - \frac{M_{i,n} \hat{P}_i^r}{2iR_n} + \frac{\hbar M_{i,n}}{2R_i R_n} \right\} \\
& \left\{ c_+(\ell_i, \Omega_i) B_{\epsilon_i}^-(\ell_i, \Omega_i + 1) - c_-(\ell_i, \Omega_i) B_{\epsilon_i}^+(\ell_i, \Omega_i - 1) \right\} \\
& + \left\{ M_{i,n} \hat{P}_i^r \hat{P}_n^r - \frac{M_{i,n}}{R_i R_n} \hbar^2 \ell_i (\ell_i + 1) \right\} B_{\epsilon_i}^o(\ell_i, \Omega_i)
\end{aligned} \tag{43}$$

(iii): Non diagonal terms for  $\Delta\Omega = \pm 1, \Delta\Omega_i = \pm 1; \Delta\ell_i = 1 \text{ or } -1$

$$\begin{aligned}
& \langle \Omega \pm 1, \dots, \Omega_i \pm 1, \ell_i + (\epsilon_i 1) \dots | \hat{\mathbf{T}}^J | \dots, \Omega_i, \ell_i, \dots \rangle = \\
& \left\{ \mp \frac{M_{i,n} \hat{P}_i^r}{2iR_n} - \frac{M_{i,n} \Omega_i}{2R_i R_n} \right\} c_{\pm}(J, \Omega) B_{\epsilon_i}^{\pm}(\ell_i, \Omega_i) \\
& + \frac{M_{i,n}}{2R_i R_n} B_{\epsilon_i}^o(\ell_i, \Omega_i \pm 1) c_{\pm}(\ell_i, \Omega_i) c_{\pm}(J, \Omega)
\end{aligned} \tag{44}$$

(iv): Non diagonal terms for  $\Delta\Omega = \pm 1$ ,  $\Delta\Omega_i = \pm 1$ ;  $\Delta\ell_i = 0$

$$\langle \Omega \pm 1, \dots, \Omega_i \pm 1, \ell_i \dots | \hat{\mathbf{T}}^J | \dots, \Omega_i, \ell_i, \dots \rangle = -\frac{M_{n,n}}{2R_n^2} c_{\pm}(\ell_i, \Omega_i) c_{\pm}(J, \Omega) \tag{45}$$

(v): Non diagonal terms for  $\Delta\Omega = 0$ ,  $\Delta\Omega_i = -\Delta\Omega_j = \pm 1$ ;  $\Delta\ell_i = \Delta\ell_j = 0$

$$\begin{aligned}
& \langle \dots, \Omega_i \pm 1, \ell_i, \dots, \Omega_j \mp 1, \ell_j \dots | \hat{\mathbf{T}}^J | \dots, \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle = \\
& c_{\pm}(\ell_i, \Omega_i) c_{\mp}(\ell_j, \Omega_j) \frac{M_{n,n}}{4R_n^2}
\end{aligned} \tag{46}$$

(vi): Non diagonal terms for  $\Delta\Omega = 0$ ,  $\Delta\Omega_i = \Delta\Omega_j = 0$ ;  $\Delta\ell_i = \pm 1$ ;  $\Delta\ell_j = 1$  or  $-1$

$$\begin{aligned}
& \langle \dots, \Omega_i, \ell_i + (\epsilon_i 1), \dots, \Omega_j, \ell_j + (\epsilon_j 1) \dots | \hat{\mathbf{T}}^J | \dots, \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle = \\
& M_{ij} \hat{P}_i^r \hat{P}_j^r B_{\epsilon_i}^o(\ell_i, \Omega_i) B_{\epsilon_j}^o(\ell_j, \Omega_j) - \frac{M_{ij} \hat{P}_j^r}{2iR_i} c_+(\ell_i, \Omega_i) B_{\epsilon_i}^-(\ell_i, \Omega_i + 1) B_{\epsilon_j}^o(\ell_j, \Omega_j) \\
& - \frac{M_{ij} \hat{P}_i^r}{2iR_j} c_+(\ell_j, \Omega_j) B_{\epsilon_j}^-(\ell_j, \Omega_j + 1) B_{\epsilon_i}^o(\ell_i, \Omega_i) \\
& + \frac{M_{ij} \hat{P}_j^r}{2iR_i} c_-(\ell_i, \Omega_i) B_{\epsilon_j}^o(\ell_j, \Omega_j) B_{\epsilon_i}^+(\ell_i, \Omega_i - 1) \\
& + \frac{M_{ij} \hat{P}_i^r}{2iR_j} c_-(\ell_j, \Omega_j) B_{\epsilon_j}^+(\ell_j, \Omega_j - 1) B_{\epsilon_i}^o(\ell_i, \Omega_i) \\
& + \frac{M_{ij}}{4R_i R_j} B_{\epsilon_i}^-(\ell_i, \Omega_i + 1) B_{\epsilon_j}^+(\ell_j, \Omega_j - 1) c_+(\ell_i, \Omega_i) c_-(\ell_j, \Omega_j) \\
& + \frac{M_{ij}}{4R_i R_j} B_{\epsilon_i}^+(\ell_i, \Omega_i - 1) B_{\epsilon_j}^-(\ell_j, \Omega_j + 1) c_-(\ell_i, \Omega_i) c_+(\ell_j, \Omega_j) \\
& - \frac{M_{ij}}{4R_i R_j} B_{\epsilon_i}^-(\ell_i, \Omega_i + 1) B_{\epsilon_j}^-(\ell_j, \Omega_j + 1) c_+(\ell_i, \Omega_i) c_+(\ell_j, \Omega_j) \\
& - \frac{M_{ij}}{4R_i R_j} B_{\epsilon_i}^+(\ell_i, \Omega_i - 1) B_{\epsilon_j}^+(\ell_j, \Omega_j - 1) c_-(\ell_i, \Omega_i) c_-(\ell_j, \Omega_j)
\end{aligned} \tag{47}$$

(vii): Non diagonal terms for  $\Delta\Omega = 0$ ,  $\Delta\Omega_i = -\Delta\Omega_j = \pm 1$ ;  $\Delta\ell_i = \pm 1$ ;  $\Delta\ell_j = 0$

$$\begin{aligned}
& \langle \dots \Omega_i \pm 1, \ell_i + (\epsilon_i 1), \dots, \Omega_j \mp 1, \ell_j \dots \mid \hat{\mathbf{T}}^J \mid \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle = \\
& \pm \frac{\hat{P}_i^r M_{i,n}}{2iR_n} B_{\epsilon_i}^\pm(\ell_i, \Omega_i) c_{\mp}(\ell_j, \Omega_j) - \left( \frac{M_{i,n}}{2R_i R_n} c_{\pm}(\ell_i, \Omega_i) c_{\mp}(\ell_j, \Omega_j) B_{\epsilon_i}^o(\ell_i, \Omega_i \pm 1) \right. \\
& \left. + \frac{M_{i,n}}{2R_i R_n} \hbar \Omega_i c_{\mp}(\ell_j, \Omega_j) B_{\epsilon_i}^\pm(\ell_i, \Omega_i) \right)
\end{aligned} \tag{48}$$

**(viii):** Non diagonal terms for  $\Delta\Omega = 0$ ,  $\Delta\Omega_i = -\Delta\Omega_j = \pm 1$ ;  $\Delta\ell_i = 0$ ;  $\Delta\ell_j = \pm 1$

$$\begin{aligned}
& \langle \dots \Omega_i \pm 1, \ell_i, \dots, \Omega_j \mp 1, \ell_j + (\epsilon_j 1) \dots \mid \hat{\mathbf{T}}^J \mid \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle = \\
& \left\{ \mp \frac{\hat{P}_j^r M_{j,n}}{2iR_n} + \frac{M_{j,n} \hbar \Omega_j}{2R_j R_n} \right\} c_{\pm}(\ell_i, \Omega_i) B_{\epsilon_j}^{\mp}(\ell_j, \Omega_j) \\
& - \frac{M_{j,n}}{2R_j R_n} c_{\pm}(\ell_i, \Omega_i) c_{\mp}(\ell_j, \Omega_j) B_{\epsilon_j}^o(\ell_j, \Omega_j \mp 1)
\end{aligned} \tag{49}$$

**(ix):** Non diagonal terms for  $\Delta\Omega = 0$ ,  $\Delta\Omega_i = -\Delta\Omega_j = \pm 1$ ;  $\Delta\ell_i = \pm 1\Delta$ ;  $\ell_j = \pm 1$

$$\begin{aligned}
& \langle \dots \Omega_i \pm 1, \ell_i + (\epsilon_i 1), \dots, \Omega_j \mp 1, \ell_j + (\epsilon_j 1) \dots \mid \hat{\mathbf{T}}^J \mid \dots \Omega_i, \ell_i, \dots, \Omega_j, \ell_j \dots \rangle = \\
& \frac{M_{ij}}{2} \left\{ \hat{P}_i^r \hat{P}_j^r \pm \frac{\hat{P}_i^r \hbar \Omega_j}{iR_j} \mp \frac{\hat{P}_j^r \hbar \Omega_i}{iR_i} + \frac{\hbar^2 \Omega_i \Omega_j}{R_i R_j} \right\} B_{\epsilon_i}^\pm(\ell_i, \Omega_i) B_{\epsilon_j}^{\mp}(\ell_j, \Omega_j) \\
& + \frac{M_{ij}}{2R_i} \left\{ \mp i \hat{P}_j^r - \frac{\hbar \Omega_j}{R_j} \right\} c_{\pm}(\ell_i, \Omega_i) B_{\epsilon_i}^o(\ell_i, \Omega_i \pm 1) B_{\epsilon_j}^{\mp}(\ell_j, \Omega_j) \\
& + \frac{M_{ij}}{2R_j} \left\{ \pm i \hat{P}_i^r - \frac{\hbar \Omega_i}{R_i} \right\} c_{\mp}(\ell_j, \Omega_j) B_{\epsilon_j}^o(\ell_j, \Omega_j \mp 1) B_{\epsilon_i}^\pm(\ell_i, \Omega_i) \\
& + \frac{M_{ij}}{2R_i R_j} c_{\pm}(\ell_i, \Omega_i) c_{\mp}(\ell_j, \Omega_j) B_{\epsilon_i}^o(\ell_i, \Omega_i \pm 1) B_{\epsilon_j}^o(\ell_j, \Omega_j \mp 1)
\end{aligned} \tag{50}$$

## VI. EXAMPLE AND DISCUSSION

The configuration of an N-atom molecule can be described by N-1 relative position vectors after elimination of the center-of-mass motion. Many sets of coordinates commonly used for describing molecules can be viewed as spherical coordinates for these vectors. The spherical angles are local, i.e. they are defined for frames which change from one vector to another. The coordinates actually consist of (i) the N-1 vector lengths, (ii) N-2 planar angles between pairs of vectors, (iii) N-3 dihedral angles between two vectors around a third one, and (iv) three Euler angles orienting the BF frame with respect to the SF frame. These 3N-3 coordinates are the local spherical coordinates for the N-1 vectors. This article has aimed at exploiting this type of parametrization.

The first innovation of the method proposed in this paper is to build a particularly compact expression of the kinetic energy. Moreover, in this expression, each term possesses its own physical meaning and is individually hermitian. This approach is absolutely general and can be applied to any system. In order to show how it is applied in a particular case, we shall consider the system (AB)CD(EF) (Figure 1) because the determination of its kinetic energy operator (for J=0) has been the subject of a recently published work[20]. In that work, Remple and Watts have followed the method initiated by Handy[22] and used valence coordinates to describe the molecular deformations. They have actually applied, with the help of Mathematica[34], the chain rule twice and obtained the developed expression of the kinetic energy containing more than 400 terms, all of them being not individually hermitian. Let us apply our approach to this system with the same coordinates, i.e. the spherical coordinates of the valence vectors  $\vec{R}_i$  represented in Figure 1. Each vector  $\vec{R}_i$  is parametrized by spherical coordinates  $R_i$ ,  $\theta_i$  and  $\phi_i$ , respectively bond lengths, bond angles and torsion angles. The correspondence between Rempe *et al*'s valence coordinates and the spherical coordinates of  $\vec{R}_i$  used in our approach is easily established since  $\vec{R}_n$  and  $\vec{R}_{n-1}$  are  $\overrightarrow{CD}$  and  $\overrightarrow{CE}$ .

$$\begin{aligned} (x, y, z) \text{ Rempe axes} &\longrightarrow (y, x, -z) \text{ axes in this paper} \\ \theta_1^{Rempe}, \theta_2^{Rempe}, \theta_3^{Rempe}, \theta_4^{Rempe}, \theta_5^{Rempe} &\longrightarrow \theta_1, \pi - \theta_2, \theta_3, \pi - \theta_4, \theta_5 \end{aligned}$$

In order to derive a compact expression of the kinetic energy operator with the angular momentum coupling terms in Eq.36, we have to determine the **M** matrix (Eq. 5) for

(AB)CD(EF). We follow the method proposed in Section 2. First a set of 5 Jacobi vectors ( $\vec{r}_i, i = 1, \dots, 5$ ) has to be defined (Figure 2). The  $\mathbf{A}$  matrix relating the valence vectors ( $\vec{R}_i, i = 1, \dots, 5$ ) parametrizing the system to the Jacobi vectors selected (Figure 2) is :

$$\begin{bmatrix} \vec{R}_1 \\ \vec{R}_2 \\ \vec{R}_3 \\ \vec{R}_4 \\ \vec{R}_5 \end{bmatrix} = \begin{bmatrix} -\frac{m_B}{m_{AB}} & 0 & -\frac{m_{EF}}{m_{ABEF}} & -1 & \frac{m_D}{m_{CD}} \\ 0 & -\frac{m_E}{m_{EF}} & \frac{m_{AB}}{m_{ABEF}} & -1 & -\frac{m_C}{m_{CD}} \\ \frac{m_A}{m_{AB}} & 0 & -\frac{m_{EF}}{m_{ABEF}} & -1 & \frac{m_D}{m_{CD}} \\ 0 & \frac{m_F}{m_{EF}} & \frac{m_{AB}}{m_{ABEF}} & -1 & -\frac{m_C}{m_{CD}} \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \vec{r}_1 \\ \vec{r}_2 \\ \vec{r}_3 \\ \vec{r}_4 \\ \vec{r}_5 \end{bmatrix} \quad (51)$$

where  $m_A, m_B, m_C, m_D, m_E$  and  $m_F$  are respectively the masses of A, B, C, D, E and F while  $m_{AB} = m_A + m_B, m_{EF} = m_E + m_F, m_{CD} = m_C + m_D$  and  $m_{ABEF} = m_A + m_B + m_E + m_F$ . Next, from Eq.5, the following  $\mathbf{M}$  matrix is obtained.

$$\mathbf{M} = \begin{bmatrix} \frac{1}{m_A} + \frac{1}{m_C} & 0 & \frac{1}{m_C} & 0 & \frac{1}{m_C} \\ 0 & \frac{1}{m_D} + \frac{1}{m_F} & 0 & \frac{1}{m_D} & -\frac{1}{m_D} \\ \frac{1}{m_C} & 0 & \frac{1}{m_B} + \frac{1}{m_C} & 0 & \frac{1}{m_C} \\ 0 & \frac{1}{m_D} & 0 & \frac{1}{m_D} + \frac{1}{m_E} & -\frac{1}{m_D} \\ \frac{1}{m_C} & -\frac{1}{m_D} & \frac{1}{m_C} & -\frac{1}{m_D} & \frac{1}{m_C} + \frac{1}{m_D} \end{bmatrix} \quad (52)$$

Consequently, the expansion including more than 400 terms proposed by Rempe and Watts can be factorized by using Eq.36, with  $n=5$  and the masses  $M_{ij}$  given in Eq.52. The compact character of the present method is thus clearly illustrated in this particular case.

The second innovation consists in obtaining analytical expressions for the action of all angular operators in the basis functions in an adequate representation. Simultaneously, getting rid of the angular singularities is a straightforward matter. The next step for completing the present formalism is the demonstration of the fact that the treatment of the angular singularities can be generalized to the radial singularities[25]. This generalization is required for studying e.g. the inversion motion of the ammonia molecule [25]. To this large amplitude motion is associated the vector linking the center of mass of  $H_3$  to the nitrogen atom. The vector length is zero when the molecule is planar and the subsequent seeming radial singularity can also be avoided. Moreover, our approach can be improved by taking into account the permutation symmetries of the system. A symmetry adapted basis can be defined. All these improvements have been used for studying the ammonia spectroscopy[25].

If there are no identical particles, the method introduced can be straightforwardly used. The flexibility of our approach is also worth mentioning : any set of vectors can be used. For instance, for the study of a  $SN_2$  reaction ( $A + CH_3B \rightarrow ACH_3 + B$ ), the combination of Jacobi and valence vectors illustrated in Figure 3 is advisable. To achieve the construction of matrix  $\mathbf{T}^J$ , radial basis functions are selected. The integrals over the radial coordinates must be numerically calculated. From that point on, the rest of the work is numerical, and the numerical effort will clearly impose limits to the size of the systems that can be actually treated. For systems free in all their deformation degrees of freedom, five particles may be treated at present. If larger systems are considered, model constraints must be introduced, such that freezing a part of the system . This subject is, to a large extent, still to be explored. In all cases, it should be emphasized that it is profitable to have a quantum FBR in which the kinetic energy matrix is sparse. Combined with a DVR for the potential, the FBR that we propose constitutes an appropriate framework for future dynamical studies of more-than-three particle molecules (see Ref[35] and Ref[36] for instance).

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# APPENDIX 1

In this appendix, the various commutators that are required for the calculations in this article are given. They can be easily obtained from the definition of the  $\hat{L}_i$  BF-components. (i=1, ..., n-2).

$$[\hat{L}_{ix}, \sin \phi_i] = i\hbar \cos^2(\phi_i) \cot \theta_i ; [\hat{L}_{ix}, \cos \phi_i] = -i\hbar \cos \phi_i \sin \phi_i \cot \theta_i \quad (53)$$

$$[\hat{L}_{ix}, \sin \theta_i] = i\hbar \sin \phi_i \cos \theta_i ; [\hat{L}_{ix}, \cos \theta_i] = -i\hbar \sin \phi_i \sin \theta_i \quad (54)$$

$$[\hat{L}_{iy}, \sin \phi_i] = i\hbar \sin \phi_i \cot \theta_i \cos \phi_i ; [\hat{L}_{iy}, \cos \phi_i] = -i\hbar \sin^2(\phi_i) \cot \theta_i \quad (55)$$

$$[\hat{L}_{iy}, \sin \theta_i] = -i\hbar \cos \phi_i \cos \theta_i ; [\hat{L}_{iy}, \cos \theta_i] = i\hbar \cos \phi_i \sin \theta_i \quad (56)$$

$$[\hat{L}_{iz}, \sin \phi_i] = -i\hbar \cos \phi_i ; [\hat{L}_{iz}, \cos \phi_i] = i\hbar \sin \phi_i \quad (57)$$

$$[\hat{L}_{iz}, \sin \theta_i] = [\hat{L}_{iz}, \cos \theta_i] = 0 \quad (58)$$



## APPENDIX 2

This appendix puts together the various formulae required for application of the kinetic energy operator upon the basis functions given in Equation (41) (see Ref. [33]).

$$\cos(\theta)\mathcal{P}_\ell^\Omega(\cos\theta) = B_+^0(\ell, \Omega)\mathcal{P}_{\ell+1}^\Omega(\cos\theta) + B_-^0(\ell, \Omega)\mathcal{P}_{\ell-1}^\Omega(\cos\theta) \quad (59)$$

$$\sin\theta\mathcal{P}_\ell^\Omega(\cos\theta) = B_+^+(\ell, \Omega)\mathcal{P}_{\ell+1}^{\Omega+1}(\cos\theta) + B_-^+(\ell, \Omega)\mathcal{P}_{\ell-1}^{\Omega+1}(\cos\theta) \quad (60)$$

$$\sin\theta\mathcal{P}_\ell^\Omega(\cos\theta) = B_+^-(\ell, \Omega)\mathcal{P}_{\ell+1}^{\Omega-1}(\cos\theta) + B_-^-(\ell, \Omega)\mathcal{P}_{\ell-1}^{\Omega-1}(\cos\theta) \quad (61)$$

$$\frac{d\mathcal{P}_\ell^\Omega(\cos\theta)}{d\theta} = B_0^+(\ell, \Omega)\mathcal{P}_\ell^{\Omega+1}(\cos\theta) + B_0^-(\ell, \Omega)\mathcal{P}_\ell^{\Omega-1}(\cos\theta) \quad (62)$$

where

$$B_+^0(\ell, \Omega) = \sqrt{\frac{(\ell - \Omega + 1)(\ell + \Omega + 1)}{(2\ell + 1)(2\ell + 3)}}; B_-^0(\ell, \Omega) = \sqrt{\frac{(\ell - \Omega)(\ell + \Omega)}{(2\ell - 1)(2\ell + 1)}} \quad (63)$$

$$B_+^+(\ell, \Omega) = -\sqrt{\frac{(\ell + \Omega + 1)(\ell + \Omega + 2)}{(2\ell + 1)(2\ell + 3)}}; B_-^+(\ell, \Omega) = \sqrt{\frac{(\ell - \Omega)(\ell - \Omega - 1)}{(2\ell - 1)(2\ell + 1)}} \quad (64)$$

$$B_+^-(\ell, \Omega) = \sqrt{\frac{(\ell - \Omega + 1)(\ell - \Omega + 2)}{(2\ell + 1)(2\ell + 3)}}; B_-^-(\ell, \Omega) = -\sqrt{\frac{(\ell + \Omega)(\ell + \Omega - 1)}{(2\ell - 1)(2\ell + 1)}} \quad (65)$$

$$B_0^+(\ell, \Omega) = \frac{1}{2}\sqrt{(\ell + \Omega + 1)(\ell - \Omega)}; B_0^-(\ell, \Omega) = -\frac{1}{2}\sqrt{(\ell + \Omega)(\ell - \Omega + 1)} \quad (66)$$

The following relationships are obtained for the spherical harmonics :

$$\cos(\theta)Y_\ell^\Omega(\theta, \phi) = B_+^0(\ell, \Omega)Y_{\ell+1}^\Omega(\theta, \phi) + B_-^0(\ell, \Omega)Y_{\ell-1}^\Omega(\theta, \phi) \quad (67)$$

$$\exp(i\phi)\sin(\theta)Y_\ell^\Omega(\theta, \phi) = B_+^+(\ell, \Omega)Y_{\ell+1}^{\Omega+1}(\theta, \phi) + B_-^+(\ell, \Omega)Y_{\ell-1}^{\Omega+1}(\theta, \phi) \quad (68)$$

$$\exp(-i\phi)\sin(\theta)Y_\ell^\Omega(\theta, \phi) = B_+^-(\ell, \Omega)Y_{\ell+1}^{\Omega-1}(\theta, \phi) + B_-^-(\ell, \Omega)Y_{\ell-1}^{\Omega-1}(\theta, \phi) \quad (69)$$

To specify how the operators  $\hat{L}_{i+}^{BF}$ ,  $\hat{L}_{i-}^{BF}$ ,  $\hat{L}_{iz}^{BF}$  and  $(\hat{L}_i^2)^{BF}$  ( $i=1, \dots, n-2$ ) act upon the spherical harmonics, the following classical expressions for the kinetic momenta are used :

$$\begin{aligned} \hat{L}_{i\pm}^{BF}Y_{\ell_i}^{\Omega_i}(\theta_i, \phi_i) &= \hbar c_i^\pm(\ell_i, \Omega_i)Y_{\ell_i}^{\Omega_i \pm 1}(\theta_i, \phi_i) \\ &= \hbar\sqrt{\ell_i(\ell_i + 1) \pm \Omega_i(\Omega_i + 1)}Y_{\ell_i}^{\Omega_i \pm 1}(\theta_i, \phi_i) \end{aligned} \quad (70)$$

$$\hat{L}_{iz}^{BF}Y_{\ell_i}^{\Omega_i}(\theta_i, \phi_i) = \hbar\Omega_i Y_{\ell_i}^{\Omega_i}(\theta_i, \phi_i)$$

$$(\hat{L}_i^2)^{BF}Y_{\ell_i}^{\Omega_i}(\theta_i, \phi_i) = \hbar\ell_i(\ell_i + 1)Y_{\ell_i}^{\Omega_i}(\theta_i, \phi_i) \quad (71)$$

whereas, for the operators  $\hat{J}_+^{BF}$ ,  $\hat{J}_-^{BF}$ ,  $\hat{J}_z^{BF}$ ,  $(\hat{J}^2)^{BF}$  fulfilling the abnormal relationships, we have :

$$\hat{J}_{\pm}^{BF} Y_J^{\Omega}(\beta, \gamma) = \hbar c_{\mp} Y_J^{\Omega \mp 1}(\beta, \gamma) = \hbar \sqrt{J(J+1) \mp \Omega(\Omega+1)} Y_J^{\Omega \mp 1}(\beta, \gamma) \quad (72)$$

$$\hat{L}_{iz}^{BF} Y_J^{\Omega}(\beta, \gamma) = \hbar \Omega Y_J^{\Omega}(\beta, \gamma) ; (\hat{L}_i^2)^{BF} Y_J^{\Omega}(\beta, \gamma) = \hbar^2 J(J+1) Y_J^{\Omega}(\beta, \gamma) \quad (73)$$

## Figure Captions

**Figure 1 :** (AB)CD(EF) system parametrized by 5 Valence vectors

**Figure 2 :** The 5 Jacobi vectors used in the calculation the matrix **M**.

**Figure 3 :** Valence vectors ( $\vec{R}_1$ ,  $\vec{R}_2$  and  $\vec{R}_3$ ) used to parametrize  $CH_3$  and Jacobi vectors ( $\vec{R}_4$  and  $\vec{R}_5$ ) describing the motion of A and B in the course of a  $SN_2$  reaction.

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## FIGURES

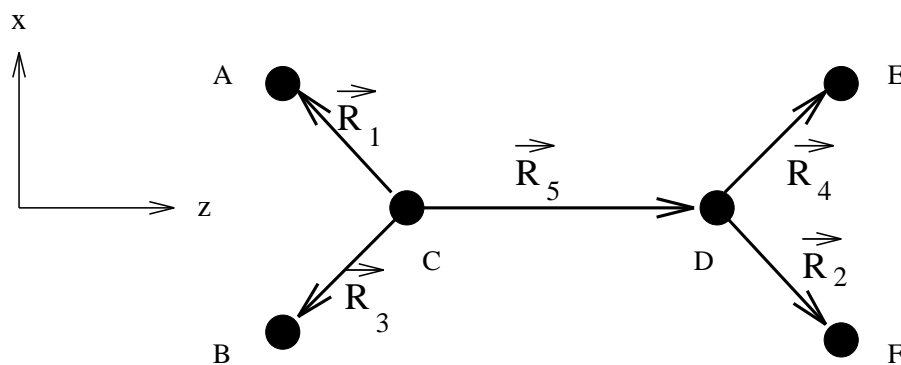


FIG. 1. .

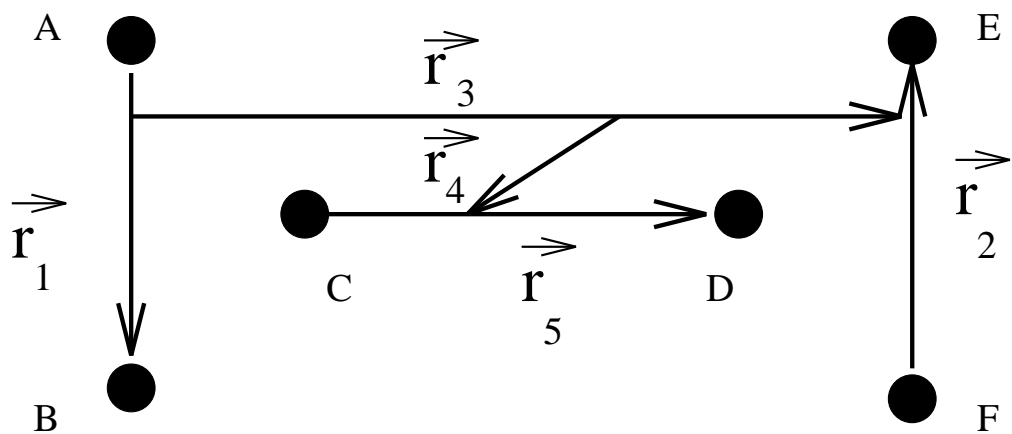


FIG. 2. .

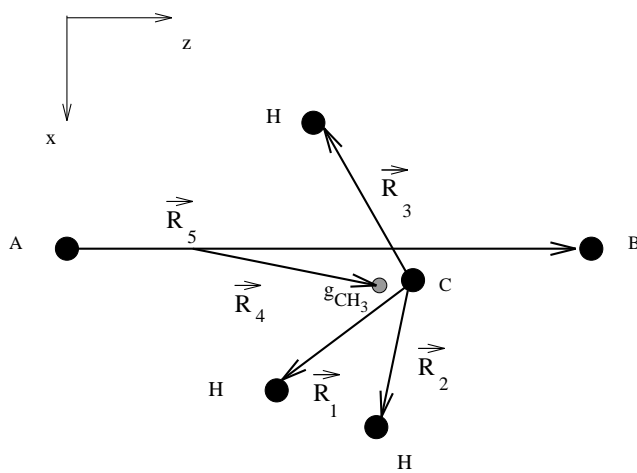


FIG. 3. .