Vector parametrization of the N-body problem in quantum mechanics: Polyspherical coordinates

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(Received 9 April 1991; revised manuscript received 3 December 1991)

The configuration of an N-body system can be entirely represented by $N-1$ relative position vectors after separation of the center-of-mass motion. Many of the sets of coordinates that are commonly used for describing molecular configurations can be viewed as spherical coordinates, for the various vectors, collected together. The spherical angles are *local*; i.e., they are defined for frames that change from one vector to another. Each particular set of coordinates of that nature (polyspherical coordinates) consists of three Euler angles for the overall rotation of the body-fixed frame and $3N-6$ internal coordinates: the $N-1$ vector lengths, $N-2$ planar angles between pairs of vectors, and $N-3$ dihedral angles between two vectors around a third one. This article aims at developing an example of this type of parametrization, where the body-fixed-frame z axis is parallel to one vector. The quantum-mechanical kinetic-energy operator for the system so described is derived. The operator action on the angular part of the functional basis set is studied (Wigner rotation matrix elements for the Euler angles and spherical harmonics for the internal angles), and the structure of the matrix representing the kinetic-energy operator is described in detail. The advantages and drawbacks of the present vector parametrization and the polyspherical coordinates are discussed. The principal advantage is in numerically calculating the matrix elements of the kinetic-energy operator: The integration over all angles turns out to be analytically achieved, so that the numerical effort is to be concentrated only on the $N-1$ radial coordinates. Radial basis functions are to be selected according to the physical context (collisonal or vibrational, or any other). Thus the angular basis set proposed constitutes an adequate finite-basis representation for the kinetic-energy operator and, combined with a discrete-variable representation for the potential energy, is likely to provide an efficient collocation framework for the dynamical study of more-than-three particle systems.

PACS number(s): 31.15.+q

I. INTRODUCTION

The growing interest in (i) the highly excited rovibrational states of polyatomic molecules, including the states where the molecules are floppy (i.e., at energies higher than isomerization barriers) or dissociative and (ii) the dynamics of van der Waals complexes, calls for exact quantum-mechanical expressions of the kinetic-energy operators for N-body systems. First, the system can be described in terms of internal (and curvilinear) coordinates. The normal-mode description of molecules [1], which is well adapted to the vibrational regime, is actually no longer well suited at high energies or for weakly bound systems. Then other treatments based on the use of curvilinear internal coordinates and differential calculus are more appropriate [2–13]. A thorough discussion of the various requirements the coordinates must fulfill for the rovibrational Hamiltonians to be adequately expressed has been presented in a recent article by Bramley, Green, and Handy [14].

Why are the matrix representations of such operators required in most cases? For bound systems, it is because the variational method has been extensively used to find rovibrational levels and wave functions. A large amount of work has been performed on triatomics using various coordinate systems (see, for instance, the reviews by Sutcliffe [15], Carney, Sprandel, and Kern [16], Carter and Handy [17], and Chapuisat, Nauts, and Brunet [18]). These systems are described in terms of (i) normal coordinates (e.g., Whitehead and Handy [19] used the Watson [20] normal coordinate kinetic-energy operator), (ii) scattering or Jacobi coordinates (Smith [21], Tennyson and Sutcliffe [22], Bacic and Light [23], and Leforestier and co-workers [24–26]), which suit isomerization processes particularly well, (iii) valence coordinates (see Refs. [18,27]), and (iv) a few others (for instance, Radau coordinates [21] and hyperspherical coordinates [28–38] which turn out to be particularly well suited for the homonuclear triatomics [39–42]). In these references, the work has been a success. In Ref. [14], a well-documented discussion of the advantages and drawbacks of all usual coordinate systems is presented, particularly with regard to the extent to which the corresponding kinetic-energy operators have or have not the two desirable properties of separability and factorizability. The requirements for vibrational coordinates and rotational coordinates are examined separately, in great detail.

In weakly bound systems, a similar approach has been used with great success, for example, for the calculation of the spectra of van der Waals complexes involving closed-shell molecules [43–58] (for reviews, see the works by Le Roy and Carley [59] and Hutson [60]). More recently, the dynamics of open-shell van der Waals complexes has been studied, for instance, the theory for atoms and open-shell Σ and Π diatomic molecules by Dubernet, Flower, and Hutson [61]. The same approach

also turned out to be successful in evaluating the molecular states in the floppy regime [62], for example, the work of Light and co-workers [63–66], Wyatt and co-workers [25], Bowman and Gadzy [67], Mladenovic and Bacic [68], and Leforestier [69].

Extending the problem to more atoms is one of the goals of this article. If no model constraints are imposed (allowing a reduction of the problem dimensionality, see Sec. VII below) and if the complete spectrum is sought (i.e., all the bands), this means four atoms, in practice, since the present state of the computational possibilities is such that the calculations would get out of hand if there are five atoms. There are a few pioneering works in that field. Maessen and Wolfsberg [70] and Handy and Carter [71] have used the Watson [20] normal coordinate operator to study H_2CO, a molecule also studied by Aoyagi, Gray, and Davis [72], Maessen, Bopp, and McLaughlin [73] have studied NH_3, Carter and Handy [74] used valence coordinates for C_2H_2, and recently Willetts *et al.* [75] and Ming-der Su *et al.* [76] have studied O_2H_2 and S_2H_2, respectively, using the same coordinates. In the field of the weakly bound systems, Hutson [77] has studied the angular momentum coupling scheme and the dynamics of the Ar-H_2O complex, by means of a coordinate system which can be considered of the Jacobi type since the water vibrations are small. For more than four particles, Iung and Leforestier have calculated, with the help of normal coordinates, the partial spectrum corresponding to the ν_1-ν_5 chromophore bands of CD_3H [78].

Getting rid of the unwieldiness of differential calculus in the derivation of exact quantum kinetic-energy operators is an important goal. A breakthrough in that field has been the use of computer algebra, as advocated by Handy [27]. The present work is an alternative attempt, at least for angular coordinates. It relies upon the fact that various sets of $N-1$ vectors can be associated with an N-body system, describing its shape as well as its orientation, and that the rovibrational motion of the system can be viewed as resulting from the rovibrational motion of each vector. These vectors can, in turn, be associated with a set of coordinates, hereafter called polyspherical coordinates, which are actually (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 (these $3N-6$ first coordinates are internal coordinates) and, finally (iv) three Eulerian angles orienting the body-fixed (BF) frame with respect to the space-fixed (SF) frame. In many practical cases, these $3N-3$ coordinates actually turn out to be local spherical coordinates for the $N-1$ vectors. Here, local means that, in order to identify spherical angles, the vectors must be viewed in frames which are not the same for all vectors. It should be emphasized that, in this work, the coordinates are mentioned only for identifying which Hamiltonians derived in terms of curvilinear coordinates actually belong to the family of the polyspherical operators introduced, thus allowing us to check our results in a few cases. However, the principal ingredients used below are clearly the algebraic (operational and matricial) considerations relevant to the rotation of the $N-1$ relative

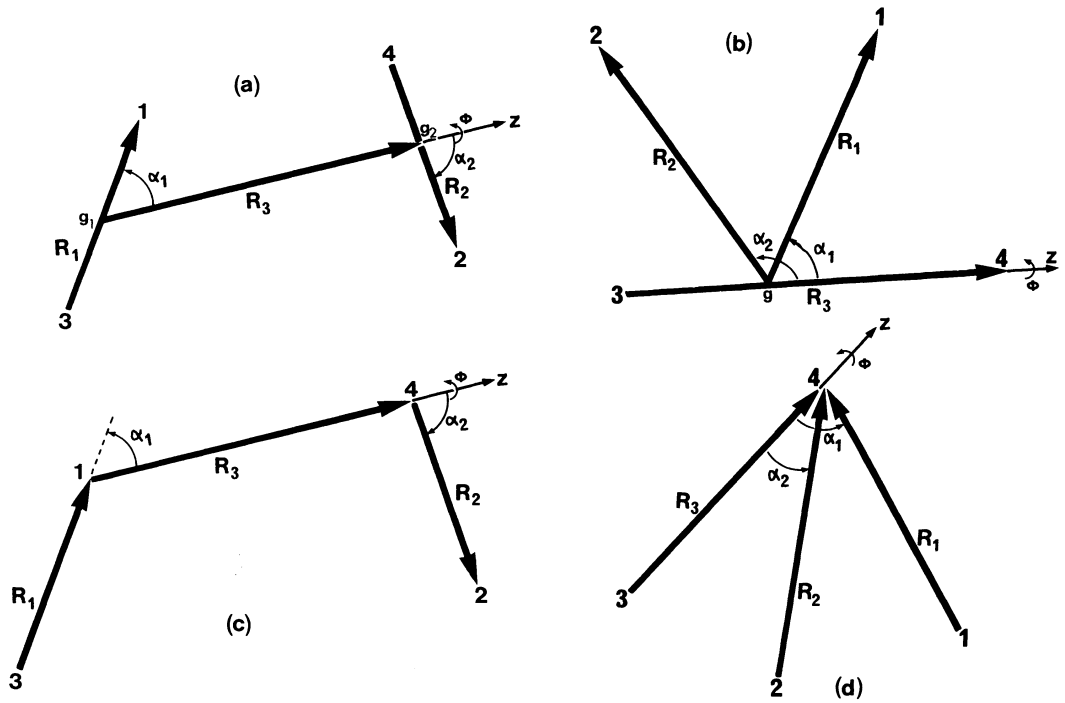

FIG. 1. Polyspherical coordinates constitute a class of internal coordinates, not a particular set of coordinates. Thus, for four particles, the four coordinate sets illustrated here are of the polyspherical type. In all cases, ϕ denotes the dihedral (internal rotation) angle between $\mathbf{R}_1$ and $\mathbf{R}_2$ around $\mathbf{R}_3$. The coordinates in (a) are advisable for a dissociative system $1234 \leftrightarrows 13+24$, for instance, a dimer; they are Jacobi coordinates. The coordinates in (b) suit well a floppy system in which particles 1 and 2 can turn around the 34 strongly bound core, and those in (c) and (d) are usual valence coordinates, respectively adapted to a linear (acetylenelike) molecule and to a branched (ammonialike) molecule.

vectors and no longer the differential calculus rules that are required for using curvilinear coordinates.

There are obvious sets of curvilinear coordinates which are not polyspherical, such as the so-called hyperspherical coordinates, initially defined for three particles by Delves [28] and Smith *et al.* [29,30], and generalized (including to more than three particles) by several authors [31–38]. However, many sets of internal coordinates, which are often resorted to for practical calculations on polyatomic molecules, are of the type considered here. This is illustrated for four-particle systems in Fig. 1, where four different sets of internal coordinates are described, all of them belonging to the polyspherical coordinate family under discussion. Let us note that Handy [27] used computer algebra to derive the kinetic-energy operators for the precise coordinate systems Figs. 1(c) and 1(d). All the coordinate systems which are of either the Jacobi type or the valence type belong to the polyspherical family.

The aim of this paper is to propose a possible parametrization of the polyspherical type. Here, one of the vectors plays a particular role; i.e., it is parallel to the z axis of the BF frame. In addition, the $N-2$ planar angles are those between this vector and the $N-2$ other vectors, and the $N-3$ dihedral angles are all taken around this vector, between a second given vector (parallel to the xz plane of the BF frame) and the $N-3$ remaining vectors.

It should be emphasized that all the raw classical as well as quantum-mechanical ingredients which are used below are basically not new. Anyone who has attended the appropriate courses in classical and quantum mechanics could, in principle, write the equations below as a lengthy exercise problem. Therefore, the interest is more in the way the problem is put and in the nature of the final solution. A generic exact quantum-mechanical kinetic-energy operator is proposed for more than three particles (there is no restriction in the number of particles), covering many different sets of internal coordinates. Furthermore, the operator derived has an advantage: the integrals over the angles appearing in the calculation of the matrix elements representing the kinetic-energy operator in an appropriate basis set are analytical. This property is well known for the Eulerian angles, with the standard basis of Wigner rotation matrix elements; it turns out to also be true for the internal angles, provided that appropriately contracted products of associated Legendre functions for the planar (bending) angles and imaginary exponentials for the dihedral (torsion) angles are used as basis functions [14]. In practice, this reduces the numerical effort for deriving the Hamiltonian matrix, concentrating it only on the integrals over the $N-1$ radial coordinates. Let us remark that (i) nearly all the work to date on triatomics and tetraatomics [27] has this desirable property, as a mark of the fact that many coordinate systems belong to the polyspherical family and (ii) the dominant numerical cost is actually matrix diagonalization.

II. CLASSICAL MECHANICAL BACKGROUND

Let $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n$ $(n=N-1)$ be Jacobi vectors (i.e., vectors pointing from one atomic group center of mass to another) describing the system uniquely. It is worth noting that the choice for a Jacobi vector set is not unique (see Appendix A for $N=4$). Let

$$\begin{bmatrix}\mathbf{R}_1\\ \mathbf{R}_2\\ \vdots\\ \mathbf{R}_n\end{bmatrix}=\mathbf{A}\begin{bmatrix}\mathbf{r}_1\\ \mathbf{r}_2\\ \vdots\\ \mathbf{r}_n\end{bmatrix} \tag{1}$$

be any vectors, also describing the system uniquely, i.e., such that $\mathbf{A}$ is a constant nonsingular matrix. In practice, $\mathbf{A}$ depends only on the masses and is of unit determinant (see Appendix A).

The classical kinetic energy is, by definition,

$$\begin{aligned}2T&=(\dot{\mathbf{r}}_1,\dot{\mathbf{r}}_2,\ldots,\dot{\mathbf{r}}_n)\boldsymbol{\mu}\begin{bmatrix}\dot{\mathbf{r}}_1\\ \dot{\mathbf{r}}_2\\ \vdots\\ \dot{\mathbf{r}}_n\end{bmatrix}\\ &=(\dot{\mathbf{R}}_1,\dot{\mathbf{R}}_2,\ldots,\dot{\mathbf{R}}_n)\mathbf{A}^{-1t}\boldsymbol{\mu}\mathbf{A}^{-1}\begin{bmatrix}\dot{\mathbf{R}}_1\\ \dot{\mathbf{R}}_2\\ \vdots\\ \dot{\mathbf{R}}_n\end{bmatrix},\end{aligned} \tag{2}$$

where $\boldsymbol{\mu}$ is the diagonal matrix of the reduced masses associated with the Jacobi vectors. Following the usual definition of the conjugate momentum vectors,

$$\begin{bmatrix}\mathbf{P}_1\\ \mathbf{P}_2\\ \vdots\\ \mathbf{P}_n\end{bmatrix}=\begin{bmatrix}\partial T/\partial\dot{\mathbf{R}}_1\\ \partial T/\partial\dot{\mathbf{R}}_2\\ \vdots\\ \partial T//\partial\dot{\mathbf{R}}_n\end{bmatrix}=\mathbf{A}^{-1t}\boldsymbol{\mu}\mathbf{A}^{-1}\begin{bmatrix}\dot{\mathbf{R}}_1\\ \dot{\mathbf{R}}_2\\ \vdots\\ \dot{\mathbf{R}}_n\end{bmatrix},$$

Eq. (2) can be rewritten in the form

$$2T=(\mathbf{P}_1,\mathbf{P}_2,\ldots,\mathbf{P}_n)\mathbf{M}\begin{bmatrix}\mathbf{P}_1\\ \mathbf{P}_2\\ \vdots\\ \mathbf{P}_n\end{bmatrix}, \tag{3}$$

where

$$\mathbf{M}=\mathbf{A}\boldsymbol{\mu}^{-1}\mathbf{A}^{t} \tag{4}$$

is a mass-dependent constant symmetric matrix.

The total angular momentum vector is defined as usual,

$$\mathbf{J}=\sum_{i=1}^{n}\mu_i\mathbf{r}_i\times\dot{\mathbf{r}}_i=\sum_{j=1}^{n}\mathbf{R}_j\times\mathbf{P}_j=\sum_{j=1}^{n}\mathbf{L}_j\ , \tag{5}$$

where $\mathbf{L}_j$ is the orbital angular momentum vector canonically associated with the position vector $\mathbf{R}_j$.

If $\mathbf{e}_i$ denotes the unit vector along $\mathbf{R}_i$, we can write

$$\mathbf{P}_i=\mathbf{e}_iP_i^r-\frac{\mathbf{e}_i\times\mathbf{L}_i}{R_i}\ , \tag{6}$$

so that

$$\mathbf{P}_i^2=(P_i^r)^2+\frac{\mathbf{L}_i^2}{R_i^2}\ , \tag{7}$$

$$\mathbf{P}_i\cdot\mathbf{P}_j=\cos\theta_{ij}P_i^rP_j^r+\frac{(\mathbf{e}_i\times\mathbf{L}_i)\cdot(\mathbf{e}_j\times\mathbf{L}_j)}{R_iR_j}$$

$$+(\mathbf{e}_i\times\mathbf{e}_j)\cdot\left[P_j^r\frac{\mathbf{L}_i}{R_i}-P_i^r\frac{\mathbf{L}_j}{R_j}\right]\ , \tag{8}$$

where θ_{ij} denotes the angle $(\mathbf{e}_i,\mathbf{e}_j)$.

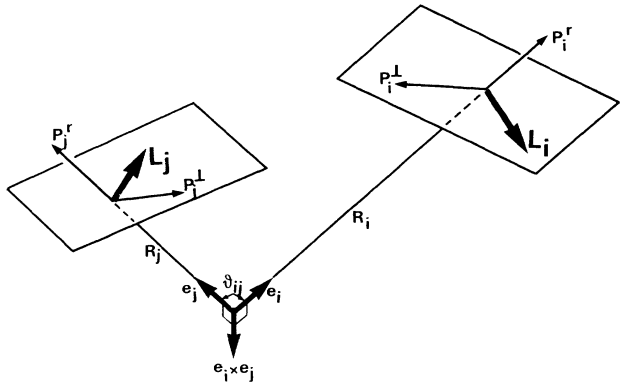

FIG. 3. Illustration of the relative orientation of the position vectors $\mathbf{R}_i$ and $\mathbf{R}_j$ $(i\neq j)$. Various vectors are also represented, the angular momentum vectors $\mathbf{L}_i$ and $\mathbf{L}_j$, on the one hand, and, on the other hand, the momentum vectors $\mathbf{P}_i$ and $\mathbf{P}_j$, by their radial $(\mathbf{P}_i^r,\mathbf{P}_j^r)$ as well as perpendicular $(\mathbf{P}_i^\perp,\mathbf{P}_j^\perp)$ vector components.

III. BODY-FIXED FRAME AND ANGULAR COORDINATES

Let the z axis of the BF frame be parallel to vector $\mathbf{R}_n$ (whence $L_n^z=0$). All angular momentum vectors being measured in the BF frame, the (purely mathematical) constraint on $\mathbf{L}_n$ (perpendicular to z) is removed by replacing $\mathbf{L}_n$ everywhere by

$$\mathbf{L}_n=\mathbf{J}-\sum_{i=1}^{n-1}\mathbf{L}_i\ , \tag{9}$$

so that

$$J^z=\sum_{i=1}^{n-1}L_i^z\ , \tag{10}$$

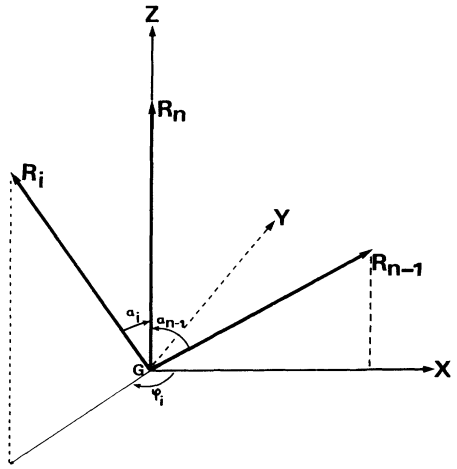

FIG. 2. The BF frame of reference, whose origin is at the center of mass G of the system, is oriented in such a way that the z axis points parallel to vector $\mathbf{R}_n$ and vector $\mathbf{R}_{n-1}$ lies parallel to xGz plane, with a positive x component. All the other vectors, $\mathbf{R}_i$ $(i=1,\ldots,n-2)$, are oriented in this frame by means of spherical angles (α_i and φ_i). The $3n-3$ internal coordinates are therefore $R_1,\ldots,R_n$, $\alpha_1,\ldots,\alpha_{n-1}$, and $\varphi_1,\ldots,\varphi_{n-2}$.

where $\mathbf{J}$ is the total angular momentum vector. In addition, the x and y axes of the moving frame are oriented in such a way that $\mathbf{R}_{n-1}$ is parallel to the xz plane, with a positive x component. Therefore, the three Euler angles defining the orientation of the BF frame relative to the SF frame are

$$\phi=\phi_n\ ,$$

$$\theta=\theta_n\ , \tag{11}$$

$$\chi=\phi_{n-1}\ ,$$

where θ_n and ϕ_n are the spherical angles for $\mathbf{R}_n$ in the SF frame; moreover, ϕ_{n-1} (a rotational angle around $\mathbf{R}_n$) and α_{n-1}, the planar angle between $\mathbf{R}_n$ and $\mathbf{R}_{n-1}$, are the spherical angles for $\mathbf{R}_{n-1}$ viewed in the intermediate frame obtained by the first two Euler rotations. Definition (11) implies that, in the BF frame,

$$\varphi_n=0\ ,$$

$$\alpha_n=0\ , \tag{12}$$

$$\varphi_{n-1}=0\ ,$$

so that the remaining nonzero spherical angles of the vectors in the BF frame, namely, $\alpha_i=(\mathbf{e}_i,\mathbf{e}_n)$ $(i=1,2,\ldots,n-1)$ and φ_i $(i=1,2,\ldots,n-2)$, can be considered pure internal coordinates (see Fig. 2). If the overall symmetry allows the permutation of identical particles, the symmetric embedding of the axes requires further study (see [14] and Sec. VII below).

From Eqs. (3)–(9), it is clear that (Fig. 3)

$$T=\tfrac{1}{2}\sum_{i=1}^{n-1}M_{ii}\left[(P_i^r)^2+\frac{\mathbf{L}_i^2}{R_i^2}\right]+\tfrac{1}{2}M_{nn}\left[(P_n^r)^2+\frac{\mathbf{J}^2-2\mathbf{J}\cdot\sum_{i=1}^{n-1}\mathbf{L}_i+\sum_{i=1}^{n-1}\mathbf{L}_i^2+2\sum_{j<i=1}^{n-1}\mathbf{L}_i\cdot\mathbf{L}_j}{\mathbf{R}_n^2}\right]$$
$$+\sum_{j<i=1}^{n-1}M_{ij}\left[\cos\theta_{ij}P_i^rP_j^r+\frac{(\mathbf{e}_i\times\mathbf{L}_i)\cdot(\mathbf{e}_j\times\mathbf{L}_j)}{R_iR_j}-(\mathbf{e}_i\times\mathbf{e}_j)\cdot\left[\frac{P_i^r\mathbf{L}_j}{R_j}-\frac{P_j^r\mathbf{L}_i}{R_i}\right]\right]$$
$$+\sum_{i=1}^{n-1}M_{ni}\left[\cos\alpha_iP_n^rP_i^r+\left\{(\mathbf{e}_i\times\mathbf{L}_i)\cdot\left[\mathbf{e}_n\times\left[\mathbf{J}-\sum_{j=1}^{n-1}\mathbf{L}_j\right]\right]\right\}\Big/R_nR_i\right.$$
$$\left.-(\mathbf{e}_n\times\mathbf{e}_i)\cdot\left[P_n^r\frac{\mathbf{L}_i}{R_i}-\left[\mathbf{J}-\sum_{j=1}^{n-1}\mathbf{L}_j\right]\frac{P_i^r}{R_n}\right]\right]. \tag{13}$$

Equation (13) can be rewritten in the form

$$T=\frac{1}{2}\frac{M_{nn}}{R_n^2}\mathbf{J}^2-\frac{\mathbf{J}}{R_n}\cdot\sum_{i=1}^{n-1}\left[\frac{M_{nn}}{R_n}\mathbf{L}_i-M_{ni}\left[\frac{\cos\alpha_i\mathbf{L}_i-\mathbf{e}_iL_i^z}{R_i}+\sin\alpha_i\mathbf{E}_iP_i^r\right]\right]$$
$$+\tfrac{1}{2}\sum_{i=1}^{n}M_{ii}(P_i^r)^2+\sum_{j<i=1}^{n}M_{ij}\cos\theta_{ij}P_i^rP_j^r+\tfrac{1}{2}\sum_{i=1}^{n-1}\left[\frac{M_{nn}}{R_m^2}+\frac{M_{ii}}{R_i^2}-2\frac{M_{ni}}{R_nR_i}\cos\alpha_i\right]\mathbf{L}_i^2$$
$$+\sum_{j<i=1}^{n-1}\left[\left[\frac{M_{nn}}{R_n^2}-\frac{M_{ni}}{R_nR_i}\cos\alpha_i-\frac{M_{nj}}{R_nR_j}\cos\alpha_j+\frac{M_{ij}}{R_iR_j}\cos\theta_{ij}\right]\mathbf{L}_i\cdot\mathbf{L}_j-\frac{M_{ij}}{R_i\cdot R_j}(\mathbf{e}_i\cdot\mathbf{L}_j)(\mathbf{e}_j\cdot\mathbf{L}_i)\right.$$
$$\left.+\frac{M_{ni}}{R_nR_i}(\mathbf{e}_i\cdot\mathbf{L}_j)L_i^z+\frac{M_{nj}}{R_nR_j}(\mathbf{e}_j\cdot\mathbf{L}_i)L_j^z\right]-\sum_{i=1}^{n}P_i^r\sum_{j=1}^{n-1}\left[\frac{M_{ij}}{R_j}(\mathbf{e}_i\times\mathbf{e}_j)+\frac{M_{ni}}{R_n}\sin\alpha_i\mathbf{E}_i\right]\cdot\mathbf{L}_j\ , \tag{14}$$

where

$$\cos\theta_{ij}=\cos\alpha_i\cos\alpha_j+\sin\alpha_i\sin\alpha_j\cos(\varphi_j-\varphi_i)$$
$$(i,j=1,2,\ldots,n-1)\ ,$$

$$\theta_{ni}=\alpha_i\quad(i=1,2,\ldots,n-1)\ ,$$

$$\sin\alpha_i\mathbf{E}_i=\mathbf{e}_n\times\mathbf{e}_i\ ,$$

and

$$\mathbf{E}_i=(\sin\varphi_i,-\cos\varphi_i,0)\quad(i=1,2,\ldots,n-1)\ .$$

IV. LINEAR MOMENTUM OPERATORS AND VOLUME ELEMENT IN $\mathbb{R}^{3n}$

The polyspherical parametrization used here consists, for each vector $\mathbf{R}_i$, of local spherical coordinates. For current spherical coordinates R,α,φ in $\mathbb{R}^3$, there is, by definition,

$$s=R^2\sin\alpha\quad\text{(Jacobian)}\ ,$$

$$\hat{p}_R=-i\hbar\frac{\partial}{\partial R}\quad\text{(linear momentum operator)}\ .$$

Now, owing to the results of Refs. [18,27,79,80], various normalization conventions can be considered. In the Euclidean case, i.e., for the volume element of $\mathbb{R}^3$, $d\tau^E=sdR\,d\alpha\,d\varphi$, the following relations hold:

$$\hat{p}_R^{\dagger}=-i\hbar\left[\frac{\partial}{\partial R}+\frac{2}{R}\right]\quad\text{(adjoint momentum operator)}\ ,$$

$$\hat{p}_R^H=-i\hbar\left[\frac{\partial}{\partial R}+\frac{1}{R}\right]$$

(Hermitian momentum operator) ,

$$\hat{p}_R^2=\hat{p}_R^{\dagger}\hat{p}_R=-\frac{\hbar^2}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}\ ,$$

$$\hat{T}_R=-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right]=-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R$$

(kinetic-energy operator)

[see Eqs. (2.17) and (2.18), (2.21) and (2.32), along with $g^{RR}=1/\mu$, in Ref. [79]].

In the general case, i.e., for the volume element $d\tau=\rho dR\,d\alpha\,d\varphi$, where ρ is any function defined in $\mathbb{R}^3$ which can be zero but only in sets of measure zero of $\mathbb{R}^3$ (i.e., surfaces), the Hermitian momentum operator and kinetic-energy operator are [see, respectively, Eqs. (4.12) and (4.21) in Ref. [79]]

$$\hat{p}_{\rho R}^H=-i\hbar\rho^{1/2}\frac{\partial}{\partial R}\rho^{-1/2}\ ,$$

$$\hat{T}_{\rho R}=s^{1/2}\rho^{-1/2}\hat{T}_R\rho^{1/2}s^{-1/2}\ ,$$

so that, in the particular case where $\rho=\sin\alpha$,

$$\hat{p}_R^H=-i\hbar\frac{\partial}{\partial R}=\hat{p}_R\ ,$$

$$\hat{T}_R=-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}\ .$$

We must, nevertheless, keep in mind that the volume element is no longer Euclidean. We shall take advantage of this later on.

In the direct product space $\mathbb{R}^{3n}=\mathbb{R}_1^3\otimes\mathbb{R}_2^3\otimes\cdots\otimes\mathbb{R}_n^3$, the volume element is $d\tau=\prod_{i=1}^n d\tau_i$. For the Euclidean volume element $d\tau_i^E=R_i^2 dR_i \sin\alpha_i d\alpha_i d\varphi_i$, $\hat{P}_i^r$ and $\hat{P}_i^{r2}$ are to be replaced in Eq. (14) by, respectively, $-i\hbar\partial/\partial R_i$ and $-(\hbar^2/R_i^2)(\partial/\partial R_i)R_i^2(\partial/\partial R_i)$. In addition, $\hat{\mathbf{L}}_i$ is the usual orbital angular momentum operator defined through its components in terms of polar angles, or, alternatively, through the commutators of its components (see Sec. VI below).

For the volume element $d\tau_i=dR_i\sin\alpha_i d\alpha_i d\varphi_i$ (and for it only), the vector operator $\hat{\mathbf{P}}_i=\mathbf{e}_i\hat{P}_i^r-(\mathbf{e}_i\times\hat{\mathbf{L}}_i)/R_i$ is Hermitian in $\mathbb{R}_i^3$ if (i) $\hat{P}_i^r=-i\hbar(\partial/\partial R_i)$ (see Sec. V) and (ii) $\hat{\mathbf{L}}_i$ is still the usual orbital angular momentum operator. Then, in virtue of

$$d\tau=\left[\prod_{i=1}^{n-2} dR_i\sin\alpha_i d\alpha_i d\varphi_i\right] dR_{n-1} \times\sin\alpha_{n-1}d\alpha_{n-1}dR_n d\chi\sin\theta\, d\theta\, d\phi\ . \tag{15}$$

Thanks to the orientation chosen for the BF frame, $d\tau$ is the product of the usual Eulerian solid-angle element (so that the overall rotation and the Coriolis effects are going to be treated in the usual way) by the following internal coordinate volume element:

$$d\tau^{\text{in}}=\prod_{i=1}^{n} dR_i \prod_{i=1}^{n-1}\sin\alpha_i d\alpha_i \prod_{i=1}^{n-2} d\varphi_i$$

and

$$d\tau^{\text{in}E}=\prod_{i=1}^{n} R_i^2 dR_i \prod_{i=1}^{n-1}\sin\alpha_i d\alpha_i \prod_{i=1}^{n-2} d\varphi_i\ ,$$

where R_i $(i=1,\ldots,n)$ denote the vector lengths, α_i $(i=1,\ldots,n-1)$ denote the planar angles between vectors $\mathbf{R}_i$ and $\mathbf{R}_n$, and finally φ_i $(i=1,\ldots,n-2)$ denote the dihedral angles between vectors $\mathbf{R}_i$ and $\mathbf{R}_{n-1}$ around $\mathbf{R}_n$. It is worth recalling here that, in particular, all Jacobi-type coordinate sets (matrices $\mathbf{A}=\mathbf{1}$ and $\mathbf{M}=\boldsymbol{\mu}$) are, by construction, polyspherical.

V. QUANTIZATION

To obtain the quantum-mechanical expression of the kinetic-energy operator, $\hat{T}^J$, we must substitute, in the classical expression, Eq. (14), P_i^r for $-i\hbar(\partial/\partial R_i)$, $(P_i^r)^2$ for either $-(\hbar^2/R_i^2)(\partial/\partial R_i)R_i^2(\partial/\partial R_i)$ or $-\hbar^2(\partial^2/\partial R_i^2)$ (depending on whether the Euclidean or the non-Euclidean normalization convention is used), and $\mathbf{L}_i$ by the vector operator $\hat{\mathbf{L}}_i$. However, when the normalization convention is not Euclidean, we must examine the question of the occurrence of an extra-potential term in $\hat{T}^J$. According to Refs. [79,80], this term is equal to $\mathcal{V}_\rho=(s^{1/2}\rho^{-1/2}\hat{T}_E^0\rho^{1/2}s^{-1/2})$, where the parentheses indicate that $\hat{T}_E^0$ does not operate beyond them, so that $\mathcal{V}_\rho$ actually is a multiplicative quantity. Here $\rho^{1/2}s^{-1/2}=(R_1\cdots R_i\cdots R_n)^{-1}$. See Appendix B for more details on the non-Euclidean normalization convention.

After relatively simple calculations, in which use is made of the familiar relations

$$\hat{\mathbf{L}}_i\cdot\hat{\mathbf{L}}_j=\hat{L}_i^z\hat{L}_j^z+\tfrac{1}{2}(\hat{L}_i^+\hat{L}_j^-+\hat{L}_i^-\hat{L}_j^+)\ ,$$

$$\mathbf{e}_i\cdot\hat{\mathbf{L}}_j=\cos\alpha_i\hat{L}_j^z+\frac{\sin\alpha_i}{2}(e^{-i\varphi_i}\hat{L}_j^+ + e^{i\varphi_i}\hat{L}_j^-)\ ,$$

where $\hat{L}_j^+=\hat{L}_j^x+i\hat{L}_j^y$ and $\hat{L}_j^-=\hat{L}_j^x-i\hat{L}_j^y$, $\hat{T}^J$ can be put in the form

$$\hat{T}^J=\hat{T}^0+\hat{T}^J_{\text{cor}}+\hat{T}^J_{\text{rot}}\ , \tag{16}$$

where

$$\hat{T}^J_{\text{rot}}=\frac{1}{2}\frac{M_{nn}}{R_n^2}\hat{\mathbf{J}}^2 \tag{17}$$

accounts for the overall rotation of the BF frame of reference and

$$\hat{T}^J_{\text{cor}}=-\frac{1}{R_n}\sum_{i=1}^{n-1}\left\{\frac{M_{nn}}{R_n}\hat{J}^z\hat{L}_i^z+\left[\frac{M_{nn}}{R_n}-\frac{M_{ni}}{R_i}\cos\alpha_i\right]\frac{\hat{J}^+\hat{L}_i^-+\hat{J}^-\hat{L}_i^+}{2} +M_{ni}\sin\alpha_i\left[\frac{\hat{L}_i^z}{R_i}\frac{e^{-i\varphi_i}\hat{J}^+ + e^{i\varphi_i}\hat{J}^-}{2}+\left[-i\hbar\frac{\partial}{\partial R_i}\right]\frac{e^{-i\varphi_i}\hat{J}^+ - e^{i\varphi_i}\hat{J}^-}{2i}\right]\right\} \tag{18}$$

accounts for the Coriolis energy.

An interesting form of the internal deformation kinetic-energy operator $\hat{T}_E^0$ is

$$\hat{T}_E^0=-\frac{\hbar^2}{2}\sum_{i=1}^{n} M_{ii}\frac{1}{R_i}\frac{\partial^2}{\partial R_i^2}R_i-\hbar^2\sum_{j<i=1}^{n} M_{ij}\cos\theta_{ij}\frac{\partial^2}{\partial R_i\partial R_j}+\tfrac{1}{2}\sum_{i=1}^{n-1}\frac{\hat{\mathbf{L}}_i^2}{I_{ii}}+\sum_{j<i=1}^{n-1}\hat{\Lambda}_{ij}+\sum_{i=1}^{n}\sum_{j=1}^{n-1}\hat{\lambda}_j^i\left[-i\hbar\frac{\partial}{\partial R_i}\right]\ , \tag{19}$$

where

$$\frac{1}{I_{ii}}=\frac{M_{nn}}{R_n^2}+\frac{M_{ii}}{R_i^2}-2\frac{M_{ni}}{R_nR_i}\cos\alpha_i\quad(i=1,2,\ldots,n-1)\ ,$$

$$\hat{\Lambda}_{ij}=a^{ij}\hat{L}_i^z\hat{L}_j^z+a_i^j\frac{e^{-i\varphi_j}\hat{L}_i^+ + e^{i\varphi_j}\hat{L}_i^-}{2}\hat{L}_j^z+a_j^i\frac{e^{-i\varphi_i}\hat{L}_j^+ + e^{i\varphi_i}\hat{L}_j^-}{2}\hat{L}_i^z+\frac{a_{ij}\hat{L}_i^+\hat{L}_j^- + a_{ij}^*\hat{L}_i^-\hat{L}_j^+}{2} -\frac{1}{2}\frac{M_{ij}}{R_iR_j}\sin\alpha_i\sin\alpha_j\frac{e^{-i(\varphi_i+\varphi_j)}\hat{L}_i^+\hat{L}_j^+ + e^{i(\varphi_i+\varphi_j)}\hat{L}_i^-\hat{L}_j^-}{2}\ , \tag{20}$$

$$\hat{\lambda}_j^i=\frac{M_{ij}}{R_j}\sin\alpha_j\left[\sin\alpha_i\sin(\varphi_i-\varphi_j)\hat{L}_j^z-\cos\alpha_i\frac{e^{-i\varphi_j}\hat{L}_j^+-e^{i\varphi_j}\hat{L}_j^-}{2i}\right]+b_j^i\frac{e^{-i\varphi_i}\hat{L}_j^+-e^{i\varphi_i}\hat{L}_j^-}{2i}\ . \tag{21}$$

The coefficient functions in Eqs. (20) and (21) are ($j<i=1,2,\ldots,n-1$)

$$\begin{aligned}
a^{ij}&=\frac{M_{nn}}{R_n^2}+\frac{M_{ij}}{R_iR_j}\sin\alpha_i\sin\alpha_j\cos(\varphi_i-\varphi_j)\ ,\\
a_j^i&=\left[\frac{M_{ni}}{R_n}-\cos\alpha_j\frac{M_{ij}}{R_j}\right]\frac{\sin\alpha_i}{R_i}\ ,\\
a_{ij}&=\frac{M_{nn}}{R_n^2}-\frac{1}{R_n}\left[\frac{M_{ni}}{R_i}\cos\alpha_i+\frac{M_{nj}}{R_j}\cos\alpha_j\right]+\frac{M_{ij}}{R_iR_j}(\cos\alpha_i\cos\alpha_j+\tfrac{1}{2}e^{-i\varphi_i}\sin\alpha_ie^{i\varphi_j}\sin\alpha_j)\ ,
\end{aligned} \tag{22}$$

and

$$\begin{aligned}
a_{ij}^*&=a_{ji}\ ,\\
b_j^i&=\left[\frac{M_{ni}}{R_n}+\frac{M_{ij}}{R_j}\cos\alpha_j\right]\sin\alpha_i\quad(i=1,2,\ldots,n,\ j=1,2,\ldots,n-1)\ .
\end{aligned} \tag{23}$$

The operators $\hat{T}_{\rm cor}^J$, $\hat{\Lambda}_{ij}$, and $\hat{\lambda}_j^i$, in the forms above, are real.

Moreover, in regard to the operator $\hat{T}_E^0$, bearing only on the internal deformations, it may be useful to rewrite it, as far as the angles α_i ($i=1,\ldots,n-1$) and φ_i ($i=1,\ldots,n-2$) are concerned, in terms of partial derivatives, and no longer in terms of angular momentum operators. The result is

$$\begin{aligned}
\hat{T}_E^0=&-\frac{\hbar^2}{2}\sum_{i=1}^{n}M_{ii}\frac{1}{R_i}\frac{\partial^2}{\partial R_1^2}R_i-\hbar^2\sum_{j<i=1}^{n}M_{ij}\cos\theta_{ij}\frac{\partial^2}{\partial R_i\partial R_j}-\frac{\hbar^2}{2}\sum_{i=1}^{n-1}\frac{1}{I_{ii}}\left[\frac{\partial^2}{\partial\alpha_i^2}+\cot\alpha_i\frac{\partial}{\partial\alpha_i}+\frac{1}{\sin^2\alpha_i}\frac{\partial^2}{\partial\varphi_i^2}\right]\\
&-\hbar^2\sum_{j<i=1}^{n-1}\left[K^{ij}\frac{\partial^2}{\partial\alpha_i\partial\alpha_j}+K_j^i\frac{\partial^2}{\partial\alpha_i\partial\varphi_j}+K_i^j\frac{\partial^2}{\partial\alpha_j\partial\varphi_i}+K_{ij}\frac{\partial^2}{\partial\varphi_i\partial\varphi_j}\right]-\hbar^2\sum_{i=1}^{n}\sum_{j=1}^{n-1}\left[N_j^i\frac{\partial}{\partial\alpha_j}+n_j^i\frac{\partial}{\partial\varphi_j}\right]\frac{\partial}{\partial R_i}\ ,
\end{aligned} \tag{24}$$

where

$$\begin{aligned}
K^{ij}=&\left[\frac{M_{nn}}{R_n^2}-\frac{M_{ni}}{R_nR_i}\cos\alpha_i-\frac{M_{nj}}{R_nR_j}\cos\alpha_j\right.\\
&\left.+\frac{M_{ij}}{R_iR_j}\cos\alpha_i\cos\alpha_j\right]\cos(\varphi_i-\varphi_j)\\
&+\frac{M_{ij}}{R_iR_j}\sin\alpha_i\sin\alpha_j\ ,\\
K_j^i=&\left[\frac{M_{nn}}{R_n^2}\cos\alpha_j-\frac{M_{ni}}{R_nR_i}\cos\alpha_i\cos\alpha_j\right.\\
&\left.-\frac{M_{nj}}{R_nR_j}+\frac{M_{ij}}{R_iR_j}\cos\alpha_i\right]\frac{\sin(\varphi_i-\varphi_j)}{\sin\alpha_j}\ ,
\end{aligned} \tag{25}$$

where $K_j^j=0$,

$$\begin{aligned}
K_{ij}=&\frac{M_{nn}}{R_n^2}+\left[\frac{M_{nn}}{R_n^2}\cos\alpha_i\cos\alpha_j-\frac{M_{ni}}{R_nR_i}\cos\alpha_j\right.\\
&\left.-\frac{M_{nj}}{R_nR_j}\cos\alpha_i+\frac{M_{ij}}{R_iR_j}\right]\frac{\cos(\varphi_i-\varphi_j)}{\sin\alpha_i\sin\alpha_j}\ ,\\
N_j^i=&\frac{M_{ni}}{R_n\sin\alpha_i}\cos(\varphi_i-\varphi_j)\\
&+\frac{M_{ij}}{R_j}[\sin\alpha_i\cos\alpha_j\cos(\varphi_i-\varphi_j)-\cos\alpha_i\sin\alpha_j]\ ,
\end{aligned} \tag{26}$$

$$n_j^i=\left[\frac{M_{ni}}{R_n}\cos\alpha_j+\frac{M_{ij}}{R_j}\right]\frac{\sin\alpha_i}{\sin\alpha_j}\sin(\varphi_i-\varphi_j)\ ,$$

where $n_j^j=0$. The expression of $\hat{T}_E^0$ in terms of internal coordinates (24) is given in order to allow the comparison with previously derived operators for four particles [27,74,80], see Appendix C. But clearly it is not the novelty of this work. What is seemingly new and will be used below is the expression [(16)–(21)] of $\hat{T}^J$ in terms of the angular momentum operators $\hat{\mathbf{J}}^2$, $\hat{J}^z$, $\hat{J}^+$, $\hat{J}^-$, $\hat{\mathbf{L}}_i^2$, $\hat{L}_i^z$, $\hat{L}_i^+$, $\hat{L}_i^-$ ($i=1,\ldots,n-1$).

VI. ANGULAR MOMENTUM OPERATORS AND ANGULAR BASIS FUNCTIONS: INTEGRATION OVER ANGULAR COORDINATES, MATRIX REPRESENTATION

The eigenfunctions of the total angular momentum vector operator $\hat{\mathbf{J}}$ are noted $|J,\Omega,M\rangle$, with the eigenvalues $\hbar^2J(J+1)$, $\hbar\Omega$, and $\hbar M$ for $\hat{J}^2$, $\hat{J}^z$, and $\hat{J}^Z$, respectively. Z denotes a SF axis and

$$\langle\phi,\theta,\chi|J,\Omega,M\rangle=\mathcal{D}_{M\Omega}^{J*}(\phi,\theta,\chi)$$

are Wigner functions. Owing to the commutation relations of the BF components of $\hat{\mathbf{J}}$, e.g., $[\hat{J}^x,\hat{J}^y]=-i\hbar\hat{J}^z$, the action of $\hat{J}^\pm$ is given by [81–83]

$$\hat{J}^\pm|J,\Omega,M\rangle=\hbar c_\mp(J,\Omega)|J,\Omega\mp1,M\rangle\ , \tag{27}$$

where

$$c_{\pm}(J,\Omega)=\sqrt{J(J+1)-\Omega(\Omega\pm1)}\ . \tag{28}$$

The eigenfunctions of the orbital angular momentum operator $\hat{\mathbf{L}}_i$ are noted $|L_i,\Omega_i\rangle$, and

$$\hat{\mathbf{L}}_i^2|L_i,\Omega_i\rangle=\hbar^2L_i(L_i+1)|L_i,\Omega_i\rangle\ ,$$

$$\hat{L}_i^z|L_i,\Omega_i\rangle=\hbar\Omega_i|L_i,\Omega_i\rangle\ ,$$

where $\langle\alpha_i,\varphi_i|L_i,\Omega_i\rangle=Y_{L_i}^{\Omega_i}(\alpha_i,\varphi_i)$ are spherical harmonics. Hereafter, the following definition of the spherical harmonics is used:

$$Y_l^m(\theta,\varphi)=(-1)^m\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}P_l^m(\cos\theta)e^{im\varphi}\ ,$$

where $P_l^{|m|}$ denotes an associated Legendre function, along with the convention $P_l^{-|m|}=(-1)^{|m|}P_l^{|m|}$. $\hat{\mathbf{L}}_i$, which operates on the internal coordinates only, is defined directly in the BF frame, with the usual commutation relations $[\hat{L}_i^x,\hat{L}_i^y]=i\hbar\hat{L}_i^z$ and so on, where $[c_{\pm}(i)=c_{\pm}(L_i,\Omega_i)]$

$$\hat{L}_i^{\pm}|L_i,\Omega_i\rangle=\hbar c_{\pm}(i)|L_i,\Omega_i\pm1\rangle\ .$$

The alignment of the BF frame z axis with $\mathbf{R}_n$ imposes that $\Omega=\sum_{i=1}^{n-1}\Omega_i$ and $J\geq\sum_{i=1}^{n-1}L_i$ (equal if, and only if $L_n=0$). Two cases are considered. (i) If the third Euler rotation is not performed, $\chi=0$, φ_{n-1} is a variable. The current angular basis function is

$$\mathcal{D}^{J*}_{M\Omega}(\phi,\theta,0)\prod_{i=1}^{n-1}Y_{L_i}^{\Omega_i}(\alpha_i,\varphi_i)\ .$$

This basis suits well asymptotic conditions corresponding to a fragmentation along $\mathbf{R}_n$. (ii) If the third Euler's rotation is carried out (see Sec. III), the following basis set is more profitable:

$$\mathcal{D}^{J*}_{M\Omega}(\phi,\theta,\chi)\left[\prod_{i=1}^{n-2}Y_{L_i}^{\Omega_i}(\alpha_i,\varphi_i)\right](-1)^{\Omega_{n-1}}\times\left[\frac{2L_{n-1}+1}{2}\frac{(L_{n-1}-|\Omega_{n-1}|)!}{(L_{n-1}+|\Omega_{n-1}|)!}\right]^{1/2}\times P_{L_{n-1}}^{\Omega_{n-1}}(\cos\alpha_{n-1})\ ,$$

where $\Omega_{n-1}=\Omega-\sum_{i=1}^{n-2}\Omega_i$. It is adapted to describe a bound state, such as those studied in ir spectroscopy or for the floppy molecular states observed by means of stimulated emission pumping techniques [25,62–69], for which the complete definition of the BF frame of reference is necessary. We write the corresponding basis function

$$|J,\Omega,M,L_1,\Omega_1,\ldots,L_{n-2},\Omega_{n-2},L_{n-1}\rangle=|J,\Omega,M\rangle\left[\prod_{i=1}^{n-2}|L_i,\Omega_i\rangle\right]\left|L_{n-1},\Omega-\sum_{i=1}^{n-2}\Omega_i\right\rangle$$

or still, in shorthand notation, $|\cdots\rangle$. It is worthwhile noting that $2n$ independent quantum numbers appear in both cases, as must be the case when describing n rotating vectors.

We calculate now $\mathbf{T}^J$, the matrix representing $\hat{T}^J$ [cf. Eqs. (16)–(21)] in the basis $\{|\cdots\rangle\}$. The integration is over the angles only, i.e., the matrix elements are expressed in terms of J, Ω, M, L_i, Ω_i $(i=1,n-2)$, and L_{n-1}, on the one hand, R_i and $\partial/\partial R_i$ $(i=1,n)$ on the other hand. J and M are fixed (in particular, the energy is independent of M, as a consequence of space isotropy in the absence of external field), i.e., $\mathbf{T}^J$ is a block at constant J. In the basis $\{|\cdots\rangle\}$, the action of $\hat{T}^J_{\rm rot}$, $\hat{T}^J_{\rm cor}$, $\hat{\mathbf{L}}_i^2$, $\hat{\Lambda}_{ij}$, and $\hat{\lambda}_j^i$ is trivial, and the matrix elements are easily derived, for instance,

$$\langle\cdots'|\hat{T}^J_{\rm rot}|\cdots\rangle=\frac{\hbar^2}{2}\frac{M_{nn}}{R_n^2}J(J+1)\delta_{\rm all',all}\ , \tag{29}$$

where $\langle\cdots'|$ denotes the current angular basis function with all quantum numbers primed, and the collective Kronecker symbol $\delta_{\rm all',all}$ indicates a pure diagonal contribution. In a similar way, we obtain

$$\begin{aligned}\langle\cdots'|\hat{T}^J_{\rm cor}|\cdots\rangle=&-\hbar^2\frac{M_{nn}}{R_n^2}\Omega^2\delta_{\rm all',all}\\&-\frac{\hbar^2}{2R_n}\left\{c_-(J,\Omega)\delta_{\Omega'\Omega-1}\sum_{i=1}^{n-1}\left[c_-(i)\left[\frac{M_{nn}}{R_n}\delta_{L_i'L_i}\delta_{\Omega_i'\Omega_i-1}-\frac{M_{ni}}{R_i}\langle L_i'\Omega_i'|\cos\alpha_i|L_i\Omega_i-1\rangle\right]\right.\right.\\&\left.+M_{ni}\left[\frac{\Omega_i}{R_i}-\frac{\partial}{\partial R_i}\right]\langle L_i'\Omega_i'|e^{-i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\Big]\delta^{(\Omega L_i\Omega_i)}_{\rm rest',rest}\\&+c_+(J,\Omega)\delta_{\Omega',\Omega+1}\sum_{i=1}^{n-1}\left[c_+(i)\left[\frac{M_{nn}}{R_n}\delta_{L_i'L_i}\delta_{\Omega_i'\Omega_i+1}-\frac{M_{ni}}{R_i}\langle L_i'\Omega_i'|\cos\alpha_i|L_i\Omega_i+1\rangle\right]\right.\\&\left.\left.+M_{ni}\left[\frac{\Omega_i}{R_i}+\frac{\partial}{\partial R_i}\right]\langle L_i'\Omega_i'|e^{i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\Big]\delta^{(\Omega L_i\Omega_i)}_{\rm rest',rest}\right\}\ ,\end{aligned} \tag{30}$$

where the collective Kronecker symbol $\delta^{(\Omega L_i \Omega_i)}_{\text{rest}',\text{rest}}$ concerns all the quantum numbers except the ones explicitly indicated as upper indices in parentheses, namely, here Ω, L_i, and Ω_i.

Remarkably, in Eq. (30) as well as in Eqs. (36)–(40) below, there appear two (and only two) types of matrix elements. These integrals can be calculated from the recursion relations of the associated Legendre functions. From

$$\cos\theta P_l^m(\cos\theta)=\frac{1}{2l+1}[(l-|m|+1)P_{l+1}^m(\cos\theta)+(l+|m|)P_{l-1}^m(\cos\theta)] ,$$

we obtain

$$\sin\theta P_l^{\pm|m|}(\cos\theta)=\pm\frac{1}{2l+1}[P_{l+1}^{\pm(|m|+1)}(\cos\theta)-P_{l-1}^{\pm(|m|+1)}(\cos\theta)] , \tag{33}$$

$$\langle L_i'\Omega_i'|e^{\pm i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle=\mp B_+^{\pm}(L_i,\Omega_i)\delta_{L_i'L_i+1}\delta_{\Omega_i'\Omega_i\pm1}\pm B_-^{\pm}(L_i,\Omega_i)\delta_{L_i'L_i-1}\delta_{\Omega_i'\Omega_i\pm1} ,$$

where

$$B_+^{\pm}(L_i,\Omega_i)=\left[\frac{(L_i\pm\Omega_i+1)(L_i\pm\Omega_i+2)}{(2L_i+1)(2L_i+3)}\right]^{1/2} ,$$
$$B_-^{\pm}(L_i,\Omega_i)=\left[\frac{(L_i\mp\Omega_i-1)(L_i\mp\Omega_i)}{(2L_i-1)(2L_i+1)}\right]^{1/2}=B_+^{\pm}(L_i-1,-\Omega_i\mp1) . \tag{34}$$

$$\langle L_i'\Omega_i'|\cos\alpha_i|L_i\Omega_i\rangle=\delta_{\Omega_i'\Omega_i}[B_+^0(L_i,\Omega_i)\delta_{L_i'L_i+1}+B_-^0(L_i,\Omega_i)\delta_{L_i'L_i-1}] , \tag{31}$$

where

$$B_+^0(L_i,\Omega_i)=\left[\frac{(L_i+\Omega_i+1)(L_i-\Omega_i+1)}{(2L_i+1)(2L_i+3)}\right]^{1/2} ,$$
$$B_-^0(L_i,\Omega_i)=\left[\frac{(L_i+\Omega_i)(L_i-\Omega_i)}{(2L_i+1)(2L_i-1)}\right]^{1/2}=B_+^0(L_i-1,\Omega_i) , \tag{32}$$

and from

Inserting Eqs. (31) and (33) into Eq. (30) yields

$$\begin{aligned}
\langle\cdots'|\hat{T}^J_{\text{cor}}|\cdots\rangle
&=-\frac{\hbar^2}{2R_n}\Bigg[\delta_{\Omega'\Omega-1}c_-(J,\Omega)\\
&\quad\times\sum_{i=1}^{n-1}\delta_{\Omega_i'\Omega_{i-1}}\Bigg\{\delta_{L_i'L_i}\frac{c_-(i)M_{nn}}{R_n}\\
&\quad-\delta_{L_i'L_i+1}\left[\frac{c_-(i)B_+^0(L_i,\Omega_i-1)}{R_i}-\left[\frac{\Omega_i}{R_i}-\frac{\partial}{\partial R_i}\right]B_+^-(L_i,\Omega_i)\right]M_{ni}\\
&\quad-\delta_{L_i'L_i-1}\left[\frac{c_-(i)B_-^0(L_i,\Omega_i-1)}{R_i}+\left[\frac{\Omega_i}{R_i}-\frac{\partial}{\partial R_i}\right]B_-^-(L_i,\Omega_i)\right]M_{ni}\Bigg\}\delta^{(\Omega L_i\Omega_i)}_{\text{rest}',\text{rest}}\\
&\quad+\delta_{\Omega'\Omega+1}c_+(J,\Omega)\sum_{i=1}^{n-1}\delta_{\Omega_i'\Omega_{i+1}}\Bigg\{\delta_{L_i'L_i}\frac{c_+(i)M_{nn}}{R_n}\\
&\quad-\delta_{L_i'L_i+1}\left[\frac{c_+(i)B_+^0(L_i,\Omega_i+1)}{R_i}+\left[\frac{\Omega_i}{R_i}-\frac{\partial}{\partial R_i}\right]B_+^+(L_i,\Omega_i)\right]M_{ni}\\
&\quad-\delta_{L_i'L_i-1}\left[\frac{c_+(i)B_-^0(L_i,\Omega_i+1)}{R_i}-\left[\frac{\Omega_i}{R_i}-\frac{\partial}{\partial R_i}\right]B_-^+(L_i,\Omega_i)\right]M_{ni}\Bigg\}\delta^{(\Omega L_i\Omega_i)}_{\text{rest}',\text{rest}}\Bigg]\\
&\quad-\hbar^2\frac{M_{nn}}{R_n^2}\Omega^2\delta_{\text{all}',\text{all}} ,
\end{aligned} \tag{35}$$

Ω varies from $-J$ to $+J$. In view of Eq. (35), $\mathbf{T}^J$ is block-tridiagonal in Ω. In the extra-diagonal blocks $\Omega,\Omega+1$ (respectively, $\Omega,\Omega-1$), the only nonzero elements are of the type Ω_i,Ω_{i+1} (respectively, Ω_i,Ω_i-1), as must be the case to

preserve the equality between Ω and the sum of the Ω_i's. Otherwise, the nonzero elements are diagonal in all the other quantum numbers, or nondiagonal in one (and only one) of them, namely, $L_i, L_i \pm 1$. Although neither SF axes nor Eckart axes [84] are used, and whatever the merits of these options recently advocated by Natanson and co-workers, see, respectively, Refs. [85,86], in view of the distribution of the nonzero elements of $\mathbf{T}^J$ owed to $\hat{T}^J_{\rm rot}$ and $\hat{T}^J_{\rm cor}$, we see no reason why the BF axes used in the present article would be liable to produce particularly large rotation-vibration couplings.

We still have to calculate $\langle \cdots' | \hat{T}^0_E | \cdots \rangle$. Equation (19) yields

$$\begin{aligned}\langle \cdots' | \hat{T}^0_E | \cdots \rangle = & -\frac{\hbar^2}{2}\delta_{\mathrm{all'},\mathrm{all}} \sum_{i=1}^{n} M_{ii} \frac{1}{R_i^2} \frac{\partial}{\partial R_i} R_i^2 \frac{\partial}{\partial R_i} - \hbar^2 \sum_{j<i=1}^{n} M_{ij} \frac{\partial^2}{\partial R_i \partial R_j} \langle \cdots' | \cos\theta_{ij} | \cdots \rangle \\ & + \frac{\hbar^2}{2} \sum_{i=1}^{n-1} L_i(L_i+1) \langle \cdots' || I_{ii}^{-1} | \cdots \rangle + \sum_{j<i=1}^{n-1} \langle \cdots' | \hat{\Lambda}_{ij} | \cdots \rangle \\ & + \sum_{i=1}^{n} \left[-i\hbar \sum_{j=1}^{n-1} \langle \cdots' | \hat{\lambda}^i_j | \cdots \rangle \right] \frac{\partial}{\partial R_i} , \end{aligned} \tag{36}$$

where

$$\langle \cdots' | \cos\theta_{ni} | \cdots \rangle = \langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i \rangle \delta^{(L_i \Omega_i)}_{\mathrm{rest}',\mathrm{rest}} \quad (i = 1, \ldots, n-1) , \tag{37a}$$

$$\begin{aligned}\langle \cdots' | \cos\theta_{ij} | \cdots \rangle = & (\langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i \rangle \langle L_j' \Omega_j' | \cos\alpha_j | L_j \Omega_j \rangle \\ & + \tfrac{1}{2} \langle L_i' \Omega_i' | e^{i\varphi_i} \sin\alpha_i | L_i \Omega_i \rangle \langle L_j' \Omega_j' | e^{-i\varphi_j} \sin\alpha_j | L_j \Omega_j \rangle \\ & + \tfrac{1}{2} \langle L_i' \Omega_i' | e^{-i\varphi_i} \sin\alpha_i | L_i \Omega_i \rangle \langle L_j' \Omega_j' | e^{i\varphi_j} \sin\alpha_j | L_j \Omega_j \rangle) \delta^{(L_i \Omega_i L_j \Omega_j)}_{\mathrm{rest}',\mathrm{rest}} \quad (i \neq j = 1, \ldots, n-1) , \end{aligned} \tag{37b}$$

$$\langle \cdots' | I_{ii}^{-1} | \cdots \rangle = \left[\frac{M_{nn}}{R_n^2} + \frac{M_{ii}}{R_i^2} \right] \delta_{\mathrm{all}',\mathrm{all}} - 2 \frac{M_{ni}}{R_n R_i} \langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i \rangle \delta^{(L_i \Omega_i)}_{\mathrm{rest}',\mathrm{rest}} \quad (i = 1, \ldots, n-1) , \tag{38}$$

$$\begin{aligned}\sum_{j<i=1}^{n-1} \langle \cdots' | \hat{\Lambda}_{ij} | \cdots \rangle = & \hbar^2 \delta_{\mathrm{all}',\mathrm{all}} \frac{M_{nn}}{R_n^2} \sum_{j<i=1}^{n-1} \Omega_i \Omega_j \\ & + \frac{\hbar^2}{2} \sum_{i \neq j=1}^{n-1} \left\{ \frac{M_{ij} \Omega_i \Omega_j}{R_i R_j} \langle L_i' \Omega_i' | e^{-i\varphi_i} \sin\alpha_i | L_i \Omega_i \rangle \langle L_j' \Omega_j' | e^{i\varphi_j} \sin\alpha_j | L_j \Omega_j \rangle \right. \\ & + \frac{\Omega_j}{R_j} \left[c_+(i) \langle L_j' \Omega_j' | e^{-i\varphi_j} \sin\alpha_j | L_j \Omega_j \rangle \right. \\ & \times \left[\frac{M_{nj}}{R_n} \delta_{L_i' L_i} \delta_{\Omega_i' \Omega_i + 1} - \frac{M_{ij}}{R_i} \langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i + 1 \rangle \right] \\ & + c_-(i) \langle L_j' \Omega_j' | e^{i\varphi_j} \sin\alpha_j | L_j \Omega_j \rangle \\ & \left. \times \left[\frac{M_{nj}}{R_n} \delta_{L_i' L_i} \delta_{\Omega_i' \Omega_i - 1} - \frac{M_{ij}}{R_i} \langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i - 1 \rangle \right] \right] \\ & + c_+(i) c_-(j) \left[\frac{M_{nn}}{R_n^2} \delta_{L_i' L_i} \delta_{\Omega_i' \Omega_i + 1} \delta_{L_j' L_j} \delta_{\Omega_j' \Omega_j - 1} \right. \\ & - \frac{M_{ni}}{R_n R_i} \delta_{L_j' L_j} \delta_{\Omega_j' \Omega_j - 1} \langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i + 1 \rangle \\ & - \frac{M_{nj}}{R_n R_j} \delta_{L_i' L_i} \delta_{\Omega_i' \Omega_1 + 1} \langle L_j' \Omega_j' | \cos\alpha_j | L_j \Omega_j - 1 \rangle \\ & + \frac{M_{ij}}{R_i R_j} (\langle L_i' \Omega_i' | \cos\alpha_i | L_i \Omega_i + 1 \rangle \\ & \times \langle L' \Omega_j' | \cos\alpha_j | L_j \Omega_j - 1 \rangle \\ & + \tfrac{1}{2} \langle L_1' \Omega_i' | e^{-i\varphi_i} \sin\alpha_i | L_i \Omega_i + 1 \rangle \\ & \left. \left. \left. \times \langle L_j' \Omega_j' | e^{i\varphi_j} \sin\alpha_j | L_j \Omega_j - 1 \rangle \right) \right] \right] \end{aligned}$$

$$-\frac{1}{4}\frac{M_{ij}}{R_iR_j}[c_+(i)c_+(j)\langle L_i'\Omega_i'|e^{-i\varphi_i}\sin\alpha_i|L_i\Omega_i+1\rangle$$

$$\times\langle L_j'\Omega_j'|e^{-i\varphi_j}\sin\alpha_j|L_j\Omega_j+1\rangle$$

$$+c_-(i)c_-(j)\langle L_i'\Omega_i'|e^{i\varphi_i}\sin\alpha_i|L_i\Omega_i-1\rangle$$

$$\times\langle L_j\Omega_j'|e^{i\varphi_j}\sin\alpha_j|L_j\Omega_j-1\rangle]\Big\}\delta_{\text{rest}',\text{rest}}^{(L_i\Omega_iL_j\Omega_j)]}, \tag{39}$$

$$-i\hbar\sum_{j=1}^{n-1}\langle\cdots'|\hat{\lambda}_j^i|\cdots\rangle=-\frac{\hbar^2}{2}\sum_{j=1}^{n-1}\left[\frac{M_{ij}\Omega_j}{R_j}(\langle L_i'\Omega_i'|e^{i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\langle L_j'\Omega_j'|e^{-i\varphi_j}\sin\alpha_j|L_j\Omega_j\rangle\right.$$

$$-\langle L_i'\Omega_i'|e^{-i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\langle L_j'\Omega_j'|e^{i\varphi_j}\sin\alpha_j|L_j\Omega_j\rangle)$$

$$+c_+(j)\left[\frac{M_{ni}}{R_n}\langle L_i'\Omega_i'|e^{-i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\delta_{L_j'L_j}\delta_{\Omega_j'\Omega_j+1}\right.$$

$$+\frac{M_{ij}}{R_j}(\langle L_i'\Omega_i'|e^{-i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\langle L_j'\Omega_j'|\cos\alpha_j|L_j\Omega_j+1\rangle$$

$$-\langle L_i'\Omega_i'|\cos\alpha_i|L_i\Omega_i\rangle$$

$$\left.\times\langle L_j'\Omega_j'|e^{-i\varphi_j}\sin\alpha_j|L_j\Omega_j+1\rangle)\right]$$

$$+c_-(j)\left[\frac{M_{ni}}{R_n}\langle L_i'\Omega_i'|e^{i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\delta_{L_j'L_j}\delta_{\Omega_j'\Omega_j-1}\right.$$

$$+\frac{M_{ij}}{R_j}(\langle L_i'\Omega_i'|e^{i\varphi_i}\sin\alpha_i|L_i\Omega_i\rangle\langle L_j'\Omega_j'|\cos\alpha_j|L_j\Omega_j-1\rangle$$

$$-\langle L_i'\Omega_i'|\cos\alpha_i|L_i\Omega_i\rangle$$

$$\left.\left.\times\langle L_j'\Omega_j'|e^{i\varphi_j}\sin\alpha_j|L_j\Omega_j-1\rangle)\right]\right]\delta_{\text{rest}',\text{rest}}^{(L_i\Omega_iL_j\Omega_j)}$$

$$(i=1,n)\,. \tag{40}$$

In particular, in view of Eqs. (29), (35), (36), (38), and (39), the current diagonal element of matrix $\mathbf{T}^J$ is

$$\langle\Omega,L_1,\Omega_1,\ldots,L_{n-2},\Omega_{n-2},L_{n-1}|\hat{T}_E^J|\Omega,L_1,\Omega_1,\ldots,L_{n-2},\Omega_{n-2},L_{n-1}\rangle$$

$$=\frac{\hbar^2}{2}\left[\frac{M_{nn}}{R_n^2}\left[J(J+1)-2\Omega^2+2\Omega\sum_{i=1}^{n-2}\Omega_i-2\sum_{j\le i=1}^{n-2}\Omega_i\Omega_j\right]\right.$$

$$\left.-\sum_{i=1}^{n}M_{ii}\frac{1}{R_i^2}\frac{\partial}{\partial R_i}R_i^2\frac{\partial}{\partial R_i}+\sum_{i=1}^{n-1}\left[\frac{M_{nn}}{R_n^2}+\frac{M_{ii}}{R_i^2}\right]L_i(L_i+1)\right]. \tag{41}$$

Moreover, the nonzero off-diagonal elements in an Ω diagonal block of $\mathbf{T}^J$ are very few. They are of two types. Those of the first type are diagonal in all quantum numbers but one, namely $L_i,L_i\pm1$ $(i=1,\ldots,n-1)$; they originate from terms (37a) and (38). The others come from terms (37b), (39) and (40): they are nondiagonal in four quantum numbers (at most), namely, L_i, Ω_i, L_j, and Ω_j $(j<i=1,\ldots,n-1)$. More precisely, all the combinations of $L_iL_i\pm1$ with $L_jL_j\pm1$ are possible, and each one is only compatible with one of the three following possibilities: (i) $\Omega_i\Omega_i$, $\Omega_j\Omega_j$; (ii) $\Omega_i\Omega_i+1$, $\Omega_j\Omega_j-1$; (iii) $\Omega_i\Omega_i-1$, $\Omega_j\Omega_j+1$. These nonzero elements make up a sparse $\mathbf{T}^J$ matrix.

It should be noted that Sutcliffe and Tennyson always give their kinetic-energy operators for triatomics in the same form as above, i.e., partially integrated over the angular coordinates, see Ref. [87] for a review. In the expression of the operators in terms of polyspherical coordinates, there are singularities, e.g., $\sin^{-2}\alpha_i$ or $\sin^{-1}\alpha_i$ $(i=1,n-1)$, see Eqs. (24) and (25). The singularities are

removed by using the appropriately contracted angular basis

$$\{|J,\Omega,M,L_1,\Omega_1,\ldots,L_{n-2},\Omega_{n-2},L_{n-1}\rangle\}$$

for representing the operators. The property is well known for the operators $\hat{\mathbf{L}}_i^2$; it is also valid for $\hat{\mathbf{L}}_i\cdot\hat{\mathbf{L}}_j$ $(i\neq j=1,\ n-1)$. Good analyses of this question are proposed by Bramley, Green, and Handy [14] for tetraatomics, and by Sutcliffe [88] for triatomics. It should be emphasized that, in Eqs. (17)–(23), where $\hat{T}^J$ is expressed in terms of angular momentum operators for the various rotating vectors, there are no longer singular coefficients. This once again illustrates the advantage of expressing the kinetic-energy operator with the help of the relative vector rotation operators as such, overmanipulating coordinates. Our proposal that the standard representation

$$|J,\Omega,M,L_1,\Omega_1,\ldots,L_{n-2},\Omega_{n-2},L_{n-1}\rangle$$

should be used for the various angular momentum operators appearing in the expression of $\hat{T}^J$, in a nonsingular way, is basically a generalization of Sutcliffe's remark for triatomics [88], according to which, using standard associated Legendre functions allows the exact cancellation of the incipiently singular terms in $\hat{T}^J$.

VII. DISCUSSION

In this article, we have introduced a quantum-mechanical kinetic-energy operator for the treatment of the internal deformations and the rotation of an N-particle system considered as a set of $n=N-1$ coupled rovibrating vectors. The system can be alternatively described in terms of polyspherical coordinates. Many coordinate systems are of the polyspherical type and our kinetic-energy operator is appropriate to all of them. For practical applications, the possibility of changing the coordinates used for the description of the system configuration without having to redo all the lengthy calculations is very appreciable: if the coordinates are also polyspherical, then all the angular parts of the problem are analytically solved and the only changes concern the mass matrix, $\mathbf{M}$ (see Appendix A 2). Moreover, owing to vector parametrization, there is no limitation on the number of particles, N, contrary to recent treatments based on the manipulation of curvilinear coordinates, which, at present, are limited to three or four particles [27,80,89].

The polyspherical parametrization is suitable for the description of bound systems (including the high-energy regime, where the motion can become completely chaotic), and weakly bound or dissociative systems, but not always for collisional systems. This limitation is a consequence of the fact that the reference vectors $\mathbf{R}_1,\ldots,\mathbf{R}_n$ are chosen *a priori,* so that a dissociation into two fragments can be suitably treated if, and only if, one reference vector points in the appropriate direction.

An important point has not been treated. If some of the particles making up the system are identical, then they are indistinguishable and the Hamiltonian must be invariant under any feasible permutation of identical particles (i.e., it must belong to the totally symmetric irreducible representation of the group of the permutations of identical particles). Thus, it is no longer possible to use independent basis functions

$$|J,\Omega,M,L_1,\Omega_1,\ldots,L_{n-2},\Omega_{n-2},L_{n-1}\rangle$$

as above: symmetry-adapted linear combinations of these functions are required. Similarly, the coordinates must be transformed into symmetry-adapted coordinates [90–97]. This is planned to be the subject of a forthcoming paper. Modern approaches to this question can be found in a few recent articles, by Frey [97], Hutson [48], and Bramley, Green, and Handy [14].

If there are no identical particles, the Hamiltonian developed above can be straightforwardly used. To achieve the construction of the $\mathbf{T}^J$ matrix, radial basis functions have to be selected, according to whether the system is bound or dissociative. The integrals over the radial coordinates R_i $(i=1,\ldots,n)$ must be numerically evaluated. 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. If the system is free in all its deformation degrees of freedom, four particles, at the most, may be treated at present. If significantly larger system are to be studied, model constraints will have to be imposed, such as freezing one bond length, or the internal geometry of a substituent group, or any other constraint that isolates a part of the system which is responsible for well-defined lines in the spectrum (e.g., a local-mode overtone series). This subject is, to a large extent, still to be explored. In all cases, it should be emphasized that it is profitable to have at one's disposal a quantum finite basis representation (FBR) in which, independently of a particular set of coordinates, the kinetic-energy matrix is sparse. Combined with a discrete variable representation (DVR) for the potential (which is a local, i.e., nondifferential, operator), the FBR that we suggest probably constitutes an appropriate framework for the future dynamical studies of more-than-three particle systems (collocation, or pseudospectral methods [98–107]). This double representation for the wave function in a quantum-dynamical problem is very similar to the duality in Fourier theory, where the spaces of positions and frequencies are strictly equivalent, through the Fourier transform and its inverse [108].

The vector formalism developed in this article has been tested by comparing our kinetic-energy operator with that directly derived for a four-body system, namely, an acetylenelike molecule in the floppy molecular regime where the terminal light atoms can overcome the isomerization energy barrier and migrate from one carbon atom to the other, thus orbiting around the heavy C_2 core [80]. This requires applying the rules of differential calculus, as are needed when using curvilinear coordinates to describe an N-body system [18,20,27,109–112]. Although the two operator derivations are of a completely different nature, the final results are identically the same. The basic elements of the comparison are presented in Appendix C.

A last point worth mentioning is that the radial coordinates $R_1,\ldots,R_n$ can be parametrized, in turn, in the

generalized spherical [SO(n)] fashion:

$$\sqrt{\mu_1}R_1=\sqrt{\mu}\rho\sin\xi_{n-1}\cdots\sin\xi_3\sin\xi_2\sin\xi_1 ,$$
$$\sqrt{\mu_2}R_2=\sqrt{\mu}\rho\sin\xi_{n-1}\cdots\sin\xi_3\sin\xi_2\cos\xi_1 ,$$
$$\sqrt{\mu_3}R_3=\sqrt{\mu}\rho\sin\xi_{n-1}\cdots\sin\xi_3\cos\xi_2 ,$$
$$\vdots$$
$$\sqrt{\mu_{n-1}}R_{n-1}=\sqrt{\mu}\rho\sin\xi_{n-1}\cos\xi_{n-2} ,$$
$$\sqrt{\mu_n}R_n=\sqrt{\mu}\rho\cos\xi_{n-1} ,$$

where $0<\rho<\infty$, $0\le\xi_1<2\pi$, and $0\le\xi_i\le\pi$ $(i=2,n-1)$ [113]. In addition, $\mu=(m_1m_2\cdots m_N)^{1/2}/M^{(N/2)-1}$ is a totally symmetric characteristic mass, $M=m_1+m_2+\cdots+m_N$ is the total mass, and μ_i is the reduced mass associated with $\mathbf{R}_i$, so as to obtain a hyperspherical description of the N-body system viewed in the BF frame, after separation of the center-of-mass motion. Here ρ is the usual hyperspherical radius:

$$\mu\rho^2=\sum_{i=1}^{n}\mu_iR_i^2 ,$$

and the $3N-4$ hyperspherical angles are divided into (i) the three Euler angles accounting for the overall rotation: (ii) $2N-5$ (i.e., $2n-3$) geometrical angles, namely, $\{\alpha_i;\ i=1,n-1\}$ and $\{\varphi_i;\ i=1,n-2\}$, accounting for relative internal orientations, and (iii) the $n-1$ (i.e., $N-2$) n-spherical angles $\{\xi_i;\ i=1,n-1\}$. These hyperspherical coordinates suit a BF description of the N-body system. We shall call them local hyperspherical coordinates. As compared with the previously defined principal-axis hyperspherical coordinates [38], which constitute a generalized version of the three-particle hyperspherical coordinates of Delves and Smith [28–30], they have the drawback that the BF frame is no longer specifically the principal-axis system. However, they can be worthwhile because their geometrical meaning is much clearer and the quantization of the Hamiltonian is straightforward, as shown above, contrary to the principal-axis hyperspherical case [114]. This subject is currently being studied in our group.

ACKNOWLEDGMENTS

Professor Claude Leforestier is cordially thanked for having stimulated, by fruitful discussions, the present work at the starting point. Dr. Sarah Jackson's helpful contribution to improving the manuscript is warmly acknowledged. The Laboratoire de Chimie Théorique de l' Université de Paris–Sud is associated with the Centre National de la Recherche Scientifique (URA 506).

APPENDIX A: MATRICES A AND M

1. Four-body systems: three vectors

Case 1. Acetylenelike molecule in the floppy molecule regime. Three vectors $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$ which are appropriate for this situation are pictured in Fig. 4, with three possible Jacobi vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. The working vector relations are here:

$$\mathbf{R}_1=\mathbf{r}_1+\frac{\mu_2}{m_3+m_4}\mathbf{r}_2 ,$$
$$\mathbf{R}_2=\mathbf{r}_2 ,$$
$$\mathbf{R}_3=\mathbf{r}_3 .$$

These relations lead to

$$\mathbf{A}=\begin{bmatrix}1 & \dfrac{\mu_2}{m_3+m_4} & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} \quad (\det\mathbf{A}=1) ,$$

and

$$\mathbf{M}=\mathbf{A}\begin{bmatrix}\dfrac{M}{m_1(M-m_1)} & 0 & 0\\ 0 & \dfrac{1}{\mu_2} & 0\\ 0 & 0 & \dfrac{1}{\mu_3}\end{bmatrix}\mathbf{A}^t$$
$$=\begin{bmatrix}\dfrac{1}{\mu_1} & \dfrac{1}{m_3+m_4} & 0\\ \dfrac{1}{m_3+m_4} & \dfrac{1}{\mu_2} & 0\\ 0 & 0 & \dfrac{1}{\mu_3}\end{bmatrix} ,$$

where

$$\frac{1}{\mu_2}=\frac{m_2+m_3+m_4}{m_2(m_3+m_4)},\quad \frac{I}{\mu_3}=\frac{m_3+m_4}{m_3m_4} ,$$
$$\frac{1}{\mu_1}=\frac{M}{m_1(M-m_1)}+\frac{\mu_2}{(m_3+m_4)^2}=\frac{m_1+m_3+m_4}{m_1(m_3+m_4)} .$$

Case 2. Acetylenelike molecule in the vibrational regime. Three vectors $\mathbf{R}_1$, $\mathbf{R}_2$ and $\mathbf{R}_3$ are pictured in Fig. 5, along with three Jacobi vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. The vector

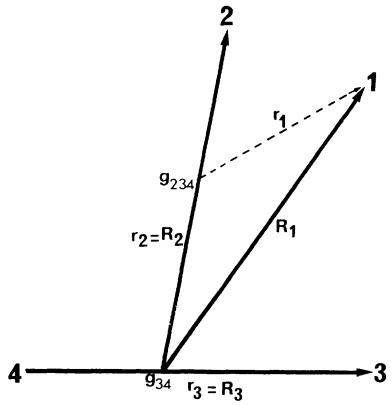

FIG. 4. The three vectors $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$ for the floppy molecule case.

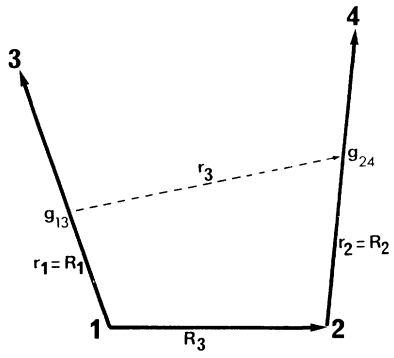

FIG. 5. Three vectors $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$, along with three Jacobi vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$.

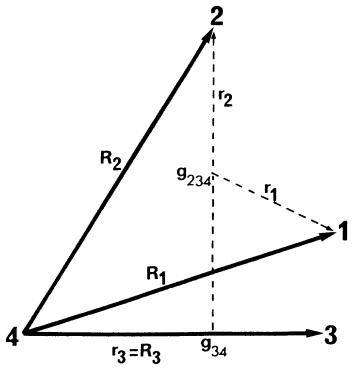

FIG. 6. The vectors $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, and $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ for the ammonialike case.

relations are now

$$\mathbf{R}_1=\mathbf{r}_1 ,$$

$$\mathbf{R}_2=\mathbf{r}_2 ,$$

$$\mathbf{R}_3=\mathbf{r}_3+\frac{\mu_1}{m_1}\mathbf{r}_1-\frac{\mu_2}{m_2}\mathbf{r}_2 .$$

They result in

$$\mathbf{A}=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \frac{\mu_1}{m_1} & -\frac{\mu_2}{m_2} & 1 \end{pmatrix} \quad (\det \mathbf{A}=1) ,$$

and

$$\mathbf{M}=\mathbf{A}\begin{pmatrix} \frac{1}{\mu_1} & 0 & 0 \\ 0 & \frac{1}{\mu_2} & 0 \\ 0 & 0 & \frac{M}{(m_1+m_3)(m_2+m_4)} \end{pmatrix}\mathbf{A}^t$$

$$=\begin{pmatrix} \frac{1}{\mu_1} & 0 & \frac{1}{m_1} \\ 0 & \frac{1}{\mu_2} & -\frac{1}{m_2} \\ \frac{1}{m_1} & -\frac{1}{m_2} & \frac{1}{\mu_3} \end{pmatrix} ,$$

where

$$\frac{1}{\mu_1}=\frac{m_1+m_3}{m_1 m_3}, \quad \frac{1}{\mu_2}=\frac{m_2+m_4}{m_2 m_4} ,$$

and

$$\frac{1}{\mu_3}=\frac{M}{(m_1+m_3)(m_2+m_4)}+\frac{\mu_1}{m_1^2}+\frac{\mu_2}{m_2^2}=\frac{m_1+m_2}{m_1 m_2} .$$

Case 3. Ammonialike molecule. The vectors $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$ and $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ are pictured in Fig. 6. The vector relations are

$$\mathbf{R}_1=\mathbf{r}_1+\frac{m_2}{m_2+m_3+m_4}\mathbf{r}_2+\frac{\mu_3}{m_4}\mathbf{r}_3 ,$$

$$\mathbf{R}_2=\mathbf{r}_2+\frac{\mu_3}{m_4}\mathbf{r}_3 ,$$

$$\mathbf{R}_3=\mathbf{r}_3 ,$$

and

$$\mathbf{A}=\begin{pmatrix} 1 & \frac{m_2}{m_2+m_3+m_4} & \frac{\mu_3}{m_4} \\ 0 & 1 & \frac{\mu_3}{m_4} \\ 0 & 0 & 1 \end{pmatrix} \quad (\det \mathbf{A}=1) ,$$

$$\mathbf{M}=\mathbf{A}\begin{pmatrix} \frac{M}{m_1(m_2+m_3+m_4)} & 0 & 0 \\ 0 & \frac{m_2+m_3+m_4}{m_2(m_3+m_4)} & 0 \\ 0 & 0 & \frac{1}{\mu_3} \end{pmatrix}\mathbf{A}^t$$

$$=\begin{pmatrix} \frac{1}{\mu_1} & \frac{1}{m_4} & \frac{1}{m_4} \\ \frac{1}{m_4} & \frac{1}{\mu_2} & \frac{1}{m_4} \\ \frac{1}{m_4} & \frac{1}{m_4} & \frac{1}{\mu_3} \end{pmatrix} ,$$

where

$$\frac{1}{\mu_3}=\frac{m_3+m_4}{m_3 m_4}, \quad \frac{1}{\mu_2}=\frac{m_2+m_3+m_4}{m_2(m_3+m_4)}+\frac{\mu_3}{m_4^2}=\frac{m_2+m_4}{m_2 m_4} ,$$

$$\frac{1}{\mu_1}=\frac{M}{m_1(m_2+m_3+m_4)}+\frac{\mu_2}{(m_3+m_4)^2}+\frac{\mu_3}{m_4^2}$$

$$=\frac{m_1+m_4}{m_1 m_4} .$$

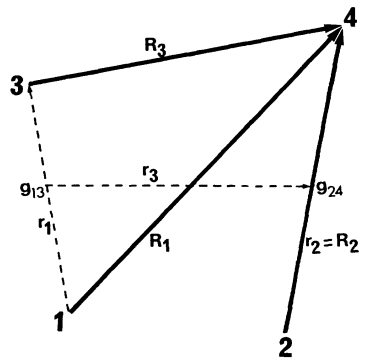

FIG. 7. Alternative vectors $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$ and $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ for the ammonialike case.

The same results could as well be obtained in starting from vectors $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$ and $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ shown in Fig. 7. The vector relations are now

$$\mathbf{R}_1=\frac{m_3}{(m_1+m_3)}\mathbf{r}_1+\frac{m_2}{(m_2+m_4)}\mathbf{r}_2+\mathbf{r}_3 ,$$

$$\mathbf{R}_2=\mathbf{r}_2 ,$$

$$\mathbf{R}_3=-\frac{m_1}{(m_1+m_3)}\mathbf{r}_1+\frac{m_2}{(m_2+m_4)}\mathbf{r}_2+\mathbf{r}_3 ,$$

and

$$\mathbf{A}=\begin{bmatrix} \frac{m_3}{(m_1+m_3)} & \frac{m_2}{(m_2+m_4)} & 1 \\ 0 & 1 & 0 \\ -\frac{m_1}{(m_1+m_3)} & \frac{m_2}{(m_2+m_4)} & 1 \end{bmatrix} \quad (\det \mathbf{A}=1) ,$$

and

$$\mathbf{M}=\mathbf{A}\begin{bmatrix} \frac{m_1+m_3}{m_1m_3} & 0 & 0 \\ 0 & \frac{m_2+m_4}{m_2m_4} & 0 \\ 0 & 0 & \frac{M}{(m_1+m_3)(m_2+m_4)} \end{bmatrix}\mathbf{A}^t$$

$$=\begin{bmatrix} \frac{1}{\mu_1} & \frac{1}{m_4} & \frac{1}{m_4} \\ \frac{1}{m_4} & \frac{1}{\mu_2} & \frac{1}{m_4} \\ \frac{1}{m_4} & \frac{1}{m_4} & \frac{1}{\mu_3} \end{bmatrix} .$$

2. N-body systems: $N-1$ vectors

If vectors $\mathbf{R}_1, \ldots, \mathbf{R}_n$ are exclusively pointing between individual particles and/or centers of mass of groups of particles, then matrix $\mathbf{M}$ has the following elements.

(i) The diagonal element M_{ii} is the inverse of the reduced mass associated with the two groups of particles whose centers of mass are joined by $\mathbf{R}_i$.

(ii) For the off-diagonal elements, $|M_{ij}|$ is the inverse of the mass of the group of particles whose center of mass is common to both $\mathbf{R}_i$ and $\mathbf{R}_j$. The sign of M_{ij} is + if the two vectors originate from or point towards the same center of mass; it is − if one originates from the center of mass towards which the other points. Otherwise, $M_{ij}=0$.

APPENDIX B: WHEN IS THE WAVE-FUNCTION NORMALIZATION CONVENTION TO BE CHANGED?

Let us suppose that the wave function Ψ_E appropriate for the kinetic-energy operator given in the text above, i.e., normalized with the help of the Euclidean volume element

$$d\tau^{\text{in}E}=\prod_{i=1}^{n} R_i^2 dR_i \prod_{i=1}^{n-1} \sin\alpha_i d\alpha_i \prod_{i=1}^{n-2} d\varphi_i ,$$

is replaced by the wave function $\Phi_{\neq E}$ normalized with the non-Euclidean volume element

$$d\tau^{\text{in}}=\prod_{i=1}^{n} dR_i \prod_{i=1}^{n-1} \sin\alpha_i d\alpha_i \prod_{i=1}^{n-2} d\varphi_i .$$

Then [79,80]

$$\Psi_E=\frac{1}{R_1\cdots R_n}\Phi_{\neq E}$$

so that the three following relationships hold:

$$\frac{\partial}{\partial R_i}\Psi_E=\frac{1}{R_1\cdots R_n}\left[-\frac{1}{R_i}+\frac{\partial}{\partial R_i}\right]\Phi_{\neq E} ,$$

$$\frac{1}{R_i}\frac{\partial^2}{\partial R_i^2}R_i\Psi_E=\frac{1}{R_1\cdots R_n}\frac{\partial^2}{\partial R_i^2}\Phi_{\neq E} ,$$

$$\frac{\partial^2}{\partial R_i\partial R_j}\Psi_E=\frac{1}{R_1\cdots R_n}\left[-\frac{1}{R_i}+\frac{\partial}{\partial R_i}\right]\times\left[-\frac{1}{R_j}+\frac{\partial}{\partial R_j}\right]\Phi_{\neq E} .$$

In virtue of these relations,

$$\hat{T}_E^0=-\frac{\hbar^2}{2}\sum_{i=1}^{n} M_{ii}\frac{1}{R_i}\frac{\partial^2}{\partial R_1^2}R_i-\hbar^2\sum_{j<i=1}^{n} M_{ij}\cos\theta_{ij}\frac{\partial^2}{\partial R_i\partial R_j}+\tfrac{1}{2}\sum_{i=1}^{n-1}\frac{\hat{\mathbf{L}}_i^2}{I_{ii}}+\sum_{j<i=1}^{n-1}\hat{\Lambda}_{ij}+\sum_{i=1}^{n}\sum_{j=1}^{n-1}\hat{\lambda}_j^i\left[-i\hbar\frac{\partial}{\partial R_i}\right]$$

must be replaced by

$$\hat{T}_{\neq E}^0=-\frac{\hbar^2}{2}\sum_{i=1}^{n} M_{ii}\frac{\partial^2}{\partial R_1^2}-\hbar^2\sum_{j<i=1}^{n} M_{ij}\cos\theta_{ij}\left[\frac{1}{R_iR_j}-\frac{1}{R_j}\frac{\partial}{\partial R_i}-\frac{1}{R_i}\frac{\partial}{\partial R_j}+\frac{\partial^2}{\partial R_i\partial R_j}\right]+\tfrac{1}{2}\sum_{i=1}^{n-1}\frac{\hat{\mathbf{L}}_i^2}{I_{ii}}+\sum_{j<i=1}^{n-1}\hat{\Lambda}_{ij}+\sum_{i=1}^{n}\sum_{j=1}^{n-1}\hat{\lambda}_j^i\left[-i\hbar\left[-\frac{1}{R_i}+\frac{\partial}{\partial R_i}\right]\right] .$$

If $M_{ij}\neq 0$ for $i\neq j$, i.e., if the vectors and the coordinates used are not of the Jacobi type, it clearly appears that it is not worth changing the normalization convention because $\hat{T}^0_{\neq E}$ turns out to be more complicated than $\hat{T}^0_E$, except for the purely quadratic part of the operator which is unchanged; particularly, it appears the so-called extra-potential term (which is nondifferential, i.e., purely multiplicative) [79,80]:

$$\mathcal{V}_{\neq E}=-\hbar^2\sum_{j<i=1}^{n} M_{ij}\frac{\cos\theta_{ij}}{R_iR_j}\ .$$

On the contrary, if (and only if) Jacobi vectors $\mathbf{r}_1,\ldots,\mathbf{r}_n$ are used, $M_{ij}=\delta_{ij}/\mu_i$ $(i=1,\ldots,n)$, changing the normalization convention significantly simplifies the expressions of the various terms in the kinetic-energy operator, without adding any extra-potential term:

$$\hat{T}^J_{\neq E\ \mathrm{rot}}=\frac{1}{2}\frac{1}{\mu_n r_n^2}\mathbf{J}^2\ ,$$

$$\hat{T}^J_{\neq E\ \mathrm{cor}}=-\frac{1}{\mu_n r_n^2}\sum_{i=1}^{n-1}\left[\hat{J}^z\hat{L}_i^z+\frac{\hat{J}^+\hat{L}_i^-+\hat{J}^-\hat{L}_i^+}{2}\right]$$
$$=-\frac{1}{\mu_n r_n^2}\sum_{i=1}^{n-1}\hat{\mathbf{J}}\cdot\hat{\mathbf{L}}_i\ ,$$

$$\hat{T}^0_{\neq E}=-\frac{\hbar^2}{2}\sum_{i=1}^{n}\frac{1}{\mu_i}\frac{\partial^2}{\partial r_i^2}+\tfrac{1}{2}\sum_{i=1}^{n-1}\frac{\hat{\mathbf{L}}_i^2}{I_{ii}}$$
$$+\frac{1}{\mu_n r_n^2}\sum_{j<i=1}^{n-1}\left[\hat{L}_i^z\hat{L}_j^z+\frac{\hat{L}_i^+\hat{L}_j^-+\hat{L}_i^-\hat{L}_j^+}{2}\right]$$
$$=-\frac{\hbar^2}{2}\sum_{i=1}^{n}\frac{1}{\mu_i}\frac{\partial^2}{\partial r_i^2}+\tfrac{1}{2}\sum_{i=1}^{n-1}\frac{\hat{\mathbf{L}}_i^2}{I_{ii}}+\frac{1}{\mu_n r_n^2}\sum_{j<i=1}^{n-1}\hat{\mathbf{L}}_i\cdot\hat{\mathbf{L}}_j\ ,$$

where

$$\frac{1}{I_{ii}}=\frac{1}{\mu_n r_n^2}+\frac{1}{\mu_i r_i^2}\quad (i=1,\ldots,n-1)\ .$$

Such expressions have been used very often in the past for three-body systems $(n=2)$ [22–26], with no crossed term $\hat{\mathbf{L}}_i\cdot\hat{\mathbf{L}}_j$ in the expression of $\hat{T}^0_{\neq E}$.

APPENDIX C: THE $J=0$ KINETIC-ENERGY OPERATOR IN TERMS OF CURVILINEAR COORDINATES

For comparing the kinetic-energy operator developed in the present article with that directly derived in applying the rules of differential calculus (as required for curvilinear coordinates), the main difficulty concerns $\hat{T}^0_E$, i.e., the part of the total Hamiltonian which remains when $\mathbf{J}=0$ (apart from the potential itself, which is nondifferential and presents no difficulty). The quantization of the radial part of the Hamiltonian has been already dealt with above (see Secs. IV and V). We still have to find quantization rules for the angular part of the kinetic-energy operator at $\mathbf{J}=0$.

First of all, let us note that, for $\mathbf{J}=0$, $\hat{T}^0_E$ is independent of the BF frame. The mathematical constraint $L_n^z=0$, which gives, in the present case,

$$\mathbf{J}=0\Longrightarrow J^z=0(L_n^z=0)\Longrightarrow 0=\sum_{i=1}^{n-1}L_i^z\Longrightarrow L_{n-1}^z=-\sum_{i=1}^{n-2}L_i^z\ ,$$

is therefore not to be considered the consequence of a particular choice of the BF frame, but rather that of the particular choice of internal coordinates. Here indeed, the dihedral angles φ_i are measured around $\mathbf{R}_n$ starting from $\mathbf{R}_{n-1}$, or still,

$$\varphi_i=\phi_i-\phi_{n-1}\quad (i=1,\ldots,n-2)\ .$$

By application of the chain rule,

$$\frac{\partial}{\partial\phi_i}=\frac{\partial}{\partial\varphi_i}\quad (i=1,\ldots,n-2)\ ,$$

$$\frac{\partial}{\partial\phi_{n-1}}=-\sum_{i=1}^{n-2}\frac{\partial}{\partial\varphi_i}\ .$$

On the basis of this preliminary remark, the angular part of the classical Hamiltonian can be quantized by using, in Eq. (14),

$$\hat{L}_i^z=-i\hbar\frac{\partial}{\partial\varphi_i}\quad (i=1,\ldots,n-2)\ . \tag{C1}$$

$$\hat{L}_{n-1}^z=+i\hbar\sum_{i=1}^{n-2}\frac{\partial}{\partial\varphi_i}\ , \tag{C2}$$

$$\hat{\mathbf{L}}_i^2=-\hbar^2\left[\frac{1}{\sin\alpha_i}\frac{\partial}{\partial\alpha_i}\sin\alpha_i\frac{\partial}{\partial\alpha_i}+\frac{1}{\sin^2\alpha_i}\frac{\partial^2}{\partial\varphi_i^2}\right]\quad (i=1,\ldots,n-2)\ , \tag{C3}$$

$$\hat{\mathbf{L}}_{n-1}^2=-\hbar^2\left[\frac{1}{\sin\alpha_{n-1}}\frac{\partial}{\partial\alpha_{n-1}}\sin\alpha_{n-1}\frac{\partial}{\partial\alpha_{n-1}}+\frac{1}{\sin^2\alpha_{n-1}}\left[\sum_{i=1}^{n-2}\frac{\partial}{\partial\varphi_i}\right]^2\right]\ , \tag{C4}$$

$$\hat{\mathbf{L}}_i\cdot\hat{\mathbf{L}}_j=-\hbar^2\left[\cos(\varphi_i-\varphi_j)\frac{\partial^2}{\partial\alpha_i\partial\alpha_j}+[1+\cot\alpha_i\cot\alpha_j\cos(\varphi_i-\varphi_j)]\frac{\partial^2}{\partial\varphi_i\partial\varphi_j}\right.$$
$$\left.-\sin(\varphi_i-\varphi_j)\left[\cot\alpha_i\frac{\partial^2}{\partial\alpha_j\partial\varphi_i}-\cot\alpha_j\frac{\partial^2}{\partial\alpha_i\partial\varphi_j}\right]\right]\quad (i,j=1,\ldots,n-2;\ i\neq j)\ . \tag{C5}$$

[In the same way as it is forbidden to apply the relation $\hat{P}_i^r \hat{P}_j^r$ to the case where $j=i$, see Sec. IV, it is forbidden to apply $\hat{\mathbf{L}}_i \cdot \hat{\mathbf{L}}_j$ given above when $j=i$; the result would be

$$-\hbar^2 \left[\frac{\partial^2}{\partial \alpha_i^2} + \frac{1}{\sin^2 \alpha_i} \frac{\partial^2}{\partial \varphi_i^2} \right] ,$$

which is wrong, cf. (C3)].

$$\hat{\mathbf{L}}_i \cdot \hat{\mathbf{L}}_{n-1} = -\hbar^2 \left[\cos\varphi_i \frac{\partial^2}{\partial \alpha_i \partial \alpha_{n-1}} - (1+\cot\alpha_i \cot\alpha_{n-1} \cos\varphi_i) \frac{\partial}{\partial \varphi_i} \sum_{j=1}^{n-2} \frac{\partial}{\partial \varphi_j} \right.$$
$$\left. - \sin\varphi_i \left[\cot\alpha_i \frac{\partial^2}{\partial \alpha_{n-1} \partial \varphi_i} + \cot\alpha_{n-1} \frac{\partial}{\partial \alpha_i} \sum_{j=1}^{n-2} \frac{\partial}{\partial \varphi_j} \right] \right] \quad (i=1,\ldots,n-2) , \tag{C6}$$

$$(\mathbf{e}_i \times \mathbf{e}_j) \cdot \hat{\mathbf{L}}_j = -i\hbar \left[[\cos\alpha_i \sin\alpha_j - \sin\alpha_i \cos\alpha_j \cos(\varphi_j - \varphi_i)] \frac{\partial}{\partial \alpha_j} + \frac{\sin\alpha_i \sin(\varphi_j - \varphi_i)}{\sin\alpha_j} \frac{\partial}{\partial \varphi_j} \right]$$
$$(i=1,\ldots,n-1;\ j=1,\ldots,n-2;\ i \neq j) , \tag{C7}$$

$$(\mathbf{e}_i \times \mathbf{e}_{n-1}) \cdot \hat{\mathbf{L}}_{n-1} = i\hbar \left[(\cos\alpha_i \sin\alpha_{n-1} - \sin\alpha_i \cos\alpha_{n-1} \cos\varphi_i) \frac{\partial}{\partial \alpha_{n-1}} + \frac{\sin\alpha_i \sin\varphi_i}{\sin\alpha_{n-1}} \sum_{j=1}^{n-2} \frac{\partial}{\partial \varphi_j} \right] \quad (i=1,\ldots,n-2) , \tag{C8}$$

$$\mathbf{E}_i \cdot \hat{\mathbf{L}}_i = i\hbar \frac{\partial}{\partial \alpha_i} \quad (i=1,\ldots,n-1) , \tag{C9}$$

$$\mathbf{E}_i \cdot \hat{\mathbf{L}}_j = i\hbar \left[\cos(\varphi_j - \varphi_i) \frac{\partial}{\partial \alpha_j} - \cot\alpha_j \sin(\varphi_j - \varphi_i) \frac{\partial}{\partial \varphi_j} \right] \quad (i=1,\ldots,n-1;\ j=1,\ldots,n-2;\ i \neq j) , \tag{C10}$$

$$\mathbf{E}_i \cdot \hat{\mathbf{L}}_{n-1} = i\hbar \left[\cos\varphi_i \frac{\partial}{\partial \alpha_{n-1}} - \cot\alpha_{n-1} \sin\varphi_i \sum_{j=1}^{n-2} \frac{\partial}{\partial \varphi_j} \right] \quad (i=1,\ldots,n-2) , \tag{C11}$$

$$\mathbf{e}_i \cdot \hat{\mathbf{L}}_j = i\hbar \left[\sin\alpha_i \sin(\varphi_j - \varphi_i) \frac{\partial}{\partial \alpha_j} + [-\cos\alpha_i + \sin\alpha_i \cot\alpha_j \cos(\varphi_j - \varphi_i)] \frac{\partial}{\partial \varphi_j} \right]$$
$$(i=1,\ldots,n-1;\ j=1,\ldots,n-2;\ i \neq j) , \tag{C12}$$

$$\mathbf{e}_i \cdot \hat{\mathbf{L}}_{n-1} = -i\hbar \left[\sin\alpha_i \sin\varphi_i \frac{\partial}{\partial \alpha_{n-1}} + (-\cos\alpha_i + \sin\alpha_i \cot\alpha_{n-1} \cos\varphi_i) \sum_{j=1}^{n-2} \frac{\partial}{\partial \varphi_j} \right] \quad (i=1,\ldots,n-2) . \tag{C13}$$

For the four-body system and the coordinates illustrated in Fig. 1(b), the operator obtained by means of the relations above is exactly the same as that in Ref. [80], Sec. 8.2. This definitely confirms the relations (C1)–(C4), (C6)–(C8), and (C12) and (C13). For confirming the others, a five-body system would have been necessary, but a direct calculation of the operator for such a system is an overwhelming task, not yet undertaken by anybody, at least to our knowledge.

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