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Principal-axis hyperspherical description of N-particle systems: Quantum-mechanical treatment

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Principal-axis hyperspherical coordinates (made up of one hyperradius and $3N-7$ angles as internal coordinates) and three Euler angles as external (rotational) coordinates [X. Chapuisat and A. Nauts, Phys. Rev. **44**, 1328 (1991)], are used to describe an N-particle system. The exact quantum-mechanical Hamiltonian of the system in terms of these coordinates is established and is very simple. Generalized angular-momentum vector operators, which allow the generation of a profitable standard representation for the angular part of the problem, are introduced. The corresponding matrix representation of the Hamiltonian operator is built.

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I. INTRODUCTION

In a recent paper [1], hereafter called I, a set of coordinates well adapted to the N-particle systems considered along the line of argument of the hyperspherical description—the so-called principal-axis hyperspherical (PAH) coordinates—has been introduced. The PAH coordinates descend directly from the old Eckart coordinates [2], recently rediscovered by Robert and Baudon [3–5]. They constitute a generalization of the hyperspherical coordinates introduced, 30 years ago, by Delves [6] and Whitten and Smith [7,8] for three particles. A wealth of information on the hyperspherical description of the three-particle systems can be found in several reviews [9–17].

In addition, in I, the *exact* classical Hamiltonian of the system, expressed in terms of the PAH coordinates, has been derived. After very long, intermediate calculations, it turned out to be remarkably simple, the only condition being that some special quasimomenta (canonically conjugate to some quasivelocities) were introduced.

The aim of the present paper is the *quantization* of this classical Hamiltonian and the derivation of the corresponding quasimomentum operators, in particular in view of establishing *a standard representation accounting analytically for all the angular part of the problem.* Therefore the numerical integration effort is to be concentrated, as far as the kinetic energy is concerned, to the only hyperradial (i.e., one-dimensional) part of the wave function.

In Sec. II some basic requirements for the quantization of a classical Hamiltonian are summarized. The exact quantum-mechanical PAH Hamiltonian is actually derived in Sec. III. A fruitful modification of the convention of normalization of the wave function is proposed in Sec. IV. Generalized angular-momentum vector operators are introduced in Sec. V; starting from the study of the commutation relationships of these operators, a standard representation is built, which allows one to generate a profitable matrix representation for the angular part of the kinetic energy operator.

II. QUANTIZATION OF A CLASSICAL HAMILTONIAN EXPRESSED IN TERMS OF QUASIMOMENTA

Let $\mathbf{q}=(q^1,q^2,\ldots,q^m)$ be a set of curvilinear coordinates well suited for the description of a dynamical system, and let $\mathbf{p}=(p_1,p_2,\ldots,p_m)$ be the corresponding conjugate momenta in classical mechanics. Quasimomenta $\mathbf{P}=(P_1,P_2,\ldots,P_m)$ are defined by

$$P_K=\sum_{i=1}^{m}[\mathbf{B}(\mathbf{q})]^i_K p_i \quad (K=1,2,\ldots,m) \tag{1}$$

where $[\mathbf{B}(\mathbf{q})]^i_K$ is the current matrix element of the nonsingular $m\times m$ matrix $\mathbf{B}(\mathbf{q})$, depending only on the coordinates. The determinant of $\mathbf{B}(\mathbf{q})$ is denoted by

$$t^{-1}(\mathbf{q})=\mathrm{Det}\mathbf{B}(\mathbf{q})\ . \tag{2}$$

In classical mechanics, the kinetic energy T can always be expressed as a quadratic form of momenta:

$$2T=\sum_{i,j=1}^{m}p_i g^{ij}(\mathbf{q})p_j \tag{3}$$

where

$$g^{ij}(\mathbf{q})=\sum_{\alpha=1}^{m}\frac{\partial q^i}{\partial x^\alpha}\frac{\partial q^j}{\partial x^\alpha}\quad (i,j=1,2,\ldots,m) \tag{4}$$

and $x^\alpha(\mathbf{q})$ is the αth mass-weighted Cartesian coordinate of the point representing the system in the (Euclidean) configuration space parametrized by $\mathbf{q}$. T can always be rewritten as

$$2T=\sum_{K,L=1}^{m}P_K g^{KL}(\mathbf{q})P_L \tag{5}$$

with

$$g^{KL}(\mathbf{q})=\sum_{i,j=1}^{m}[\mathbf{B}^{-1}(\mathbf{q})]^K_i g^{ij}(\mathbf{q})[\mathbf{B}^{-1}(\mathbf{q})]^L_j \quad (K,L=1,2,\ldots,m) \tag{6}$$

so that if

$$g(\mathbf{q})=\mathrm{Det}[g^{ij}(\mathbf{q})] \tag{7a}$$

and

$$\tilde{g}(\mathbf{q})=\mathrm{Det}[g^{KL}(\mathbf{q})] \tag{7b}$$

there is

$$g(\mathbf{q})=\tilde{g}(\mathbf{q})t^{-2}(\mathbf{q}) \ . \tag{8}$$

In quantum mechanics, p_i is to be replaced by the partial derivative operator:

$$\hat{p}_i=-i\hbar\frac{\partial}{\partial q^i} \quad (i=1,2,\ldots,m) \ . \tag{9}$$

In keeping, for the quasimomentum operators, with the same definition as above

$$\hat{P}_K=\sum_{i=1}^{m}[\mathbf{B}(\mathbf{q})]^i_K\hat{p}_i \quad (K=1,2,\ldots,m) \tag{10}$$

it is established that [18,19], as long as the Euclidean volume element of the configuration space

$$d\tau_1=dx^1dx^2\cdots dx^m=[g(\mathbf{q})]^{-1/2}dq^1dq^2\cdots dq^m$$

is used for the calculation of the matrix elements as integrals, the kinetic energy operator must be written as

$$2\hat{T}_1=\sum_{K,L=1}^{m}[\hat{P}_K+\Lambda_K(\mathbf{q})]g^{KL}(\mathbf{q})\hat{P}_L \tag{11a}$$

where

$$\Lambda_K(\mathbf{q})=\mathbf{B}^i_K(g^{1/2}\hat{p}_i g^{-1/2})+(\hat{p}_i\mathbf{B}^i_K) \ . \tag{11b}$$

Here, the derivative operators appearing in parentheses are supposed not to operate beyond the parentheses, so that the Λ_K are multiplicative (i.e., nondifferential) operators. Equations (11a) and (11b) can be readily rewritten in the form

$$2\hat{T}_1=\sum_{K,L=1}^{m}g^{KL}(\mathbf{q})\hat{P}_K\hat{P}_L+\sum_{L=1}^{m}\Gamma^L_1(\mathbf{q})\hat{P}_L \tag{12}$$

where

$$\Gamma^L_1(\mathbf{q})=\sum_{i=1}^{m}\{[\hat{p}_i+\Lambda_i(\mathbf{q})][\mathbf{B}(\mathbf{q})]^i_K g^{KL}(\mathbf{q})\} \tag{13}$$

and

$$\Lambda_i(\mathbf{q})=(\tilde{g}^{1/2}\hat{p}_i\tilde{g}^{-1/2})+(t^{-1}\hat{p}_i t) \tag{14a}$$

$$=-i\hbar g^{1/2}\frac{\partial g^{-1/2}}{\partial q^i}=-i\hbar\Lambda^*_i(\mathbf{q}) \ . \tag{14b}$$

If a classical Hamiltonian is known in the form

$$H=T(\mathbf{q},\mathbf{P})+V(\mathbf{q}) \tag{15}$$

where $T(\mathbf{q},\mathbf{P})$ is written as in Eq. (5), its quantization simply amounts to rewriting it as in Eq. (12), by means of the quantities in Eqs. (13) and (14), that are to be explicitly calculated. This is precisely the case for the classical Hamiltonian derived in I, where Eq. (65) on the one hand, and Eqs. (3) and (66a) on the other hand, are, respectively, formally of the type (12) and (1) of the present article. [In the following, we will use an abbreviation for equation numbers from paper I: Eq. (I-65) denotes Eq. (65) of I, e.g.]

For more details on the PAH coordinates and quasimomenta, see I.

III. THE QUANTUM-MECHANICAL PAH HAMILTONIAN

We actually have, from Eq. (I-65),

$$[g^{KL}(\mathbf{q})]=\begin{bmatrix} \mathbf{s}(\mathbf{q}) & 0 & 0 & \cdots & 0 & 0 \\ 0 & \frac{1}{\rho^2}\mathbf{b}(\mathbf{q}) & 0 & & 0 & \frac{1}{\rho^2}\mathbf{d}(\mathbf{q}) \\ 0 & 0 & \frac{1}{\rho^2}\mathbf{e}(\mathbf{q}) & & 0 & 0 \\ \vdots & & & \ddots & & \\ 0 & 0 & 0 & & \frac{1}{\rho^2}\mathbf{e}(\mathbf{q}) & 0 \\ 0 & \frac{1}{\rho^2}\mathbf{d}(\mathbf{q}) & 0 & & 0 & \frac{1}{\rho^2}\mathbf{b}(\mathbf{q}) \end{bmatrix} \tag{16}$$

where each element in the matrix above denotes a 3×3 diagonal matrix, respectively,

$$\mathbf{s}(\mathbf{q})=\begin{bmatrix}1 & 0 & 0\\ 0 & \frac{1}{\rho^2} & 0\\ 0 & 0 & \frac{1}{\rho^2\sin^2\theta}\end{bmatrix} \tag{17a}$$

$$\mathbf{b}(\mathbf{q})=\begin{bmatrix}\frac{\cos^2\theta+\sin^2\theta\sin^2\phi}{(\cos^2\theta-\sin^2\theta\sin^2\phi)^2} & 0 & 0\\ 0 & \frac{\cos^2\theta+\sin^2\theta\cos^2\phi}{(\cos^2\theta-\sin^2\theta\cos^2\phi)^2} & 0\\ 0 & 0 & \frac{1}{\sin^2\theta\cos^2 2\phi}\end{bmatrix} \tag{17b}$$

$$\mathbf{d}(\mathbf{q})=\begin{bmatrix}\frac{\sin^2\theta\sin\phi}{(\cos^2\theta-\sin^2\theta\sin^2\phi)^2} & 0 & 0\\ 0 & \frac{\sin 2\theta\cos\phi}{(\cos^2\theta-\sin^2\theta\cos^2\phi)^2} & 0\\ 0 & 0 & \frac{\sin 2\phi}{\sin^2\theta\cos^2 2\phi}\end{bmatrix} \tag{17c}$$

and

$$\mathbf{e}(\mathbf{q})=\begin{bmatrix}\frac{1}{\sin^2\theta\cos^2\phi} & 0 & 0\\ 0 & \frac{1}{\sin^2\theta\sin^2\phi} & 0\\ 0 & 0 & \frac{1}{\cos^2\theta}\end{bmatrix}. \tag{17d}$$

ρ, θ, and ϕ are the three spherical coordinates which allow the parametrization of the three mass-weighted gyration radii of the system (see I, Fig. 1). The following result is readily obtained:

$$\tilde{g}(\mathbf{q})=\frac{16^{n-2}}{[\rho^{3n-1}\sin^n\theta\sin^{n-3}2\theta\cos 2\phi\sin^{n-3}2\phi(4\cos^2\theta\cos 2\theta+\sin^4\theta\sin^2 2\phi)]^2}\quad (n\geq 3)\ . \tag{18}$$

Here, $n=N-1$ is the number of Jacobi vectors describing the internal conformation of the system, and N is the number of particles. In the matrix of Eq. (16), there are $n-3$ diagonal blocks $(1/\rho^2)\mathbf{e}(\mathbf{q})$.

In addition, we have from Eqs. (I-62) and (I-66a)

$$\begin{bmatrix}\hat{K}_x\\ \hat{K}_y\\ \hat{K}_z\\ \hat{N}_{x4}\\ \hat{N}_{y4}\\ \hat{N}_{z4}\\ \hat{N}_{x5}\\ \hat{N}_{y5}\\ \hat{N}_{z5}\\ \\ \hat{N}_{xn}\\ \hat{N}_{yn}\\ \hat{N}_{zn}\end{bmatrix}=-i\hbar[\tilde{\mathbf{B}}(\theta_1,\theta_2,\ .\ .\ .\ ,\theta_{3n-7})]^T\cdot\begin{bmatrix}\partial/\partial\theta_1\\ \partial/\partial\theta_2\\ \partial/\partial\theta_3\\ \partial/\partial\theta_4\\ \partial/\partial\theta_5\\ \partial/\partial\theta_6\\ \partial/\partial\theta_7\\ \partial/\partial\theta_8\\ \partial/\partial\theta_9\\ \vdots\\ \partial/\partial\theta_{3n-8}\\ \partial/\partial\theta_{3n-7}\\ \partial/\partial\theta_{3n-6}\end{bmatrix} \tag{19a}$$

where the $(3n-6)$-dimensional matrix $[\tilde{\mathbf{B}}(\theta_1,\theta_2,\ldots,\ \theta_{3n-7})]^T$ actually is

$$\begin{bmatrix} \Omega^{-1} & 0 & 0 & \cdots & 0 \\ -\Phi\cdot D_4^T\cdot\Xi^T & \Phi\cdot A_{44}^T & 0 & \cdots & 0 \\ -\Phi\cdot D_5^T\cdot\Xi^T & \Phi\cdot A_{45}^T & \Phi\cdot A_{55}^T & \cdots & 0 \\ \vdots & & & \ddots & \vdots \\ -\Phi\cdot D_n^T\cdot\Xi^T & \Phi\cdot A_{4n}^T & \Phi\cdot A_{5n}^T & \cdots & \Phi\cdot A_{nn}^T \end{bmatrix} .$$

All blocks, and all matrices in the blocks, are still 3×3 matrices. $\tilde{\mathbf{B}}(\theta_1,\theta_2,\ldots,\theta_{3n-7})$ appears, in the expression of $\mathbf{B}(\mathbf{q})$, the overall matrix transforming the momenta into quasimomenta, as follows:

$$\mathbf{B}(\mathbf{q})_{3n\times 3n}=\begin{bmatrix} \mathbf{1}_{3\times 3} & \mathbf{0}_{3\times(3n-6)} & \mathbf{0}_{3\times 3} \\ \mathbf{0}_{(3n-6)\times 3} & \tilde{\mathbf{B}}(\theta_1,\theta_2,\ldots,\theta_{3n-7})_{(3n-6)\times(3n-6)} & \mathbf{0}_{(3n-6)\times 3} \\ \mathbf{0}_{3\times 3} & \mathbf{0}_{3\times(3n-6)} & \Omega^{-1}(\gamma,\beta)_{3\times 3} \end{bmatrix} . \quad (19b)$$

This corresponds to the fact that (i) the operators in the left-hand column vector of Eq. (19a) are actually the quasimomentum operators to be used, (ii) the 3×3 unit matrix in the upper left corner of $\mathbf{B}(\mathbf{q})$ in Eq. (19b) is for $\hat{p}_\rho=-i\hbar\partial/\partial\rho$, $\hat{p}_\theta=-i\hbar\partial/\partial\theta$, and $\hat{p}_\phi=-i\hbar\partial/\partial\phi$, which are unaffected by the transformation, and (iii) $\Omega^{-1}(\gamma,\beta)$ in the lower right corner is for the overall-rotation angular-momentum vector operator definition.

In the present article, Ω replaces ω^* of I. Ω^{-1} is equal to

$$\Omega^{-1}(\theta_1,\theta_2)=\begin{bmatrix} -\sin\theta_1\cot\theta_2 & \cos\theta_1 & \dfrac{\sin\theta_1}{\sin\theta_2} \\ -\cos\theta_1\cot\theta_2 & -\sin\theta_1 & \dfrac{\cos\theta_1}{\sin\theta_2} \\ 1 & 0 & 0 \end{bmatrix} . \quad (20)$$

This matrix stands for the transformation of angular (quasi) velocities into angular (quasi) momenta, namely,

$$\begin{bmatrix} \hat{K}_x \\ \hat{K}_y \\ \hat{K}_z \end{bmatrix}=-i\hbar\Omega^{-1}(\theta_1,\theta_2)\cdot\begin{bmatrix} \partial/\partial\theta_1 \\ \partial/\partial\theta_2 \\ \partial/\partial\theta_3 \end{bmatrix} \quad (21a)$$

as well as

$$\begin{bmatrix} \hat{J}_x \\ \hat{J}_y \\ \hat{J}_z \end{bmatrix}=-i\hbar\Omega^{-1}(\gamma,\beta)\cdot\begin{bmatrix} \partial/\partial\gamma \\ \partial/\partial\beta \\ \partial/\partial\alpha \end{bmatrix} . \quad (21b)$$

$\hat{\mathbf{K}}$ is the so-called pseudo-angular-momentum vector operator (see Refs. [20] and I), which concerns the internal motion of the system (the hyperangles θ_1, θ_2, and θ_3 are actually internal coordinates), whereas $\hat{\mathbf{J}}$ is the usual total-angular-momentum operator for the overall rotation of the system (Eulerian angles α, β, and γ). This results in

$$\hat{J}_z=-i\hbar\frac{\partial}{\partial\gamma} , \quad (22a)$$

$$\hat{\mathbf{J}}^2=-\hbar^2\left[\frac{1}{\sin^2\beta}\left[\frac{\partial^2}{\partial\gamma^2}+\frac{\partial^2}{\partial\alpha^2}-2\cos\beta\frac{\partial^2}{\partial\gamma\partial\alpha}\right]+\frac{\partial^2}{\partial\beta^2}+\cot\beta\frac{\partial}{\partial\beta}\right] \quad (22b)$$

and similar expressions for $\hat{\mathbf{K}}$, by substituting θ_1, θ_2, and θ_3 for γ, β, and α.

In addition, according to I, Eq. (19a) must be read with

$$\Phi(\theta_1,\theta_2,\theta_3)=\begin{bmatrix} \cos\theta_1\cos\theta_3-\sin\theta_1\cos\theta_2\sin\theta_3 & \cos\theta_1\sin\theta_3+\sin\theta_1\cos\theta_2\cos\theta_3 & \sin\theta_1\sin\theta_2 \\ -\sin\theta_1\cos\theta_3-\cos\theta_1\cos\theta_2\sin\theta_3 & -\sin\theta_1\sin\theta_3+\cos\theta_1\cos\theta_2\cos\theta_3 & \cos\theta_1\sin\theta_2 \\ \sin\theta_2\sin\theta_3 & -\sin\theta_2\cos\theta_3 & \cos\theta_2 \end{bmatrix} , \quad (23)$$

$$\Xi^T(\theta_2,\theta_3)=\Phi^T(\theta_1,\theta_2,\theta_3)\cdot\Omega^{-1}(\theta_1,\theta_2)$$

$$=\begin{bmatrix} \dfrac{\sin\theta_3}{\sin\theta_2} & \cos\theta_3 & -\cot\theta_2\sin\theta_3 \\ -\dfrac{\cos\theta_3}{\sin\theta_2} & \sin\theta_3 & \cot\theta_2\cos\theta_3 \\ 0 & 0 & 1 \end{bmatrix} , \quad (24)$$

$$
\begin{aligned}
&\mathbf{A}_{ff}(\theta_4,\theta_5,\ldots,\theta_{3f-7})\\
&=(-1)^{f+1}\begin{pmatrix}
\displaystyle\sum_{f'=4}^{f-1}\Gamma^{3,f'}_{3f'-6}\left[\frac{\Gamma^{f',f}_{3f'-8}}{\sin\theta_{3f'-7}}+\cot\theta_{3f'-7}\sum_{f''=f'+1}^{f-1}\Gamma^{f',f''}_{3f''-7}\Gamma^{f'',f}_{3f''-8}\right] & \displaystyle\sum_{f'=4}^{f-1}\Gamma^{3,f'}_{3f'-7}\Gamma^{f',f}_{3f'-8} & \dfrac{1}{\prod_{j=4}^{f-1}\sin\theta_{3j-8}}\\
\dfrac{1}{\sin\theta_{3f-8}}\displaystyle\sum_{f'=4}^{f-1}\Gamma^{3,f'}_{3f'-6}\Gamma^{f',f}_{3f'-7} & \dfrac{1}{\sin\theta_{3f-8}\prod_{j=4}^{f-1}\sin\theta_{3j-7}} & 0\\
\dfrac{1}{\sin\theta_{3f-8}\sin\theta_{3f-7}\prod_{j=4}^{f-1}\sin\theta_{3j-6}} & 0 & 0
\end{pmatrix}
\end{aligned}
$$

$$(4\le f\le n)\ , \qquad (25a)$$

$$
\begin{aligned}
&\mathbf{A}_{f'f}(\theta_4,\theta_5,\ldots,\theta_{3f-7})\\
&=(-1)^{f+1}\\
&\begin{pmatrix}
-\Gamma^{f',f}_{3f-8}\left[\dfrac{\Gamma^{3,f'}_{3f'-6}}{\sin\theta_{3f'-7}}+\cot\theta_{3f'-7}\displaystyle\sum_{f''=4}^{f'-1}\Gamma^{3,f''}_{3f''-6}\Gamma^{f'',f'}_{3f''-7}\right] & -\Gamma^{3,f'}_{3f'-7}\Gamma^{f',f}_{3f-8} & 0\\
\begin{aligned}&-\Gamma^{3,f'}_{3f'-6}\left[\dfrac{\Gamma^{f',f}_{3f-7}}{\sin\theta_{3f-8}}+\cot\theta_{3f-8}\displaystyle\sum_{f''=f'+1}^{f-1}\Gamma^{f',f''}_{3f''-7}\Gamma^{f'',f}_{3f''-8}\right.\\ &\qquad\left.+\cot\theta_{3f'-8}\Gamma^{f',f}_{3f-8}\displaystyle\sum_{f''=4}^{f'-1}\Gamma^{3,f''}_{3f''-6}\Gamma^{f'',f'}_{3f''-7}\right]\end{aligned} & \dfrac{\cot\theta_{3f'-8}\Gamma^{f',f}_{3f-8}}{\prod_{j=4}^{f-1}\sin\theta_{3j-7}} & 0\\
\begin{aligned}&\dfrac{\cot\theta_{3f'-7}}{\prod_{j=4}^{f'-1}\sin\theta_{3j-6}}\left[\dfrac{\Gamma^{f',f}_{3f-7}}{\sin\theta_{3f-8}}+\cot\theta_{3f-8}\displaystyle\sum_{f''=f'+1}^{f-1}\Gamma^{f',f''}_{3f''-7}\Gamma^{f'',f}_{3f''-8}\right.\\ &\qquad\left.+\dfrac{\cot\theta_{3f'-8}\Gamma^{f',f}_{3f-8}}{\sin\theta_{3f'-7}\prod_{j=4}^{f'-1}\sin\theta_{3j-6}}\right]\end{aligned} & 0 & 0
\end{pmatrix}
\end{aligned}
$$

$$(4\le f'<f\le n)\ , \qquad (25b)$$

i.e., all $\mathbf{A}$ matrices are 3×3 triangular matrices with respect to the second diagonal. Finally, the $\mathbf{D}$ matrices appearing in $\tilde{\mathbf{B}}$, Eq. (19a), are

$$\mathbf{D}_f(\theta_4,\theta_5,\ldots,\theta_{3f-7})=(-1)^f\begin{pmatrix}
0 & \Gamma^{3,f}_{3f-8} & 0\\
-\Gamma^{3,f}_{3f-8} & 0 & 0\\
\dfrac{\Gamma^{3,f}_{3f-7}}{\sin\theta_{3f-8}}+\cot\theta_{3f-8}\displaystyle\sum_{f'=4}^{f-1}\Gamma^{3,f'}_{3f'-7}\Gamma^{f',f}_{3f'-8} & 0 & 0
\end{pmatrix}\quad(4\le f\le n)\ . \qquad (26)$$

The following notation is used throughout:

$$\Gamma^{k,l}_{3f-i}=\frac{\cot\theta_{3f-i}}{\prod_{j=k+1}^{l-1}\sin\theta_{3j-i}}\quad(k\le l-2) \qquad (27)$$

in keeping with the convention that, in the denominator $\prod_{j=k+1}^{l-1}$ (argument) is 1 if $k=l-1$, whatever the argument is.

Let us come back to the quantization problem. Since (i) $\mathbf{B}$ is block triangular [see Eqs. (19)], and (ii) $\mathbf{\Phi}$ is an orthogonal matrix, we have

$$t^{-1}=\mathrm{Det}\mathbf{\Omega}^{-1}(\theta_1,\theta_2)\mathrm{Det}\,\mathbf{A}_{44}\cdots\mathrm{Det}\,\mathbf{A}_{nn}\mathrm{Det}\mathbf{\Omega}^{-1}(\gamma,\beta)\ . \qquad (28a)$$

Now

$$\text{Det}\,\mathbf{A}_{ff}=\frac{(-1)^f}{\sin\theta_{3f-7}\sin^2\theta_{3f-8}}\frac{1}{\sin\theta_{3f-9}\sin\theta_{3f-10}\sin\theta_{3f-11}\cdots\sin\theta_4}\quad (f>5)$$

and

$$\text{Det}\,\mathbf{A}_{44}=\frac{1}{\sin\theta_5\sin^2\theta_4}$$

so that

$$|t^{-1}|=\frac{1}{\sin\beta}\frac{1}{\sin\theta_2}\frac{1}{\sin\theta_{3n-7}\sin^2\theta_{3n-8}}$$
$$\times\frac{1}{\sin\theta_{3n-9}\sin^2\theta_{3n-10}\sin^3\theta_{3n-11}\cdots\sin^{n-5}\theta_9\sin^{n-4}\theta_8\sin^{n-3}\theta_7\sin^{n-4}\theta_6\sin^{n-3}\theta_5\sin^{n-2}\theta_4} \quad (28b)$$

and Eqs. (8) and (18) yield ($n\geq 3$)

$$[g(\mathbf{q})]^{-1/2}=\rho^{3n-1}\sin^n\theta\sin^{n-3}2\theta\cos2\phi\sin^{n-3}2\phi(4\cos^2\theta\cos2\theta+\sin^4\theta\sin^2 2\phi)$$
$$\times\sin\theta_2\sin^{n-2}\theta_4\sin^{n-3}\theta_5\sin^{n-4}\theta_6\sin^{n-3}\theta_7\sin^{n-4}\theta_8\sin^{n-5}\theta_9\cdots$$
$$\times\sin^3\theta_{3n-11}\sin^2\theta_{3n-10}\sin\theta_{3n-9}\sin^2\theta_{3n-8}\sin\theta_{3n-7}\sin\beta\,. \quad (29)$$

g clearly does not depend on θ_1, θ_3, θ_{3n-6}, γ, and α, whence, from Eq. (14b)

$$\Lambda^*_\rho=\frac{3n-1}{\rho}\,,$$
$$\Lambda^*_\theta=n\cot\theta+2(n-3)\cot2\theta-2\sin2\theta\frac{4\cos^2\theta+2\cos2\theta-\sin^2\theta\sin^2 2\phi}{4\cos^2\theta\cos2\theta+\sin^4\theta\sin^2 2\phi}\,,$$
$$\Lambda^*_\phi=2\left[(n-3)\cot2\phi-tn\,2\phi+\frac{\sin^4\theta\sin4\phi}{4\cos^2\theta\cos2\theta+\sin^4\theta\sin^2 2\phi}\right],$$
$$\Lambda^*_1=\Lambda^*_3=0\,,$$
$$\Lambda^*_2=\cot\theta_2\,, \quad (30)$$
$$\left.\begin{aligned}\Lambda^*_{3f-8}&=(n-f+2)\cot\theta_{3f-8}\\ \Lambda^*_{3f-7}&=(n-f+1)\cot\theta_{3f-7}\\ \Lambda^*_{3f-6}&=(n-f)\cot\theta_{3f-6}\end{aligned}\right\}(4\leq f\leq n)$$
$$\Lambda^*_\alpha=\Lambda^*_\gamma=0\,,$$
$$\Lambda^*_\beta=\cot\beta\,.$$

Now, for the Euclidean volume element of the configuration space,

$$d\tau_1=[g(\mathbf{q})]^{-1/2}d\rho\,d\theta\,d\phi\,d\theta_1 d\theta_2\cdots d\theta_{3n-6}d\gamma\,d\beta\,d\alpha\,,$$

if $n\geq 3$, i.e., for systems with four particles or more, the PAH Hamiltonian is written as

$$\hat{H}_1=\hat{T}_1+V(\rho,\theta,\phi,\theta_1,\theta_2,\ldots,\theta_{3n-6}) \quad (31a)$$

with the following kinetic energy operator:

$$2\hat{T}_1=-\hbar^2\left[\frac{\partial^2}{\partial\rho^2}+\frac{3n-1}{\rho}\frac{\partial}{\partial\rho}\right]+\frac{[\hat{\Lambda}^2_{3n-1}]_1}{\rho^2}=-\hbar^2\hat{\Delta}_{3n}\,, \quad (31b)$$

$\hat{\Delta}_{3n}$ being the Laplacian. $[\hat{\Lambda}^2_{3n-1}]_1$ is the so-called "grand-angular-momentum" operator, for the $(3n-1)$-dimensional hypersphere embedded into the $3n$-dimensional configuration space of the n mass-weighted Jacobi vectors describing the system, after separation of the center of mass. In applying the quantization rules given in Sec. II above, $[\hat{\Lambda}^2_{3n-1}]_1$ can be written as

$$[\hat{\Lambda}^2_{3n-1}]_1=-\hbar^2\left[\frac{\partial^2}{\partial\theta^2}+\Lambda^*_\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2}+\Lambda^*_\phi\frac{\partial}{\partial\phi}\right]\right]$$
$$+\sum_{g=x,y,z}\left[b_g(\hat{J}^2_g+\hat{K}^2_g)+2d_g\hat{J}_g\hat{K}_g+e_g\sum_{f=4}^{n}(\hat{N}^2_{gf}+C^*_{gf}\hat{N}_{gf})\right] \quad (31c)$$

where the b_g, d_g, and e_g's depend on θ and ϕ only [they are given in Eqs. (17b), (17c), and (17d), respectively], and

Λ_θ^* and Λ_ϕ^* are given in Eq. (30).

Obviously, the part of $\hat{T}_1$ that is linear in $\partial/\partial\theta_1, \ldots, \partial/\partial\theta_{3n-6}$, as it comes out of Eq. (12), i.e., the $\Gamma^L(\mathbf{q})$ coefficients in Eq. (13), has been entirely reexpressed in terms of the quasimomentum operators $\hat{\mathbf{K}}_g$ and $\hat{\mathbf{N}}_{gf}$ ($g=x,y,z$; $f=4,5,\ldots,n$), defined in Eq. (19a). All the difficulty was therefore concentrated on the derivation of the coefficients $C_{gf}^*(\mathbf{q})$. Long and tedious calculations (demonstration not given here) have yielded the following result:

$$\begin{bmatrix} C_{xf}^* \\ C_{yf}^* \\ C_{zf}^* \end{bmatrix} = (-1)^f i\hbar(n-f)\Phi(\theta_1,\theta_2,\theta_3)\cdot \begin{bmatrix} C_{xf}^\circ \\ C_{yf}^\circ \\ C_{zf}^\circ \end{bmatrix} \tag{32}$$

where the C_{gf}°'s depend on $\theta_4, \theta_5, \ldots, \theta_{3n-6}$, but are independent of n:

$$\begin{aligned} C_{xf}^\circ = &-\frac{1}{\sin\theta_{3f-8}}\left[\frac{\Gamma_{3f-6}^{3,f}}{\sin\theta_{3f-7}} + \cot\theta_{3f-7}\sum_{f'=4}^{f-1}\Gamma_{3f'-6}^{3,f'}\Gamma_{3f'-7}^{f',f}\right] \\ &+\cot\theta_{3f-8}\sum_{f'=4}^{f-1}\Gamma_{3f'-6}^{3,f'}\left[\frac{\Gamma_{3f'-8}^{f',f}}{\sin\theta_{3f'-7}} + \cot\theta_{3f'-7}\sum_{f''=f'+1}^{f-1}\Gamma_{3f''-7}^{f',f''}\Gamma_{3f''-8}^{f'',f}\right], \\ C_{yf}^\circ = &\frac{\Gamma_{3f-7}^{3,f}}{\sin\theta_{3f-8}} + \cot\theta_{3f-8}\sum_{f'=4}^{f-1}\Gamma_{3f'-7}^{3,f'}\Gamma_{3f'-8}^{f',f}, \\ C_{zf}^\circ = &\Gamma_{3f-8}^{3,f} \end{aligned} \tag{33}$$

with the convention that $\sum_{j=k+1}^{l-1}$ (argument) is 0 if $k=l-1$, whatever the argument is. The few first applications of the above formulas yield

$$C_{x4}^\circ = \frac{\cot\theta_6}{\sin\theta_4\sin\theta_5}, \quad C_{y4}^\circ = \frac{\cot\theta_5}{\sin\theta_4}, \quad C_{z4}^\circ = \cot\theta_4, \tag{34a}$$

$$\begin{aligned} C_{x5}^\circ &= \frac{\cot\theta_9}{\sin\theta_6\sin\theta_7\sin\theta_8} + \frac{\cot\theta_5\cot\theta_6\cot\theta_8}{\sin\theta_7} + \frac{\cot\theta_4\cot\theta_6\cot\theta_7}{\sin\theta_5}, \\ C_{y5}^\circ &= \frac{\cot\theta_8}{\sin\theta_5\sin\theta_7} + \cot\theta_4\cot\theta_5\cot\theta_7, \quad C_{z5}^\circ = \frac{\cot\theta_7}{\sin\theta_4}, \end{aligned} \tag{34b}$$

$$\begin{aligned} C_{x6}^\circ = &\frac{\cot\theta_{12}}{\sin\theta_6\sin\theta_9\sin\theta_{10}\sin\theta_{11}} + \left[\frac{\cot\theta_8\cot\theta_9}{\sin\theta_6} + \frac{\cot\theta_5\cot\theta_6}{\sin\theta_8}\right]\frac{\cot\theta_{11}}{\sin\theta_{10}} \\ &+ \left[\frac{\cot\theta_7\cot\theta_9}{\sin\theta_6\sin\theta_8} + \frac{\cot\theta_4\cot\theta_6}{\sin\theta_5\sin\theta_7}\right]\cot\theta_{10} + \cot\theta_5\cot\theta_6\cot\theta_7\cot\theta_8\cot\theta_{10}, \\ C_{y6}^\circ = &\frac{\cot\theta_{11}}{\sin\theta_5\sin\theta_8\sin\theta_{10}} + \left[\frac{\cot\theta_7\cot\theta_8}{\sin\theta_5} + \frac{\cot\theta_4\cot\theta_5}{\sin\theta_7}\right]\cot\theta_{10}, \\ C_{z6}^\circ = &\frac{\cot\theta_{10}}{\sin\theta_4\sin\theta_7} \end{aligned} \tag{34c}$$

thus allowing us to express the PAH Hamiltonian operator up to $n=7$, i.e., eight particles [recall that C_{g7}^* is identically zero if $n=7$, see Eq. (32)].

It should be emphasized here that all the effort so far has allowed us to write an exact quantum-mechanical expression of the Hamiltonian operator for any N-particle system described by means of a special set of curvilinear coordinates, the so-called PAH coordinates. Here the important word is "exact." Indeed, even if, in a few cases, this Hamiltonian operator can be used as such, it is not easy to manipulate just because the quasimomentum operators $\hat{\mathbf{N}}_{gf}$ ($g=x,y,z$; $f=4,5,\ldots,n$) defined in Eq. (19a) are themselves rather complicated expressions in terms of $\theta_1, \theta_2, \ldots, \theta_{3n-6}$. It is therefore very important to go on studying the algebraic properties of the operators $\hat{\mathbf{N}}_{gf}$, in order to derive a representation in which the matrix elements of the kinetic energy operator would be calculated in a rather straightforward manner, at least for the angular part $(\theta,\phi,\theta_1,\theta_2,\ldots,\theta_{3n-6},\gamma,\beta,\alpha)$ of the problem.

This aim we have not yet been able to reach in all generality. We have been able only to propose appropriate exact answers in the cases where $n=3$ and 4, i.e., for four and five particles. This preliminary approach will be developed in Sec. V below. Before doing it, it is worthwhile proposing a change of the normalization convention for the wave function that significantly simplifies the expression of the PAH Hamiltonian operator.

IV. ALTERNATIVE CONVENTION OF NORMALIZATION OF THE WAVE FUNCTION, AND SIMPLIFIED EXPRESSION OF THE PAH HAMILTONIAN OPERATOR

Up to now, the wave functions $\Psi_1(\mathbf{q})$ onto which the Hamiltonian $\hat{H}_1$ operates, are supposed to be normalized with the help of the Euclidean volume element, expressed as

$$d\tau_1 = dx^1dy^1dz^1 \cdots dx^ndy^ndz^n = [g(\mathbf{q})]^{-1/2}d\mathbf{q} \ , \tag{35a}$$

$$d\mathbf{q} = d\rho\, d\theta\, d\phi\, d\theta_1 d\theta_2 \cdots d\theta_{3n-6}d\gamma\, d\beta\, d\alpha \tag{35b}$$

where (x^i,y^i,z^i) denote the mass-weighted Cartesian components of the ith Jacobi vector in the principal-axis system. $[g(\mathbf{q})]^{-1/2}$ is given in Eq. (29).

The quantities that are physically relevant are (i) the norm:

$$1 = \int [\Psi_1(\mathbf{q})]^*\Psi_1(\mathbf{q})d\tau_1 \ ; \tag{36a}$$

(ii) the spectrum of the eigenvalues:

$$\hat{H}_1\Psi_1(\mathbf{q}) = E\Psi_1(\mathbf{q}) \ ; \tag{36b}$$

(iii) the matrix elements:

$$H_{12} = \int [\Psi_1(\mathbf{q})]_1^*\{\hat{H}_1[\Psi_1(\mathbf{q})]_2\}d\tau_1 \ . \tag{36c}$$

If we change the wave function according to

$$\Psi_\xi(\mathbf{q}) = [\xi(\mathbf{q})]^{1/2}\Psi_1(\mathbf{q}) \tag{37}$$

where $\xi(\mathbf{q})$ is any real function different from zero, except (possibly) on sets of measure zero, we preserve (i) the norm, in changing the volume element, i.e.,

$$1 = \int [\Psi_\xi(\mathbf{q})]^*\Psi_\xi(\mathbf{q})d\tau_\xi \ ;$$

if, and only if

$$d\tau_\xi = [\xi(\mathbf{q})]^{-1}[g(\mathbf{q})]^{-1/2}d\mathbf{q} \ , \tag{38a}$$

(ii) the spectrum, in changing the Hamiltonian operator, i.e.,

$$\hat{H}_\xi\Psi_\xi(\mathbf{q}) = E\Psi_\xi(\mathbf{q}) \ ;$$

if, and only if

$$\hat{H}_\xi = [\xi(\mathbf{q})]^{1/2}\hat{H}_1[\xi(\mathbf{q})]^{-1/2} \ , \tag{38b}$$

(iii) the matrix elements, i.e.,

$$H_{12} = \int [\Psi_\xi(\mathbf{q})]_1^*\{\hat{H}_\xi[\Psi_\xi(\mathbf{q})]_2\}d\tau_\xi \ . \tag{38c}$$

$\hat{H}_1$ being the sum of the potential energy function $V(\mathbf{q})$, which is a multiplicative operator, and of the kinetic energy operator $\hat{T}_1$ which is purely differential (recall that it is proportional to the Laplacian), an extra potential term appears in the expression of $\hat{T}_\xi$, i.e., a nondifferential term, namely [18],

$$\mathcal{V}_\xi(\mathbf{q}) = ([\xi(\mathbf{q})]^{1/2}\hat{T}_1[\xi(\mathbf{q})]^{-1/2}) \ .$$

More explicitly, if we rewrite $\hat{H}_1$ in the form [see Eq. (12) with no quasimomenta]

$$\hat{H}_1 = -\frac{\hbar^2}{2}\sum_{i=1}^{m}\left[\sum_{j=1}^{m} g^{ij}(\mathbf{q})\frac{\partial^2}{\partial q^i\partial q^j} + \Gamma_1^i(\mathbf{q})\frac{\partial}{\partial q^i}\right] + V(\mathbf{q}) \tag{39}$$

then we have for $\hat{H}_\xi$

$$\hat{H}_\xi = -\frac{\hbar^2}{2}\sum_{i=1}^{m}\left[\sum_{j=1}^{m} g^{ij}(\mathbf{q})\frac{\partial^2}{\partial q^i\partial q^j} + \Gamma_\xi^i(\mathbf{q})\frac{\partial}{\partial q^i}\right] + \mathcal{V}_\xi(\mathbf{q}) + V(\mathbf{q}) \tag{40a}$$

where

$$\Gamma_\xi^i(\mathbf{q}) = \Gamma_1^i(\mathbf{q}) - \sum_{j=1}^{m} g^{ij}(\mathbf{q})\xi_j(\mathbf{q}) \ , \tag{40b}$$

$$\mathcal{V}_\xi(\mathbf{q}) = -\frac{\hbar^2}{4}\sum_{i=1}^{m}\left[-\Gamma_1^i(\mathbf{q})\xi_j(\mathbf{q}) + \sum_{j=1}^{m} g^{ij}(\mathbf{q})[\tfrac{3}{2}\xi_i(\mathbf{q})\xi_j(\mathbf{q}) - \xi_{ij}(\mathbf{q})]\right] . \tag{40c}$$

$\xi_i(\mathbf{q}) = [1/\xi(\mathbf{q})]\partial\xi(\mathbf{q})/\partial q^i$ and $\xi_{ij}(\mathbf{q}) = [1/\xi(\mathbf{q})]\partial^2\xi(\mathbf{q})/\partial q^i\partial q^j$ are, respectively, logarithmic first and second derivatives of $\xi(\mathbf{q})$.

Let us apply this transformation to the particular PAH coordinate problem, with [see Eq. (29) for comparison]

$$d\tau_\xi = \sin\theta\sin\theta_2\sin^{n-2}\theta_4\sin^{n-3}\theta_5\sin^{n-4}\theta_6\sin^{n-3}\theta_7 \times\sin^{n-4}\theta_8\sin^{n-5}\theta_9\cdots\sin^2\theta_{3n-8}\sin\theta_{3n-7} \times\sin\beta\, d\rho\, d\theta\, d\phi\, d\theta_1 d\theta_2\cdots d\theta_{3n-6}d\gamma\, d\beta\, d\alpha \tag{41a}$$

or still

$$\xi(\rho,\theta,\phi) = \rho^{3n-1}\sin^{n-1}\theta\sin^{n-3}2\theta\cos2\phi\sin^{n-3}2\phi \times(4\cos^2\theta\cos2\theta + \sin^4\theta\sin^2 2\phi) \ . \tag{41b}$$

Then we have

$$\xi_\rho = \frac{3n-1}{\rho}, \quad \xi_\theta = \Lambda_\theta^* - \cot\theta, \quad \xi_\phi = \Lambda_\phi^* \ ,$$

$$\xi_{\rho\rho} = \frac{(3n-1)(3n-2)}{\rho^2} \ ,$$

$$\xi_{\theta\theta} = (\Lambda_\theta^* - \cot\theta)^2 + \frac{1}{\sin^2\theta} + \frac{\partial\Lambda_\theta^*}{\partial\theta} \ ,$$

and

$$\xi_{\phi\phi} = (\Lambda_\phi^*)^2 + \frac{\partial\Lambda_\phi^*}{\partial\phi} \ ,$$

so that

$$2\hat{T}_\xi = -\hbar^2\frac{\partial^2}{\partial\rho^2} + \frac{[\hat{\Lambda}_{3n-1}^2]_\xi}{\rho^2} + 2\mathcal{V}_\xi(\rho,\theta,\phi) \tag{42a}$$

where

$$[\hat{\Lambda}^2_{3n-1}]_\xi=\hat{\mathcal{L}}^2(\theta,\phi)+\sum_{g=x,y,z}\left[b_g(\theta,\phi)(\hat{J}^2_g+\hat{K}^2_g)+2d_g(\theta,\phi)\hat{\mathbf{J}}_g\hat{\mathbf{K}}_g+e_g(\theta,\phi)\sum_{f=4}^{n}(\hat{N}^2_{gf}+C^*_{gf}\hat{N}_{gf})\right] \tag{42b}$$

and

$$\hat{\mathcal{L}}^2(\theta,\phi)=-\hbar^2\left[\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{42c}$$

is the regular angular-momentum operator in spherical coordinates, whose eigenvalues are $\hbar^2 l(l+1)$ and eigenfunctions are the spherical harmonics $\mathcal{Y}^m_l(\theta,\phi)$. In classical mechanics, θ and ϕ are spherical angles parametrizing the system gyration radii, see I, Fig. 1 and Eq. (31), so that $\theta\in[0,\pi/2]$ and $\phi\in[0,\pi/2]$. In quantum mechanics, the Hamiltonian operator must be invariant, not only by translation and rotation, but also by inversion of the momenta and the positions [with respect to the center of mass, i.e., in the body-fixed (BF) frame], and finally by permutation of the positions of identical particles [21]. The group of the Hamiltonian is the direct product of the groups to which the transformations above belong. For deformable systems, the point-group irreducible representations are no longer adequate symmetry labels; permutation-inversion groups must be used (whose point groups are subgroups), so as to appropriately describe the interferences between equivalent permuted structures [21,22]. In the present case, this can be achieved in extending the domain of definition in (θ,ϕ) to $\theta\in[0,\pi]$ and $\phi\in[0,2\pi]$ [20]. Therefore the $\mathcal{Y}^m_l(\theta,\phi)$ are regular spherical harmonics.

In addition, the following extra potential term appears:

$$\mathcal{V}_\xi(\rho,\theta,\phi)=\frac{\hbar^2}{8\rho^2}\left[(3n-1)(3n-5)+F_\theta(\theta,\phi)+\frac{F_\phi(\theta,\phi)}{\sin^2\theta}\right] \tag{43a}$$

where

$$F_\iota(\theta,\phi)=1+(\Lambda^*_\iota)^2+2\frac{\partial\Lambda^*_\iota}{\partial\iota}\quad(\iota=\theta,\phi)\ . \tag{43b}$$

The physical meaning of the extra potential term is the following. By playing the role of a potential although being of kinetic origin, the extra potential term $\mathcal{V}_\xi$ sets up (virtual) energy barriers that prevent the wave function Ψ_ξ from expanding over certain regions of the configuration space. This counterbalances the absence of the Euclidean weight function $[g(\mathbf{q})]^{-1/2}$ on those regions where it is zero or very small. In particular, Ψ_ξ is strictly zero in all those regions of the configuration space (of measure zero), where singularities arise (for example, when the molecule becomes linear or planar). This is a confirmation of the convergence of the matrix elements of the kinetic energy operator as integrals, which is physically necessary since a particular conformation of the system (e.g., linear or coplanar) is *a priori* not singular. For further details on the domain of definition in θ and ϕ, and the particular configurations of the system, see Appendix A.

V. GENERALIZED ANGULAR-MOMENTUM OPERATORS: FOUR- AND FIVE-PARTICLE SYSTEMS

Equation (19a) can be rewritten as follows:

$$\begin{bmatrix}\hat{K}_x\\ \hat{K}_y\\ \hat{K}_z\end{bmatrix}=-i\hbar\mathbf{\Omega}^{-1}(\theta_1,\theta_2)\cdot\begin{bmatrix}\partial/\partial\theta_1\\ \partial/\partial\theta_2\\ \partial/\partial\theta_3\end{bmatrix} \tag{44}$$

on the one hand, and on the other hand

$$\begin{bmatrix}\hat{N}_{xf}\\ \hat{N}_{yf}\\ \hat{N}_{zf}\end{bmatrix}=-i\hbar\mathbf{\Phi}(\theta_1,\theta_2,\theta_3)\cdot\left[-\mathbf{D}^T_f(\theta_4,\theta_5,\ldots,\theta_{3f-7})\cdot\mathbf{\Xi}^T(\theta_2,\theta_3)\begin{bmatrix}\partial/\partial\theta_1\\ \partial/\partial\theta_2\\ \partial/\partial\theta_3\end{bmatrix}+\sum_{f'=4}^{f}\mathbf{A}^T_{f'f}(\theta_4,\theta_5,\ldots,\theta_{3f-7})\cdot\begin{bmatrix}\partial/\partial\theta_{3f'-8}\\ \partial/\partial\theta_{3f'-7}\\ \partial/\partial\theta_{3f'-6}\end{bmatrix}\right]\quad(4\le f\le n) \tag{45}$$

where the 3×3 matrices $\mathbf{D}^T_f$ and $\mathbf{A}^T_{f'f}$ $(4\le f'\le f\le n)$ are given in Eqs. (26) and (25), respectively.

A. Four particles [20]

In the case of four particles, $n=3$, Eq. (42b) is

$$[\hat{\Lambda}^2_8]_\xi=\hat{\mathcal{L}}^2(\theta,\phi)+\sum_{g=x,y,z}[b_g(\theta,\phi)(\hat{J}^2_g+\hat{K}^2_g)+2d_g(\theta,\phi)\hat{J}_g\hat{K}_g]\ . \tag{46}$$

Here, all the operators are well known, along with appropriate standard representations: (i) $\hat{\mathcal{L}}^2$ operates on θ and ϕ:

$$\hat{\mathcal{L}}^2|l,m\rangle=\hbar^2 l(l+1)|l,m\rangle \tag{47}$$

where l is a positive or zero integer, m a degeneracy integer index, $m \in [-l, +l]$, and $\langle \theta,\phi | l,m \rangle = \mathcal{Y}_l^m(\theta,\phi)$ are spherical harmonics; (ii) $\hat{\mathbf{K}}$ operates on θ_1, θ_2, and θ_3. It is the so-called "pseudo-angular-momentum" vector operator [20], which concerns internal deformation properties. Being algebraically an angular-momentum vector operator, there is for it the usual standard representation $\{|K,k\rangle\}$ such that [23,24]

$$\begin{aligned}
&\hat{\mathbf{K}}^2|K,k\rangle = \hbar^2 K(K+1)|K,k\rangle ,\\
&\hat{\mathbf{K}}_z|K,k\rangle = \hbar k|K,k\rangle ,\\
&\hat{\mathbf{K}}_+|K,k\rangle = (\hat{\mathbf{K}}_x + i\hat{\mathbf{K}}_y)|K,k\rangle = \hbar\sqrt{K(K+1)-k(k-1)}|K,k-1\rangle ,\\
&\hat{\mathbf{K}}_-|K,k\rangle = (\hat{\mathbf{K}}_x - i\hat{\mathbf{K}}_y)|K,k\rangle = \hbar\sqrt{K(K+1)-k(k+1)}|K,k+1\rangle
\end{aligned} \tag{48}$$

where K is a positive or zero integer, $k \in [-K, +K]$, and $\langle \theta_1,\theta_2,\theta_3 | K,k\rangle = \mathcal{D}_K^{pk}(\theta_3,\theta_2,\theta_1)$ denotes a Wigner matrix element (for the kinetic energy, and for it only, p is an integer degeneracy index); (iii) $\hat{\mathbf{J}}$ operates on γ, β, and α. It is the rotational angular-momentum vector operator, with the standard representation $\{|J,j\rangle\}$ such that

$$\begin{aligned}
&\hat{\mathbf{J}}^2|J,j\rangle = \hbar^2 J(J+1)|J,j\rangle ,\\
&\hat{\mathbf{J}}_z|J,j\rangle = \hbar j|J,j\rangle ,\\
&\hat{J}_+|J,j\rangle = [\hat{\mathbf{J}}_x + i\hat{\mathbf{J}}_y]|J,j\rangle = \hbar\sqrt{J(J+1)-j(j-1)}|J,j-1\rangle ,\\
&\hat{\mathbf{J}}_-|J,j\rangle = \{\hat{\mathbf{J}}_x - i\hat{\mathbf{J}}_y\}|J,j\rangle = \hbar\sqrt{J(J+1)-j(j+1)}|J,j+1\rangle
\end{aligned} \tag{49}$$

where J is a positive or zero integer, $j \in [-J, +J]$, and $\langle \gamma,\beta,\alpha | J,j\rangle = \mathcal{D}_J^{rj}(\alpha,\beta,\gamma)$. r is a degeneracy index, denoting the space-fixed Z component of $\mathbf{J}$, which is physically immaterial because of space isotropy.

With the help of the operators defined above, Eq. (46) can be rewritten in the form

$$\begin{aligned}
[\hat{\Lambda}_8^2]_\xi = \hat{\mathcal{L}}^2 + \frac{b_x+b_y}{2}(\hat{\mathbf{J}}^2+\hat{\mathbf{K}}^2) + \left[b_z - \frac{b_x+b_y}{2}\right](\hat{J}_z^2+\hat{K}_z^2) + \frac{b_x-b_y}{4}(\hat{J}_+^2+\hat{J}_-^2+\hat{K}_+^2+\hat{K}_-^2) + 2d_z\hat{J}_z\hat{K}_z \\
+ \frac{d_x+d_y}{2}(\hat{\mathbf{J}}_+\hat{\mathbf{K}}_- + \hat{\mathbf{J}}_-\hat{\mathbf{K}}_+) + \frac{d_x-d_y}{2}(\hat{\mathbf{J}}_+\hat{\mathbf{K}}_+ + \hat{\mathbf{J}}_-\hat{\mathbf{K}}_-) .
\end{aligned} \tag{50}$$

The following equation is readily derived from Eqs. (47)–(50):

$$\begin{aligned}
\hbar^{-2}[\hat{\Lambda}_8^2]_\xi|l,m,K,k,J,j\rangle = \Bigg[& l(l+1) + \frac{b_x+b_y}{2}[K(K+1)+J(J+1)] \\
& + \left[b_z - \frac{b_x+b_y}{2}\right](j^2+k^2) + 2d_z kj \Bigg] |l,m,K,k,J,j\rangle \\
& + \frac{b_x-b_y}{4}\{ \sqrt{[K(K+1)-k(k+1)][K(K+1)-(k+1)(k+2)]}|l,m,K,k+2,J,j\rangle \\
& + \sqrt{[K(K+1)-k(k-1)][K(K+1)-(k-1)(k-2)]} \\
& \quad \times |l,m,K,k-2,J,j\rangle \\
& + \sqrt{[J(J+1)-j(j+1)][J(J+1)-(j+1)(j+2)]} \\
& \quad \times |l,m,K,k,J,j+2\rangle \\
& + \sqrt{[J(J+1)-j(j-1)][J(J+1)-(j-1)(j-2)]} \\
& \quad \times |l,m,K,k,J,j-2\rangle \} \\
& + \frac{d_x+d_y}{2}[\sqrt{(K-k)(K+k+1)(J+j)(J-j+1)}|l,m,K,k+1,J,j-1\rangle \\
& + \sqrt{(K+k)(K-k+1)(J-j)(J+j+1)}|l,m,K,k-1,J,j+1\rangle] \\
& + \frac{d_x-d_y}{2}[\sqrt{(K-k)(K+k+1)(J-j)(J+j+1)}|l,m,K,k+1,J,j+1\rangle \\
& \qquad + \sqrt{(K+k)(K-k+1)(J+j)(J-j+1)}|l,m,K,k-1,J,j-1\rangle] .
\end{aligned} \tag{51}$$

After integration over all the angles, we obtain

$$
\begin{aligned}
&\hbar^{-2}\langle l',m',K',k',J',j'|[\hat{\Lambda}_8^2]_\xi|l,m,K,k,J,j\rangle \\
&=\delta_{K'K}\delta_{J'J}\Bigg\{\Bigg[l(l+1)\delta_{m'm}\delta_{l'l}+\frac{b_x^{l'lm'm}+b_y^{l'lm'm}}{2}[K(K+1)+J(J+1)] \\
&\quad+\left[b_z^{l'lm'm}-\frac{b_x^{l'lm'm}+b_y^{l'lm'm}}{2}\right](k^2+j^2)+2d_z^{l'lm'm}kj\Bigg]\delta_{k'k}\delta_{j'j} \\
&\quad+\frac{b_x^{l'lm'm}-b_y^{l'lm'm}}{4}\{[\sqrt{(K+k+2)(K+k+1)(K-k)(K-k-1)}\delta_{k'k+2} \\
&\qquad+\sqrt{(K+k)(K+k-1)(K-k+2)(K-k+1)}\delta_{k'k-2}]\delta_{j'j} \\
&\qquad+[\sqrt{(J+j+2)(J+j+1)(J-j)(J-j-1)}\delta_{j'j+2} \\
&\qquad+\sqrt{(J+j)(J+j-1)(J-j+2)(J-j+1)}\delta_{j'j-2}]\delta_{k'k}\} \\
&\quad+\frac{d_x^{l'lm'm}+d_y^{l'lm'm}}{2}[\sqrt{(K-k)(K+k+1)(J+j)(J-j+1)}\delta_{k'k+1}\delta_{j'j-1} \\
&\qquad+\sqrt{(K+k)(K-k+1)(J-j)(J+j+1)}\delta_{k'k-1}\delta_{j'j+1}] \\
&\quad+\frac{d_x^{l'lm'm}-d_y^{l'lm'm}}{2}[\sqrt{(K-k)(K+k+1)(J-j)(J+j+1)}\delta_{k'k+1}\delta_{j'j+1} \\
&\qquad+\sqrt{(K+k)(K-k+1)(J+j)(J-j+1)}\delta_{k'k-1}\delta_{j'j-1}]\Bigg\}
\end{aligned}
\tag{52}
$$

where

$$b_g^{l'lm'm}=\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\, d\theta[\mathcal{Y}_{l'}^{m'}(\theta,\phi)]^* \times b_g(\theta,\phi)\mathcal{Y}_l^m(\theta,\phi)\quad (g=x,y,z)\ ,$$

and the same for $d_g^{l'lm'm}$. The matrix representing $[\hat{\Lambda}_8^2]_\xi$ is therefore *diagonal in K and J*. As far as the quantum numbers k and j are concerned, the only *nonzero* coupling matrix elements are (i) $kj\leftrightarrow kj$ (i.e., diagonal), (ii) $kj\leftrightarrow k\pm 2j$ and $kj\leftrightarrow kj\pm 2$, (iii) $kj\leftrightarrow k\pm 1j\mp 1$, and (iv) $kj\leftrightarrow k\pm 1j\pm 1$. This indicates that the matrix has a block structure, with only few blocks that are not identically zero (see Fig. 1). Each block $kj\leftrightarrow k'j'$ which is not identically zero is *a priori* a full matrix (with indices lm and $l'm'$ for the rows and the columns). Indeed, all the integrals $b_g^{l'lm'm}$ and $d_g^{l'lm'm}$ are *a priori* nonzero, i.e., all couplings $lm\leftrightarrow l'm'$ can be effective.

See Appendix B for the radial close-coupled equations.

B. Five particles

For five particles, $n=4$, we have [see Eqs. (42b) and (46), and recall that C_{g4}^* is then identically zero]

$$[\hat{\Lambda}_{11}^2]_\xi=[\hat{\Lambda}_8^2]_\xi+\sum_{g=x,y,z}e_g(\theta,\phi)\hat{N}_{g4}^2 \tag{53}$$

where, from Eqs. (45)

$$\begin{pmatrix}\hat{N}_{x4}\\ \hat{N}_{y4}\\ \hat{N}_{z4}\end{pmatrix}=-i\hbar\Phi(\theta_1,\theta_2,\theta_3)\cdot\begin{pmatrix}\hat{n}_{x4}\\ \hat{n}_{y4}\\ \hat{n}_{z4}\end{pmatrix} \tag{54a}$$

and

$$
\begin{aligned}
\hat{n}_{x4}&=-\cot\theta_4\left[\frac{\cos\theta_3}{\sin\theta_2}\frac{\partial}{\partial\theta_1}-\sin\theta_3\frac{\partial}{\partial\theta_2}-\cot\theta_2\cos\theta_3\frac{\partial}{\partial\theta_3}\right]-\frac{\cot\theta_5}{\sin\theta_4}\frac{\partial}{\partial\theta_3}-\frac{1}{\sin\theta_4\sin\theta_5}\frac{\partial}{\partial\theta_6}\ ,\\
\hat{n}_{y4}&=-\cot\theta_4\left[\frac{\sin\theta_3}{\sin\theta_2}\frac{\partial}{\partial\theta_1}+\cos\theta_3\frac{\partial}{\partial\theta_2}-\cot\theta_2\sin\theta_3\frac{\partial}{\partial\theta_3}\right]-\frac{1}{\sin\theta_4}\frac{\partial}{\partial\theta_5}\ ,\\
\hat{n}_{z4}&=-\frac{\partial}{\partial\theta_4}\ .
\end{aligned}
\tag{54b}
$$

It is easy to check that

$$[\hat{n}_{x4},\hat{n}_{y4}]=-\frac{\cot\theta_5}{\sin\theta_4}\hat{n}_{x4}+\frac{\partial}{\partial\theta_3}\ ,$$

$$[\hat{n}_{z4},\hat{n}_{x4}]=\cot\theta_4\hat{n}_{x4}-\left[\frac{\cos\theta_3}{\sin\theta_2}\frac{\partial}{\partial\theta_1}-\sin\theta_3\frac{\partial}{\partial\theta_2}-\cot\theta_2\cos\theta_3\frac{\partial}{\partial\theta_3}\right]\ , \tag{55}$$

$$[\hat{n}_{y4},\hat{n}_{z4}]=-\cot\theta_4\hat{n}_{y4}+\left[\frac{\sin\theta_3}{\sin\theta_2}\frac{\partial}{\partial\theta_1}+\cos\theta_3\frac{\partial}{\partial\theta_2}-\cot\theta_2\sin\theta_3\frac{\partial}{\partial\theta_3}\right]\ .$$

Now, with the help of relations of the type

$$\Phi_{xx}\Phi_{yy}-\Phi_{xy}\Phi_{yx}=\Phi_{zz},\quad \Phi_{yx}\Phi_{zz}-\Phi_{yz}\Phi_{zx}=-\Phi_{xy},\ldots,$$

$$(\hat{n}_{x4}\Phi_{yx})=\cot\theta_4\Phi_{yz}+\frac{\cot\theta_5}{\sin\theta_4}\Phi_{yy},\quad (\hat{n}_{x4}\Phi_{zy})=-\frac{\cot\theta_5}{\sin\theta_4}\Phi_{zx},\quad (\hat{n}_{y4}\Phi_{zx})=0,\ldots$$

the following relations are obtained for the commutators of the quasimomentum operators $\hat{N}_{g4}$:

$$[\hat{N}_{x4},\hat{N}_{y4}]=-\hbar^2\frac{\partial}{\partial\theta_1}=-i\hbar\hat{K}_z\ ,$$

$$[\hat{N}_{y4},\hat{N}_{z4}]=-\hbar^2\left[\frac{\sin\theta_1}{\sin\theta_2}\frac{\partial}{\partial\theta_3}+\cos\theta_1\frac{\partial}{\partial\theta_2}-\sin\theta_1\cot\theta_2\frac{\partial}{\partial\theta_1}\right]$$
$$=-i\hbar\hat{K}_x \tag{56a}$$
$$[\hat{N}_{z4},\hat{N}_{x4}]=-\hbar^2\left[\frac{\cos\theta_1}{\sin\theta_2}\frac{\partial}{\partial\theta_3}-\sin\theta_1\frac{\partial}{\partial\theta_2}-\cos\theta_1\cot\theta_2\frac{\partial}{\partial\theta_1}\right]$$
$$=-i\hbar\hat{K}_y\ .$$

This remarkable result, rewritten in the form

$$[\hat{N}_{x4},\hat{N}_{y4}]=[\hat{K}_x,\hat{K}_y]\ ,$$
$$[\hat{N}_{y4},\hat{N}_{z4}]=[\hat{K}_y,\hat{K}_z]\ , \tag{56b}$$
$$[\hat{N}_{z4},\hat{N}_{x4}]=[\hat{K}_z,\hat{K}_x]$$

(recall that $\hat{\mathbf{K}}$ is algebraically an angular-momentum vector operator), is at the origin of the construction of a new standard representation for the angular part of the problem, that greatly simplifies the structure of the matrix representing the kinetic energy operator. Indeed, whatever f, we have also

$$[\hat{K}_x,\hat{N}_{xf}]=0,\quad [\hat{K}_y,\hat{N}_{xf}]=+i\hbar\hat{N}_{zf},\quad [\hat{K}_z,\hat{N}_{xf}]=-i\hbar\hat{N}_{yf}\ ,$$
$$[\hat{K}_x,\hat{N}_{yf}]=-i\hbar\hat{N}_{zf},\quad [\hat{K}_y,\hat{N}_{yf}]=0,\quad [\hat{K}_z,\hat{N}_{yf}]=+i\hbar\hat{N}_{xf}\ , \tag{57}$$
$$[\hat{K}_x,\hat{N}_{zf}]=+i\hbar\hat{N}_{yf},\quad [\hat{K}_y,\hat{N}_{zf}]=-i\hbar\hat{N}_{xf},\quad [\hat{K}_z,\hat{N}_{zf}]=0\ .$$

Equations (56b) and (57) yield

$$[\hat{N}_{x4}\pm\hat{K}_x,\hat{N}_{y4}\pm\hat{K}_y]=\mp 2i\hbar(\hat{N}_{z4}\pm\hat{K}_z)\ ,$$
$$[\hat{N}_{y4}\pm\hat{K}_y,\hat{N}_{z4}\pm\hat{K}_z]=\mp 2i\hbar(\hat{N}_{x4}\pm\hat{K}_x)\ , \tag{58a}$$
$$[\hat{N}_{z4}\pm\hat{K}_z,\hat{N}_{x4}\pm\hat{K}_x]=\mp 2i\hbar(\hat{N}_{y4}\pm\hat{K}_y)\ ,$$

$$[(\hat{\mathbf{N}}_4\pm\hat{\mathbf{K}})^2,\hat{N}_{g4}\pm\hat{K}_g]=0\quad (\forall g\in[x,y,z])\ , \tag{58b}$$

$$[\hat{N}_{g4}\pm\hat{K}_g,\hat{N}_{g'4}\mp\hat{K}_{g'}]=-0\quad (\forall g,g'\in[x,y,z])\ . \tag{58c}$$

This strongly suggests introducing, for the angular part of the problem (in $\theta_1,\theta_2,\ldots,\theta_6$), two new vector operators replacing $\hat{\mathbf{K}}$ and $\hat{\mathbf{N}}_4$, respectively,

$$\hat{\mathbf{L}}^+=\tfrac{1}{2}(\hat{\mathbf{N}}_4+\hat{\mathbf{K}})\ ,$$
$$\hat{\mathbf{L}}^-=\tfrac{1}{2})\hat{\mathbf{N}}_4-\hat{\mathbf{K}})\ . \tag{59}$$

Equations (58) become

$$[\hat{L}_x^\pm,\hat{L}_y^\pm]=\mp i\hbar\hat{L}_z^\pm\ ,$$
$$[\hat{L}_y^\pm,\hat{L}_z^\pm]=\mp i\hbar\hat{L}_x^\pm\ , \tag{60a}$$
$$[\hat{L}_z^\pm,\hat{L}_x^\pm]=\mp i\hbar\hat{L}_y^\pm\ ,$$

$$[(\hat{\mathbf{L}}^\pm)^2,\hat{L}_g^\pm]=0\quad (\forall g\in[x,y,z])\ , \tag{60b}$$

$$[\hat{L}_g^\pm,\hat{L}_{g'}^\mp]=0\quad (\forall g,g'\in[x,y,z])\ . \tag{60c}$$

Equations (60) definitely allow us to state that (i) both $\hat{\mathbf{L}}^+$ and $\hat{\mathbf{L}}^-$ are, algebraically, angular-momentum vector operators; (ii) $(\hat{\mathbf{L}}^+)^2$, $(\hat{\mathbf{L}}^-)^2$, $\hat{L}_z^+$, and $\hat{L}_z^-$ make up a complete set of commuting observables.

We have now in hand all the elements of the new representation. By replacing $\hat{\mathbf{K}}$ and $\hat{\mathbf{N}}_4$ by, respectively, $\hat{\mathbf{L}}^+-\hat{\mathbf{L}}^-$ and $\hat{\mathbf{L}}^++\hat{\mathbf{L}}^-$, Eq. (53) is rewritten as

$$[\hat{\Lambda}_{11}^2]_\xi=\hat{\mathcal{L}}^2(\theta,\phi)+\sum_{g=x,y,z}\{b_g(\theta,\phi)\hat{J}_g^2+[e_g(\theta,\phi)+b_g(\theta,\phi)][(\hat{L}_g^+)^2+(\hat{L}_g^-)^2]$$
$$+2d_g(\theta,\phi)\hat{J}_g(\hat{L}_g^+-\hat{L}_g^-)+2[e_g(\theta,\phi)-b_g(\theta,\phi)]\hat{L}_g^+\hat{L}_g^-\}\ . \tag{61}$$

From here on, we introduce for $\hat{\mathbf{L}}^+$ and $\hat{\mathbf{L}}^-$ the angular-momentum standard representations, $\{|L^+,l^+\rangle\}$ and $\{|L^-,l^-\rangle\}$, respectively. Therefore, in considering carefully the difference in the commutation relations for $\hat{\mathbf{L}}^+$ and $\hat{\mathbf{L}}^-$ [see Eq. (60a)], we have

$$(\hat{\mathbf{L}}^\pm)^2|L^\pm,l^\pm\rangle=\hbar^2L^\pm(L^\pm+l)|L^\pm,l^\pm\rangle\ ,$$

$$\hat{\mathbf{L}}_z^\pm|L^\pm,l^\pm\rangle=\hbar l^\pm|L^\pm,l^\pm\rangle\ ,$$

$$\hat{L}_+^\pm|L^\pm,l^\pm\rangle=(\hat{L}_x^\pm+i\hat{L}_y^\pm)|L^\pm,l^\pm\rangle$$
$$=\hbar[L^\pm(L^\pm+1)-l^\pm(l^\pm\mp 1)]^{1/2}|L^\pm,l^\pm\mp 1\rangle,$$
$$\hat{L}_-^\pm|L^\pm,l^\pm\rangle=(\hat{L}_x^\pm-i\hat{L}_y^\pm)|L^\pm,l^\pm\rangle$$
$$=\hbar[L^\pm(L^\pm+1)-l^\pm(l^\pm\pm 1)]^{1/2}|L^\pm,l^\pm\pm 1\rangle\ .$$

$[\hat{\Lambda}_{11}^2]_\xi$ can be straightforwardly rewritten in such a way that only $(\hat{\mathbf{L}}^\pm)^2$, $\hat{L}_z^\pm$, $\hat{L}_+^\pm$, and $\hat{L}_-^\pm$ appear in its expression (analogous to Eq. (50) for $[\hat{\Lambda}_8^2]_\xi$). Next, a general expression can also be given for the current matrix element

$$\langle l',m',L^{+\prime},l^{+\prime},L^{-\prime}l^{-\prime},J',j'|[\hat{\Lambda}_{11}^2]_\xi|l,m,L^+,l^+,L^-,l^-,J,j\rangle\ ,$$

in terms of all the quantum numbers, and also of $b_x^{l'lm'm}$, and so on [analogous to Eq. (52)]. In this representation, J, L^+, and L^- are obviously conserved quantum numbers, as far as the kinetic energy operator is only concerned. The kinetic coupling scheme in $(l^+l^-j\leftrightarrow l^{+\prime}l^{-\prime}j')$ (analogous to that schematically represented in Fig. 1) can be given as well. This we shall not do here for the sake of brevity. But it should be emphasized that the problem is nevertheless entirely solved for five particles.

VI. DISCUSSION

We have attempted to treat the six-particle problem (angles θ_i up to $i=9$) in following the same approach as above for five. The intermediate calculations, done by hand, turned out to be overwhelming, and we have not been successful, most likely just because of a few mistakes in the calculation. It nevertheless allowed us to observe many algebraic structures for the operators $\hat{N}_{g\alpha}$ and $\alpha=5$. We have reached a point, in the development of this algebra, at which, were it not for the aforementioned calculation errors, we can conjecture a recursive demonstration. With all the caution that a conjecture requires (we clearly do not claim that it is a demonstrated result), the conjecture is the following.

For N particles, $n=N-1$, Eqs. (42) being applicable, $[\hat{\Lambda}_{3n-1}^2]_\xi$ can be reexpressed in terms of new quasi-momentum vector operators that are linear combinations of $\hat{\mathbf{K}},\hat{\mathbf{N}}_4,\ldots,\hat{\mathbf{N}}_n$, according to the irreducible representations of the $(n-2)$-dimensional cyclic group, C_{n-2}. For example, for six particles, $n-2=3$, the linear combinations could be

$$\hat{\mathbf{L}}^A\propto\hat{\mathbf{N}}_5+\hat{\mathbf{N}}_4+\hat{\mathbf{K}}\ ,$$

$$\hat{\mathbf{L}}^{E_1}\propto\hat{\mathbf{N}}_5-\hat{\mathbf{N}}_4\ ,$$

$$\hat{\mathbf{L}}^{E_2}\propto\hat{\mathbf{N}}_5+\hat{\mathbf{N}}_4-2\hat{\mathbf{K}}\ .$$

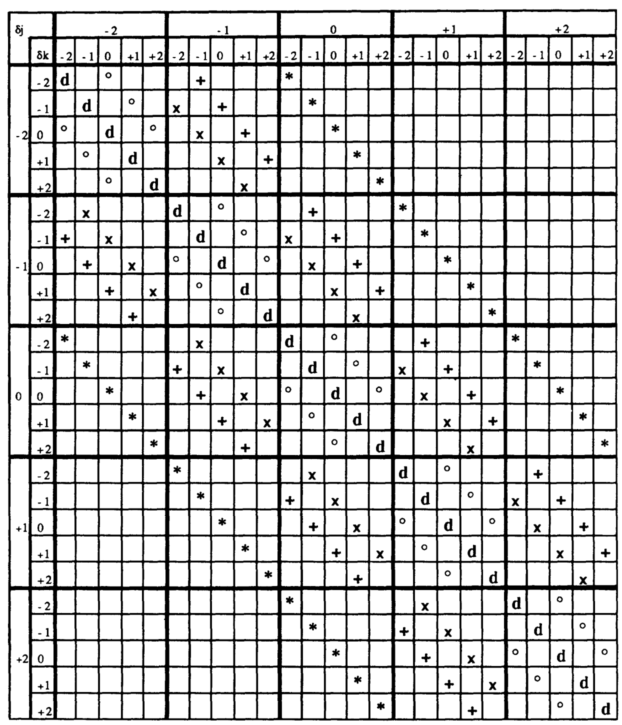

FIG. 1. Schematic illustration of the block structure (with respect to the quantum numbers j and k) of the matrix representing $[\hat{\Lambda}_8^2]_\xi$ in the basis $\{|l,m,K,p,k,J,r,j\rangle\}$. For $[\hat{\Lambda}_8^2]_\xi$, J and K are conserved quantum numbers, and r and p are pure degeneracy indices. The various nonidentically zero blocks are (i) $kj\leftrightarrow kj$ (diagonal blocks, **d**); (ii) $kj\leftrightarrow k\pm 2j$ (∘): internal deformation couplings; (iii) $kj\leftrightarrow kj\pm 2$ (✱): overall rotation terms; (iv) $kj\leftrightarrow k\pm 1j\mp 1$ (×): Coriolis couplings; (v) $kj\leftrightarrow k\pm 1j\pm 1$ (+): Coriolis couplings. δk and δj, as row $(\delta k_1\delta j_1)$ and column $(\delta k_2\delta j_2)$ indices, allow one to identify the blocks $(k+\delta k_1 j+\delta j_1\leftrightarrow k+\delta k_2 j+\delta j_2)$. The array is arbitrarily limited to $(|\delta k|,|\delta j|)\le 2$ for the sake of brevity. Each block that is nonzero is *a priori* full, i.e., all coupling matrix elements $lm\leftrightarrow l'm'$ can be nonzero.

After multiplication by appropriate constants, the new operators are algebraically pure angular-momentum vector operators. From that point on, all the rest of the work would be long and perhaps tedious, but straightforward.

For demonstrating the conjecture, two steps are probably necessary. (i) Reattempt to solve the problem for six particles in playing with coordinates and the rules of differential calculus. This will be the starting point of a possible recursive demonstration. Indeed, this strategy has always worked until now. But, this time, owing to the very intricate character of the intermediate analytical operations, advantage should be taken by using one of the powerful computerized routines based on symbolic manipulation that allow practical analytical calculations (MACSYMA, MAPLE, MATHEMATICA, etc.). (ii) Reinvestigate, from the very beginning, the vectorial structure of the problem described in I. A particularly interesting approach of that sort has been recently proposed by Robert [25]. Then the quantization should be studied along the line of argument of Lie algebra, i.e., within a pure linear algebra context.

The quantum-mechanical treatment of the PAH description of the N-body systems is therefore still an open question. This description, as far as the kinetic energy is only concerned, seems to be optimal, i.e., it leads to a representation in which many quantum numbers are conserved. The present article has simply aimed at (i) putting the problem in a physically and mathematically appropriate way, and (ii) solving it for four and five particles. The latter case is the one for which the general N-particle regime really applies, as marked by the appearance of the first $\hat{\mathbf{N}}_\alpha$-type operators. Four Jacobi vectors describe this system; the fourth one is necessarily linearly dependent on the first three [25].

Last but not least, it should be emphasized that the standard representation developed in the present paper provides a quantum finite-basis representation (FBR) in which the kinetic energy matrix is probably optimally sparse. Combined with a discrete variable representation (DVR) for the potential (which is local, i.e., nondifferential), it will make up an attractive collocation scheme for more-than-three-particle systems (cf. pseudospectral methods [26–35]. This double discretized representation for a quantum dynamical problem is very advisable since the fast Fourier transform and the inverse are now commonly implemented on supercomputers [36].

APPENDIX A: LINEAR AND PLANAR CONFIGURATIONS

In Eckart's classical treatment [2], the three gyration radii of the system, a_x, a_y, and a_z, are positive length-dimensioned quantities, to which the x, y, and z components of all Jacobi vectors are proportional, see I, Fig. 1. In addition, in I, a spherical parametrization of the gyration radii has been introduced, which achieves the hyperspherical description of the system:

$$\left.\begin{array}{l} a_x=\rho\sin\theta\cos\phi \\ a_y=\rho\sin\theta\sin\phi \\ a_z=\rho\cos\theta \end{array}\right\} \Longrightarrow \left\{\begin{array}{l} \rho\in[0,\infty] \\ \theta\in\left[0,\dfrac{\pi}{2}\right] \\ \phi\in\left[0,\dfrac{\pi}{2}\right] \end{array}\right. .$$

In the quantum treatment above, in order to make sure that the Hamiltonian operator has all the prescribed invariance properties [21], the domain of definition of θ and ϕ has been extended:

$$\theta\in[0,\pi] \text{ and } \phi\in[0,2\pi] .$$

However, for any Jacobi vector $\mathbf{r}_i'$ ($i=1,2,\ldots,n=N-1$), we still have

$$r_{ix}' \propto \rho\sin\theta\cos\phi ,$$

$$r_{iy}' \propto \rho\sin\theta\sin\phi ,$$

$$r_{iz}' \propto \rho\cos\theta$$

so that [recall that the BF frame is the principal-axis system (PAS)] (a) if $\theta=\pi/2$, the system is xy planar; (b) if $\phi=0$ or π, the system is xz planar; (c) if $\phi=\pi/2$ or $3\pi/2$, the system is yz planar; (d) if $\theta=0$ or π, the system is z linear; (e) if $\theta=\pi/2$ and $\phi=0$ or π, the system is x linear; (f) if $\theta=\pi/2$ and $\phi=\pi/2$ or $3\pi/2$, the system is y linear. Figure 2 gives an illuminating illustration of all the particular system configurations, as determined by the θ and ϕ values.

APPENDIX B: RADIAL CLOSE-COUPLED EQUATIONS

For four particles, $n=3$, we have [see Eq. (41a)]

$$d\tau_\xi=\sin\theta\sin\theta_2\sin\beta\, d\rho\, d\theta\, d\phi\, d\theta_1 d\theta_2 d\theta_3 d\gamma\, d\beta\, d\alpha .$$

If the wave function $(\Psi_\xi)_r^J$ is written in the form

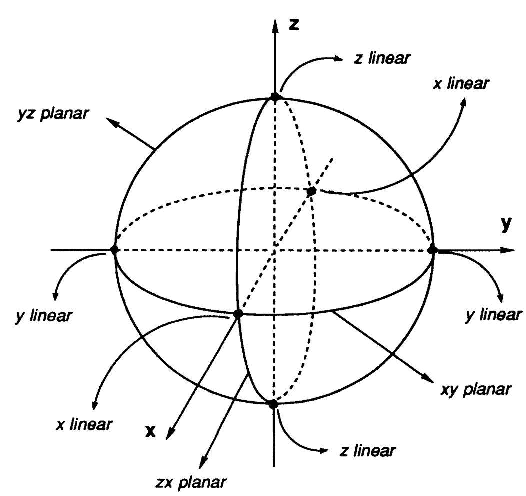

FIG. 2. Spherical representation of the range of variation for the angles θ and ϕ, in the quantum problem. In this representation, the planar configurations of the system, in the xy or yz or zx planes of the PAS, correspond to circles in the xy, yz, and zx planes, respectively; and the linear configurations along the x or y or z axes of the PAS correspond to points on the x, y, and z axes.

$$(\Psi_\xi)_r^J(E)=\frac{\sqrt{2J+1}}{8\pi^2}\sum_j \mathcal{D}_r^{j}(\alpha,\beta,\gamma)\sum_{l,m}\mathcal{Y}_l^m(\theta,\phi)\sum_{K,p,k}\sqrt{2K+1}\mathcal{D}_K^{pk}(\theta_3,\theta_2,\theta_1)\mathcal{R}_{lmKpk}^j(\rho)$$

where E is the total energy, J is the conserved rotational quantum number, and r is an index accounting for the $(2J+1)$ degeneracy of the level $|J,E\rangle$ owed to space isotropy, then the close-coupled equations for the radial wave functions $\mathcal{R}_{lmKpk}^j(\rho)$ are, cf. Eq. (52),

$$\begin{aligned}0=&\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial\rho^2}-E+\mathcal{V}_\xi^{llmm}(\rho)+\frac{\hbar^2}{2\rho^2}\left\{l(l+1)+\frac{b_x^{llmm}+b_y^{llmm}}{2}[K(K+1)-k^2+J(J+1)-j^2]\right.\right.\\&\left.\left.+b_z^{llmm}(k^2+j^2)+2d_z^{llmm}kj\right\}\right]\mathcal{R}_{lmKpk}^j(\rho)\\&+\sum_{l',m'(\neq l,m)}\left[\mathcal{V}_\xi^{l'lm'm}(\rho)+\frac{\hbar^2}{2\rho^2}\left\{\frac{b_x^{l'lm'm}+b_y^{l'lm'm}}{2}[K(K+1)-k^2+J(J+1)-j^2]\right.\right.\\&\left.\left.+b_z^{l'lm'm}(k^2+j^2)+2d_z^{l'lm'm}kj\right\}\right]\mathcal{R}_{l'm'Kpk}^j(\rho)\\&+\frac{\hbar^2}{4\rho^2}\sum_{l',m'}\left\{\frac{b_x^{l'lm'm}-b_y^{l'lm'm}}{2}\left[\sqrt{(K+k+2)(K+k+1)(K-k)(K-k-1)}\mathcal{R}_{l'm'Kpk+2}^j(\rho)\right.\right.\\&+\sqrt{(K+k)(K+k-1)(K-k+2)(K-k+1)}\mathcal{R}_{l'm'Kpk-2}^j(\rho)\\&+\sqrt{(J+j+2)(J+j+1)(J-j)(J-j-1)}\mathcal{R}_{l'm'Kpk}^{j+2}(\rho)\\&\left.+\sqrt{(J+j)(J+j-1)(J-j+2)(J-j+1)}\mathcal{R}_{l'm'Kpk}^{j-2}(\rho)\right]\\&+(d_x^{l'lm'm}+d_y^{l'lm'm})\left[\sqrt{(K+k+1)(K-k)(J+j)(J-j+1)}\mathcal{R}_{l'm'Kpk+1}^{j-1}(\rho)\right.\\&\left.+\sqrt{(K+k)(K-k+1)(J+j+1)(J-j)}\mathcal{R}_{l'm'Kpk-1}^{j+1}(\rho)\right]\\&+(d_x^{l'lm'm}-d_y^{l'lm'm})\left[\sqrt{(K+k+1)(K-k)(J+j+1)(J-j)}\mathcal{R}_{l'm'Kpk+1}^{j+1}(\rho)\right.\\&\left.\left.+\sqrt{(K+k)(K-k+1)(J+j)(J-j+1)}\mathcal{R}_{l'm'Kpk-1}^{j-1}(\rho)\right]\right\}\\&+\frac{1}{8\pi^2}\sum_{l',m'}\sum_{K',p',k'}\sqrt{(2K+1)(2K'+1)}V_{K'Kp'pk'k}^{l'lm'm}(\rho)\mathcal{R}_{l'm'K'p'k'}^j(\rho)\end{aligned}$$

where

$$\mathcal{V}_\xi^{l'lm'm}(\rho)=\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\, d\theta[\mathcal{Y}_{l'}^{m'}(\theta,\phi)]^*\mathcal{V}_\xi(\rho,\theta,\phi)\mathcal{Y}_l^m(\theta,\phi)\ ,$$

$$\begin{aligned}V_{K'Kp'pk'k}^{l'lm'm}(\rho)=&\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\, d\theta[\mathcal{Y}_{l'}^{m'}(\theta,\phi)]^*\mathcal{Y}_l^m(\theta,\phi)\int_0^{2\pi}d\theta_1\int_0^{\pi}\sin\theta_2 d\theta_2\int_0^{2\pi}d\theta_3[\mathcal{D}_{K'}^{p'k'}(\theta_1,\theta_2,\theta_3)]^*\mathcal{D}_K^{pk}(\theta_1,\theta_2,\theta_3)\\&\times V(\rho,\theta,\phi,\theta_1,\theta_2,\theta_3)\ .\end{aligned}$$

It should be emphasized that, although they are on the same footing in the kinetic energy terms, the quantum numbers J and K on the one hand (j and k on the other hand) are appearing in a completely different way in the potential energy term (e.g., J is conserved, whereas K is not), just because the potential energy function V depends on θ_1, θ_2, and θ_3 (which are internal coordinates), but not on α, β, and γ (the Eulerian angles), because the potential V is by definition rotation invariant. It is an indication that the standard representation introduced in this paper, which gives for the kinetic energy a sparse matrix (in which the quantum numbers K and p are conserved), has not been built for representing the potential energy in a simple way. This once again suggests that a double representation is advisable for the dynamical treatment of polyatomic systems (collocation methods [26–35]: a grid expansion of the wave function (DVR) allows one to take advantage of the local character of the potential, whereas a state expansion (FBR) is to be used in order to make the kinetic energy matrix as sparse as possible.

[1] X. Chapuisat and A. Nauts, Phys. Rev. A **44**, 1328 (1991).
[2] C. Eckart, Phys. Rev. **46**, 383 (1934).
[3] J. Robert and J. Baudon, J. Phys. B **19**, 171 (1986).
[4] J. Robert and J. Baudon, J. Phys. (Paris) **47**, 631 (1986).
[5] J. Robert and J. Baudon, Europhys. Lett. **2**, 363 (1986).
[6] L. M. Delves, Nucl. Phys. **9**, 391 (1959); **20**, 275 (1960).
[7] F. T. Smith, J. Chem. Phys. **31**, 1352 (1959); Phys. Rev. **120**, 1058 (1960); J. Math. Phys. **3**, 735 (1962).

[8] R. C. Whitten and F. T. Smith, J. Math. Phys. **9**, 1103 (1968).
[9] R. D. Amado, in *Elementary Particle Physics and Scattering Theory,* edited by M. Chretien and S. Schweber (Gordon and Breach, New York, 1970), Vol. 2.
[10] J. D. Louck and H. W. Galbraith, Rev. Mod. Phys. **44**, 540 (1972).
[11] Y. A. Simonov, in *The Nuclear Many Body Problem,* edited by F. Calogero and C. Ciofi degli Atti (Editrice, Bologna, 1973).
[12] L. Ballott and M. Fabre de la Ripelle, Ann. Phys. **127**, 62 (1980).
[13] M. Fabre de la Ripelle, Ann. Phys. **147**, 281 (1983).
[14] J. Avery, B. L. Christensen-Dalsgaard, P. S. Larsen, and S. Hengyi, Int. J. Quantum Chem. Symp., **18**, 321 (1984).
[15] J. Manz, Comments At. Mol. Phys. **17**, 91 (1985).
[16] A. Kuppermann, in *Theory of Chemical Reaction Dynamics,* edited by D. C. Clary (Reidel, Dordrecht, 1986).
[17] V. Aquilanti, in *Theory of Chemical Reaction Dynamics,* edited by D. C. Clary (Reidel, Dordrecht, 1986).
[18] A. Nauts and X. Chapuisat, Mol. Phys. **55**, 1287 (1985).
[19] X. Chapuisat, J. P. Brunet, and A. Nauts, Mol. Phys. **72**, 1 (1991).
[20] X. Chapuisat, A. Nauts, and J. P. Brunet, Chem. Phys. Lett. **136**, 153 (1987).
[21] H. C. Longuet-Higgins, Mol. Phys. **6**, 445 (1963).
[22] J. G. Frey, Mol. Phys. **70**, 145 (1990).
[23] A. S. Davydov, *Quantum Mechanics* (Pergamon, Oxford, 1965), pp. 157–161.
[24] L. C. Biedenharn and J. D. Louck, *Angular Momentum in Quantum Physics* (Addison-Wesley, Reading, MA, 1982), pp. 527–535.
[25] J. Robert, Thèse d'etat, Université de Paris–Nord, 1990.
[26] D. Harris, G. Engerholm, and W. Gwinn, J. Chem. Phys. **43**, 1515 (1965).
[27] P. Endress, J. Chem. Phys. **47**, 798 (1967).
[28] A. S. Dickinson and P. R. Certain, J. Chem. Phys. **49**, 4209 (1968).
[29] J. V. Lill, G. A. Parker, and J. C. Light, Chem. Phys. Lett. **89**, 483 (1982).
[30] D. Kosloff and R. Kosloff, J. Comput. Phys. **52**, 35 (1983); J. Chem. Phys. **79**, 1823 (1983).
[31] J. C. Light, L. P. Hamilton, and J. V. Lill, J. Chem. Phys. **82**, 1400 (1985).
[32] R. A. Friesner, J. Chem. Phys. **85**, 1462 (1986).
[33] R. Kosloff, J. Chem. Phys. **92**, 2087 (1988).
[34] J. C. Light, R. M. Whitnell, T. J. Park, and S. E. Choi, in *Supercomputer Algorithms for Reactivity Dynamics and Kinetics of Small Molecules,* edited by A. Laganà (Kluwer, Dordrecht, 1989), p. 187.
[35] F. LeQuéré and C. Leforestier, J. Chem. Phys. **94**, 1118 (1991).
[36] F. LeQuéré, Ph.D. thesis, Université de Paris–Sud, 1991.