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Coordinates for molecular dynamics: Orthogonal local systems

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Systems of orthogonal coordinates for the problem of the motion of three or more particles in classical or in quantum mechanics are considered from the viewpoint of applications to intramolecular dynamics and chemical kinetics. These systems, for which the kinetic energy of relative motion is diagonal, are generated by making extensive use of the concept of kinematic rotations, which act on coordinates of different particles and describe their rearrangements. An explicit representation of these rotations by mass dependent matrices allows to relate different particle couplings in the Jacobi scheme, and to build up alternative systems (such as those based on the Radau-Smith vectors or variants thereof): this makes it possible to obtain coordinates which, while being rigorously orthogonal, may approximate closely the local ones, which are based on actual interparticle distances and are in general nonorthogonal. It is also briefly shown that by defining as variables the parameters describing the kinematic rotations it is possible to obtain nonorthogonal systems of coordinates, which are useful in the treatment of collective modes.

I. INTRODUCTION

The treatment of the motion of three or more particles involves the solution of formidable partial differential equations, either in classical or in quantum mechanics, and the progress in the analysis of these equations has not been so substantial to outdate what Jacobi, in his *Lectures on Dynamics*,¹ wrote: "The main difficulty in integrating a given differential equation lies in introducing convenient variables, which there is no rule for finding. Therefore, we must travel the reverse path, and after finding some noticeable substitution, look for problems to which it can be successfully applied."

The present availability of powerful computational facilities allows us to add that the search for convenient variables is a prerequisite to any numerical approach. Furthermore, especially since the advent of quantum mechanics, it is clear that the choice of proper coordinate systems not only must capitalize on exact symmetries, but also on the approximate symmetries of a given problem, in order to find useful procedures to build up solutions starting from exact or approximate separability of some variables. This procedure, although not leading to the usually impossible complete solution to a given problem, nevertheless may lead to both a qualitative understanding of the behavior of solutions and to useful starting points for quantitative numerical approaches.

In this and the following² paper, we consider systems of orthogonal coordinates for the problem of the motion of three or more particles in classical or in quantum mechanics. The motivation for this work comes from our interest in problems arising in intramolecular and intermolecular dynamics. The usual approach to intramolecular dynamics,³ such as is pursued in the treatment of vibrational relaxation and unimolecular reactions, starts from the analysis of normal modes around the equilibrium positions: this inevitably leads to a picture of the molecular motion not directly related to vibrations of specific bonds, and therefore it is not very useful where large amplitude vibrations are of interest. A local picture, on the other hand, exploits the use of bond distances as coordinates: this involves the introduction of

nonorthogonality effects and therefore it is appropriate only when coupling terms in the kinetic energy can be neglected. In the theory of elementary processes of chemical reactions, a useful concept, that of the reaction path⁴ joining reactants and products through the saddles corresponding to transition states, leads naturally to the introduction of curvilinear coordinates, which turn out to be not especially convenient when the reaction path itself has sharp curvatures or bifurcates.

The present investigation stresses the possibility of constructing alternative sets of orthogonal coordinates which diagonalize the kinetic energy of relative motion. The actual choice will eventually be dictated by the particular system being investigated. One of our main purposes has been to give the explicit construction of the various systems, and to provide in detail the connections between them.

The plan of the present paper is as follows: in Sec. II we recall the concept of kinematic rotations,^{5,6} which will constitute the key for building up alternative sets of orthogonal coordinates. In Sec. III, Jacobi type of coordinates are discussed, and it is shown how elementary kinematic rotations describe changes in particle coupling schemes. In Sec. IV, coordinate systems corresponding to a more localized picture of molecular bond vibrations are described. Conclusions follow in Sec. V. The Appendix shows that sets of coordinates, especially useful for describing collective motions, can also be introduced by considering as coordinates the angles of spatial and kinematic rotations: these systems are in general nonorthogonal and do not always lead to a simple expression of the conservation of total angular momentum.

The following paper² will deal explicitly with the hyperspherical formulation of these coordinate systems and with the mapping of kinetic and potential energy upon hyperspheres.

II. KINEMATIC ROTATIONS

Consider N particles in a D -dimensional Euclidean space ($D = 1$ for a line, $D = 2$ for a plane, $D = 3$ for the

space). Their positions with respect to the origin are given by vectors \mathbf{r}_i , and their masses are denoted by m_i ($i = 1, 2, \dots, N$). The kinetic energy operator can be written in nonrelativistic quantum mechanics

$$T = -\frac{\hbar^2}{2} \sum_i (m_i)^{-1} \nabla_{\mathbf{r}_i}^2, \quad (1)$$

where the Laplacian operators $\nabla_{\mathbf{r}_i}^2$ act in a D -dimensional space. It is convenient to transform this expression so as to make it appear as involving the Laplacian of an $N \times D$ dimensional Euclidean space. This can be effected by the usual mass scaling

$$\mathbf{q}_i = \left(\frac{m_i}{m}\right)^{1/2} \mathbf{r}_i \quad (2)$$

which introduces the D -dimensional vectors \mathbf{q}_i and an essentially arbitrary mass m , which for definiteness we will here take as the total mass $m = \sum_i m_i$. The kinetic energy operator now reads

$$T = -\frac{\hbar^2}{2m} \sum_i \nabla_{\mathbf{q}_i}^2 = -\frac{\hbar^2}{2m} \nabla_{\mathbf{Q}}^2, \quad (3)$$

where \mathbf{Q} is an $N \times D$ dimensional vector, whose components are obtained from the D components of each of the $N_{\mathbf{q}_i}$ vectors.

This procedure has of course an analog in classical mechanics, where the scaling (2) allows to transform the kinetic energy

$$T = \frac{1}{2} \sum_i m_i \left(\frac{d}{dt} \mathbf{r}_i\right)^2 \quad (1')$$

into

$$T = \frac{m}{2} \sum_i \left(\frac{d\mathbf{q}_i}{dt}\right)^2 = \frac{m}{2} \left(\frac{d}{dt} \mathbf{Q}\right)^2. \quad (3')$$

It reduces the study of the motion of N particles in D space to that of the motion of a single particle in an $N \times D$ space.

The diagonal character of the kinetic energy, i.e., the absence of cross terms in Eqs. (3) and (3'), is preserved under $O(D \times N)$, the group of the proper and improper rotations in the full $N \times D$ space. However, particular subgroups are of interest, as will now be shown.

It is well known that invariance properties with respect to rotations in the D Euclidean space, belonging to the $O(D)$ group, lead to conservation of angular momentum, and therefore to an essential reduction of the dimensionality of the problem. In the following, we will describe in detail how special "kinematic" rotations^{5,6} in a $(N-1)$ -dimensional subspace allow the introduction of several alternatives for the representations of the N -body problem: these rotations mix the components of different \mathbf{q}_i vectors, include operations such as particle permutations and will be represented by matrices $\mathbf{K}^N \subset O(N)$. The conservation of linear momentum, which follows from invariance with respect to overall translation, can also be enforced by a kinematic rotation, and therefore the problem can be effectively reduced into an $(N-1)$ dimensional space.

In terms of the mass scaled vectors \mathbf{q}_i , the relative distances between two particles can be written as vectors

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j = m^{1/2} (m_i^{-1/2} \mathbf{q}_i - m_j^{-1/2} \mathbf{q}_j)$$

or

$$\mathbf{r}_{ij} = \sum_k S_{ij,k} (\mathbf{I}^N) \mathbf{q}_k, \quad i, j, k = 1, 2, \dots, N, \quad (4)$$

where we have defined⁷

$$S_{ij,k} (\mathbf{I}^N) = (m/m_i)^{1/2} \delta_{ik} - (m/m_j)^{1/2} \delta_{jk}, \quad (5)$$

δ_{ik} and δ_{jk} being elements of the N -dimensional identity matrix \mathbf{I}^N . The square of the modulus of the distance vector, from which the interaction between the particles depends, becomes

$$r_{ij}^2 = \sum_{k,k'} S_{ij,k} (\mathbf{I}^N) \mathbf{q}_k \cdot \mathbf{q}_{k'} S_{ij,k'} (\mathbf{I}^N), \quad (6)$$

where the scalar product can be written explicitly in terms of the components of the vectors \mathbf{q}_k and $\mathbf{q}_{k'}$,

$$\mathbf{q}_k \cdot \mathbf{q}_{k'} = \sum_l q_{kl} q_{lk'}, \quad l = 1, \dots, D. \quad (7)$$

The components q_{kl} and $q_{lk'}$ can be considered as elements of a matrix $\mathbf{q}^{D \times N}$ having D rows and N columns. We can now linearly combine the components of the \mathbf{q}_i vectors, by means of an orthogonal $N \times N$ matrix $\mathbf{K}^N \subset O(N)$, thus generating N new vectors \mathbf{x}_i , whose components are arranged in a matrix $\mathbf{x}^{D \times N}$,

$$\mathbf{x}^{D \times N} = \mathbf{q}^{D \times N} \mathbf{K}^N. \quad (8)$$

In terms of the new vectors \mathbf{x}_i , the formulas for distances become

$$\mathbf{r}_{ij} = \sum_k S_{ij,k} (\mathbf{K}^N) \mathbf{x}_k, \quad (4')$$

$$r_{ij}^2 = \sum_{k,k'} S_{ij,k} (\mathbf{K}^N) \mathbf{x}_k \cdot \mathbf{x}_{k'} S_{ij,k'} (\mathbf{K}^N), \quad (6')$$

where

$$S_{ij,k} (\mathbf{K}^N) = (m/m_i)^{1/2} K_{ik} - (m/m_j)^{1/2} K_{jk}. \quad (5')$$

A proper choice of a column of the \mathbf{K}^N matrix generates a vector which does not appear in the distance formulas (4') and (6'). Specifically, let this vector be \mathbf{x}_N . Taking $K_{iN} = \pm (m_i/m)^{1/2}$ we have $S_{ij,k} (\mathbf{K}^N) = 0$, and \mathbf{x}_N is recognized as the vector which joins the origin of the coordinates to the center of mass of the system of the particles. It points toward the center of mass for the plus sign, and toward the origin for the minus sign.

Since the coordinates of the center of mass vector do not appear in the expression for distances, they will not appear in the potential energy, and therefore in the kinetic energy of the system we can exclude the contribution of the center of mass, considering in Eqs. (3) and (3') the index i running from 1 to $N-1$. The remaining $N-1$ vectors which enter in the columns of the $\mathbf{x}^{D \times N}$ matrix can be defined in several alternative ways, that depend on the definition we give to the elements of the orthogonal \mathbf{K}^N matrix.

The \mathbf{K}^N matrix describes rotations in an N -dimensional space. Such kinematic rotations play a very different role from rotations in the physical D dimension, which, as it is well known, are represented by $SO(D)$ matrices. In general, a rotation in the N -dimensional space is parametrized by up to $N(N-1)/2$ Euler angles,⁸ corresponding to a sequence

of the same number of planar rotations. However, the Jacobi procedure shows that $N - 1$ planar rotations are sufficient for the present problem. Various ways of achieving this are described next.

III. JACOBI COORDINATES

A. The standard Jacobi vectors

In the standard procedure, which generalizes Jacobi's treatment of the three-body problem, one starts by numbering particles, and then defines \mathbf{y}_1 as the vector that joins the particles 1 and 2, and is directed towards 1. The other $N - 2$ vectors \mathbf{y}_i are directed from the i th particle towards the center of mass of the first $(i - 1)$ particles [Fig. 1(a)]:

$$\begin{aligned} \mathbf{y}_1 &= (m_1 m_2 / m M_2)^{1/2} (\mathbf{r}_1 - \mathbf{r}_2), \\ \mathbf{y}_2 &= (m_3 / m M_2 M_3)^{1/2} (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2 - M_2 \mathbf{r}_3), \\ &\dots \end{aligned} \quad (9)$$

$$\mathbf{y}_{N-1} = (m_N / m M_{N-1} M_N)^{1/2} \left(\sum_{i=1}^{N-1} m_i \mathbf{r}_i - M_{N-1} \mathbf{r}_N \right),$$

$$\mathbf{y}_N = m^{-1} \sum_{i=1}^N m_i \mathbf{r}_i,$$

where $M_i = m_i + M_{i-1}$ (and thus $M_N = m$).

In this case, Eq. (8) becomes

$$\mathbf{y}^{D \times N} = \mathbf{q}^{D \times N} \mathbf{J}^N, \quad (10)$$

where the elements of the kinematic rotation matrix \mathbf{J}^N are immediately verified to be⁷

$$\begin{aligned} J_{jk}^N &= (m_j m_{k+1} / M_k M_{k+1})^{1/2}, \quad j < k \\ J_{k+1,k}^N &= (M_k / M_{k+1})^{1/2}, \\ J_{jk}^N &= 0, \quad j > k + 1, \\ J_{jN}^N &= (m_j / m)^{1/2}. \end{aligned} \quad (11)$$

The Jacobi procedure is thus a constructive proof that the matrices of kinematic rotation corresponding to any ordering of the N particles can be specified by $N - 1$ "angles"

rather than the $N(N - 1)/2$ Euler angles which in general are needed for parametrizing a rotation in N -dimensional space.⁸ In fact, we will verify that the \mathbf{J}^N matrix can be obtained multiplying $N - 1$ matrices of $SO(N)$, each of them depending on one parameter only (a particular combination of masses).

For the specific example of three particles ($N = 3$) the matrix can be considered as given by a product of two $SO(3)$ matrices parametrized by

$$\begin{aligned} \mathbf{J}^3 &= \begin{pmatrix} \cos \alpha_{12} & \sin \alpha_{12} & 0 \\ -\sin \alpha_{12} & \cos \alpha_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ &\times \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha_{23} & \sin \alpha_{23} \\ 0 & -\sin \alpha_{23} & \cos \alpha_{23} \end{pmatrix} \\ &= \mathbf{G}^{12}(\alpha_{12}) \mathbf{G}^{23}(\alpha_{23}) \end{aligned} \quad (12)$$

with the following choice of angles:

$$\cos \alpha_{12} = (m_2 / M_2)^{1/2}, \quad \sin \alpha_{12} = (m_1 / M_2)^{1/2}, \quad (13)$$

$$\cos \alpha_{23} = (m_3 / M_3)^{1/2}, \quad \sin \alpha_{23} = (M_2 / M_3)^{1/2}.$$

When there are more than three particles, the procedure consists in adding further planar rotations

$$\mathbf{J}^N = \mathbf{G}^{12}(\alpha_{12}) \mathbf{G}^{23}(\alpha_{23}) \dots \mathbf{G}^{N-1,N}(\alpha_{N-1,N}), \quad (14)$$

where $\mathbf{G}^{j,j+1}(\alpha_{j,j+1})$ has 1 for diagonal elements and 0 for the off-diagonal ones, except for the elements

$$G_{jj} = G_{j+1,j+1} = \cos \alpha_{j,j+1} = (m_{j+1} / M_{j+1})^{1/2} \quad (15)$$

and

$$G_{j,j+1} = -G_{j+1,j} = \sin \alpha_{j,j+1} = (M_j / M_{j+1})^{1/2}. \quad (15')$$

Different couplings of particles are possible, and examples will be given in the following: it should be obvious by now that any particle permutations and changes in coupling

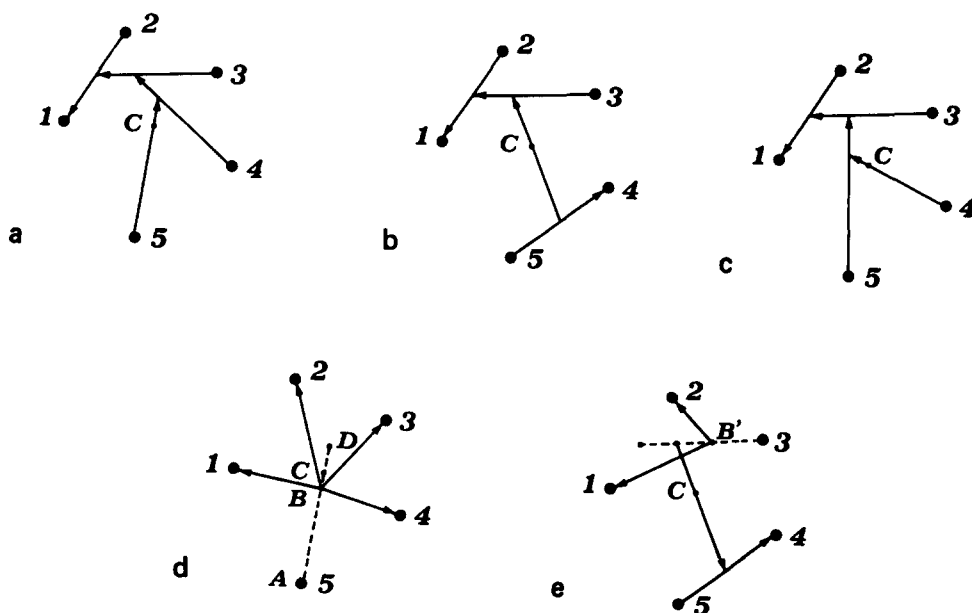


FIG. 1. Several alternatives for vectors describing the kinematics of five particles. a is the standard Jacobi scheme [Eq. (9)]; b is an alternative scheme [see Eqs. (19) and (20)]; it can be obtained from a by a change in the particle coupling scheme, through the kinematic rotation (21); c is obtained from a by a permutation of particles 4 and 5, through the kinematic rotation (17); d is the Radau-Smith scheme obtained by kinematic rotations C^+ in Sec. IV. 1; B is the "canonical point" for particle 5; e is an example of the mixed systems of Sec. IV. 2: the Radau-Smith construction is only for particles 1 and 2 "symmetrized" with respect to particle 3, and B' is the corresponding canonical point. The drawing is indicative: for five equal masses lying on the plane it is reasonably realistic.

schemes will be described by sequences of kinematic rotations depending on masses only. Specifically, it will be shown that they will be given by products of matrices having the structure of the $G^{j,j+1}$ matrices introduced above.

B. Particle permutations and alternative coupling schemes

In the standard Jacobi construction just outlined, each $G^{j,j+1}$ matrix creates two vectors, the vector which joins the $(j+1)$ particle to the center of mass of the previous j particles, and the center of mass vector for the $j+1$ particles. An alternative possibility is to divide the particle as in disjoint sets and to build up vectors according to the above procedure within each set. The G matrices belonging to different sets obviously commute. The procedure is then completed by defining vectors which join the centers of mass of the sets.

Let two such sets contain particles designated from 1 to k and from $k+1$ to N , respectively (see Fig. 1b where $N=5$ and $k=3$). It is now possible to create the vector which joins the centers-of-mass of the two sets of particles, and the center-of-mass vector for all the N particles. Such an operation, which corresponds again to a kinematic rotation, is performed by means of a matrix $G^{kN}(\alpha_{kN})$, where

$$\cos \alpha_{kN} = \left(\frac{M_N - M_k}{M_N} \right)^{1/2}; \quad \sin \alpha_{kN} = \left(\frac{M_k}{M_N} \right)^{1/2}. \quad (16)$$

Note that the $G^{j,j+1}(\alpha_{j,j+1})$ defined above are particular cases of these.

The above machinery can now be applied to deal with particle permutations and with changes in particle coupling schemes, which are of interest for rearrangement collisions.^{5,9-11} These operations will be effected by sequences of elementary kinematic rotations, described by matrices, having the same simple structure as the G matrices defined above.

The simplest elementary operation is a change in sign of a vector. Let this vector be y_k : the operation is performed through a diagonal matrix which has -1 as the k diagonal element, and 1 in the other ones. It is therefore an improper rotation, belonging to $O(N)$.

Any particle permutation can be obtained by a finite number of permutations of two neighboring particles (Fig. 1c where, with respect to Fig. 1a, particles 4 and 5 have been interchanged in the standard Jacobi construction). But the permutation between the k th and $(k+1)$ th particle involves only a kinematic rotation of the vectors y_{k-1} and y_k to give new vectors y_k^1 . Again, this is an improper rotation, and can be shown to be given by

$$\begin{pmatrix} y_{k-1}^1 \\ y_k^1 \end{pmatrix} = \begin{pmatrix} \cos \beta & \sin \beta \\ \sin \beta & -\cos \beta \end{pmatrix} \begin{pmatrix} y_{k-1} \\ y_k \end{pmatrix}, \quad (17)$$

where

$$\cos \beta = [(m_{k+1}m_k)/M_k(M_{k-1} + m_{k+1})]^{1/2}, \quad (18)$$

$$\sin \beta = [(M_{k-1}M_{k+1})/M_k(M_{k-1} + m_{k+1})]^{1/2}.$$

Besides the kinematic rotations needed for computing changes in sign of vectors and permutations of particles, it is necessary to consider also the kinematic rotations needed to

perform changes in particle coupling schemes. It is immediate that, in order to cover this type of situations, it is sufficient to show how to obtain from the standard Jacobi vectors involving particles k and $k+1$, y_{k-1} and y_k (Fig. 1b), two other alternative vectors, one which couples k and $k+1$,

$$y''_{k-1} = [m_k m_{k+1} / m(m_k + m_{k+1})]^{1/2} (r_k - r_{k+1}) \quad (19)$$

and the second one which joins the center of mass of the particles from 1 to $k-1$ to the center of mass of particles k and $k+1$,

$$y''_k = \left[\frac{(m_k + m_{k+1})M_{k-1}}{mM_{k+1}} \right]^{1/2} \times \left(\frac{\sum_{i=1}^{k-1} m_i r_i}{M_{k-1}} - \frac{m_k r_k + m_{k+1} r_{k+1}}{m_k + m_{k+1}} \right). \quad (20)$$

The connection between the two sets of vectors can again be written in matrix form:

$$\begin{pmatrix} y''_{k-1} \\ y''_k \end{pmatrix} = \begin{pmatrix} -\cos \gamma & \sin \gamma \\ \sin \gamma & \cos \gamma \end{pmatrix} \begin{pmatrix} y_{k-1} \\ y_k \end{pmatrix}, \quad (21)$$

where

$$\cos \gamma = [M_{k-1}m_{k+1}/M_k(m_k + m_{k+1})]^{1/2}, \quad (22)$$

$$\sin \gamma = [m_k M_{k+1}/M_k(m_k + m_{k+1})]^{1/2}.$$

These transformations are extremely useful in chemical reaction dynamics: in this context, γ is recognized as the skewing angle^{5,9-11} for a reactive collision involving the exchange of a particle.

IV. NON-JACOBI ORTHOGONAL COORDINATES

A. Radau-Smith vectors

Besides Jacobi vectors, other sets of orthogonal vectors have been considered in the literature. According to the procedure we have established in the previous sections, we will derive in the following alternative coordinate systems having specific symmetry properties by making a systematic use of kinematic rotations.

Recently, renewed interest has arisen for modified heliocentric or Radau coordinates,¹² which treat symmetrically the motion of $N-1$ particles with respect to the N th particle: see Fig. 1d. The matrices describing kinematic rotations are symmetrical in this case: following Smith,¹³ who also discusses some of the properties of these coordinates, the corresponding matrices can be defined in two essentially different ways, which will be written as C_{\pm}^N . Their elements are

$$C_{ij}^{\pm} = (m_i m_j)^{1/2} / [(m m_N)^{1/2} \pm m] \mp \delta_{ij}. \quad (23)$$

Let us show how these matrices are connected by kinematic rotations to the standard Jacobi ones:

$$C_{\pm}^N = J^N S_{\pm}^N. \quad (24)$$

The orthogonal matrix S_{\pm}^N can be obtained generalizing the following procedure for three particles: multiplying J^3 as in Eq. (12) by

$$S_{\pm}^3 = \begin{pmatrix} \mp \cos \alpha_{12} & \pm \sin \alpha_{12} & 0 \\ -\sin \alpha_{12} & -\cos \alpha_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv H_{\pm}^{12}(\alpha_{12}) \quad (25)$$

gives a symmetrical matrix

$$C_{\pm}^3 = J^3 S_{\pm}^3 = G^{12}(\alpha_{12}) G^{23}(\alpha_{23}) H_{\pm}^{12}(\alpha_{12}). \quad (26)$$

Note that $H_{\pm}^{12}(\alpha_{12})$ can be also written as $G^{12}(\pi - \alpha_{12})$, and therefore $C_{+}^3 \subset SO(3)$ while $H_{-}^{12}(\alpha_{12})$ is an improper rotation, and $C_{-}^3 \subset O(3)$.

For N particles, C_{\pm}^N is easily found to be

$$\begin{aligned} C_{\pm}^N &= G^{12}(\alpha_{12}) \dots G^{N-3, N-2}(\alpha_{N-3, N-2}) \\ &\times G^{N-1, N}(\alpha_{N-1, N}) H_{\pm}^{N-2, N-1}(\alpha_{N-2, N-1}) \\ &\times \tilde{G}^{N-3, N-2}(\alpha_{N-3, N-2}) \dots \tilde{G}_{12}(\alpha_{12}), \end{aligned} \quad (27)$$

where the tilde indicates matrix transposition.

The matrix manipulations in the above treatment are reminiscent of very well known procedures: the standard Jacobi construction actually proceeds via a sequence of steps similar to the ones which allow the orthogonalization of vectors in the Schmidt method, as noted by Dahler and Hirschfelder.¹⁰ On the other hand, the symmetric C_{\pm}^N matrices are of the Householder type, used for example for reducing symmetric matrices to a tridiagonal form: this was noted by Öhrn and Linderberg.⁷

It should be apparent by now that the combined use of these manipulations allows to construct orthogonal vectors in a variety of ways, and therefore it is pointed out that a proper choice of the coordinate systems will be dictated by the problem at hand. For an elementary chemical reaction,¹⁴ for example, $A + BC \rightarrow AB + C$ it may be convenient to use the vectors defined in this section where A and C are treated symmetrically with respect to atom B.

Actually, the Radau vectors were reconsidered in recent times in order to deal with the vibrational spectroscopy of molecules having a central atom, such as CH_4 , SF_6 ,... For them, it is apparent the advantage of treating symmetrically all the atoms with respect to the central one: in general, and the more so the heavier this atom is with respect to the others, the Radau vectors will be very similar to the chemical bonds.

The geometrical interpretation of the above construction, also discussed by Smith¹³ can be given in terms of the canonical points introduced by Radau: they are in number as many as the particles. Suppose that the symmetrization is made with respect to the particle A (the sun, in the heliocentric formulation): the total center-of-mass C lies on the line joining A and the center-of-mass of all the other particles D (the planets). The canonical point B is defined as the geometrical mean of segments on the line, $\overline{BD}^2 = \overline{AD} \times \overline{CD}$ (Fig. 1d); it has the interpretation of a shifted heliocenter, from which the orthogonal vectors point toward the planets. The distance from B of a planet of mass m_i is simply given by the corresponding vector, multiplied by $m_i^{1/2}$.

B. Orthogonal local coordinates

In many cases, a proper blend of the above treatments may turn out to be convenient (Fig. 1e). Consider, for exam-

ple, formaldehyde (Fig. 2), a four particle system to be described by three vectors. Any choice of three Jacobi vectors is obviously not useful in this case, nor does it appear to be useful to the three Radau-Smith vectors, which would treat the two hydrogen atoms and the oxygen atom on an equal footing. However, it is possible to define two Radau-Smith vectors describing symmetrically the hydrogen atoms with respect to the carbon atom, and a third Jacobi vector between the oxygen atom and the center-of-mass of the CH_2 group. The corresponding kinematic rotation, $K^4 \subset SO(4)$, looks as follows:

$$K^4 = G^{12} G^{23} H_{+}^{12} G^{34}, \quad (28)$$

where the numbers 1 to 4 are associated to the atoms as in Fig. 2. The sequence of elementary G matrices forms three vectors which, once properly mass scaled, are close to the distance vectors [which can be obtained by Eqs. (4') and (5')]: unlike the distance vectors, however, they provide an orthogonal coordinate set, with no cross terms in the quantum kinetic energy operators, Eq. (3), or in the classical kinetic energy, Eq. (3'). Equation (6') gives the connection between these vectors and the modulus of the distance vectors, which is the quantity needed for the definition of the potential energy surface.

The generalization of the above example to deal with molecules having different geometries is straightforward: a more complicated example is the acetic acid (Fig. 3), for

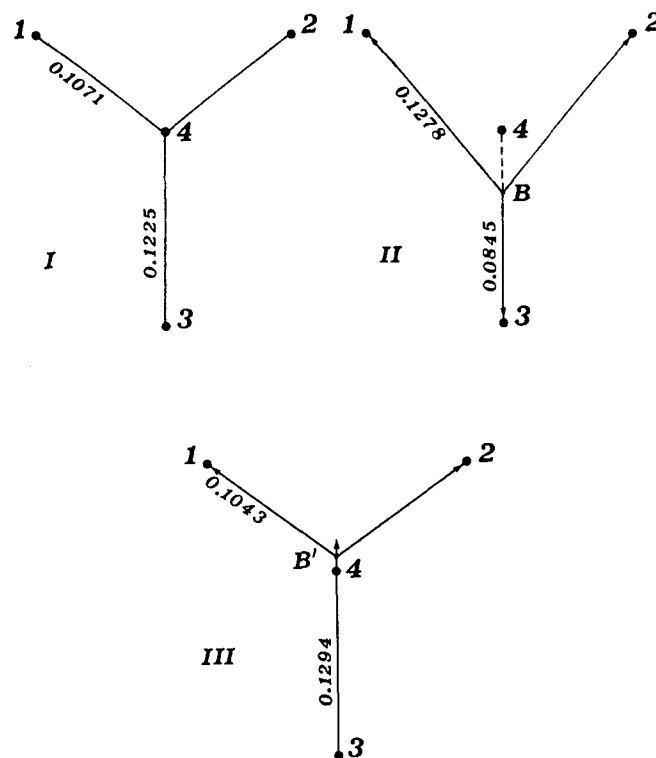


FIG. 2. The formaldehyde molecule, with atoms numbered as needed in Sec. IV. 2 (1 and 2 for H, 3 for O, 4 for C). At equilibrium [G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, New York, 1945), p. 440] the molecule lies in a plane and the HCH angle is $123^{\circ}26'$. In I, bond lengths are indicated. In II (Radau-Smith construction) vectors are measured from the canonical point B, and their lengths are indicated. In III, B' is the canonical point for the hydrogen atoms symmetrized with respect to the carbon, and the third vector joins O and the center-of-mass of CH_2 .

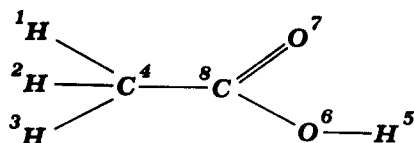


FIG. 3. The numbering of atoms of acetic acid, Sec. IV B.

which the convenient choice may be three Radau-Smith vectors for the hydrogen atoms around the first carbon atom (labeled as 4 in Fig. 3), a Jacobi vector for the O-H bond, two Radau vectors for the oxygen atom and the oxydriol group around the second carbon atom (labeled as 8 in Fig. 3), and finally a Jacobi vector joining the methyl and carboxyl group. The kinematic rotation matrix, $\mathbf{K}^8 \subset SO(8)$, can be checked to be

$$\mathbf{K}^8 = \mathbf{G}^{12} \mathbf{G}^{23} \mathbf{G}^{34} \mathbf{H}_+^{23} \tilde{\mathbf{G}}^{12} \mathbf{G}^{56} \mathbf{G}^{67} \mathbf{G}^{78} \mathbf{H}_+^{67} \mathbf{G}^{48}. \quad (29)$$

In general, when there are no cycles in the molecule, the number of vectors, not including the center of mass vector, is the same as the number of bonds, and the procedure allows to build up representations where the local character of bond vibrations can be exploited by constructing vectors which are very close to the actual distances.

V. SUMMARY AND CONCLUSIONS

In this paper, we have generated alternative sets of orthogonal coordinate systems for the many body problem by making a systematic use of kinematic rotations depending only on masses. These kinematic rotations belong to the full group $O(N)$, but a main result of this paper is to show how to resolve such rotations in terms of $O(2)$ ones.

For any of the vector systems discussed in this paper, the expressions of the kinetic energy can be easily written as to make explicit the angular momentum. Let x_i be the length of vectors \mathbf{x}_i , which are now taken to be three dimensional ($D = 3$). The quantum mechanical kinetic energy operator can be written

$$\mathbf{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N-1} \left(x_i^{-2} \frac{\partial}{\partial x_i} x_i^2 \frac{\partial}{\partial x_i} + \frac{\mathbf{l}_i^2}{x_i^2} \right), \quad (30)$$

where \mathbf{l}_i^2 is an angular momentum operator: for example, in the polar angles θ_i and φ_i of the vector \mathbf{x}_i :

$$\mathbf{l}_i^2 = \frac{1}{\sin \theta_i} \frac{\partial}{\partial \theta_i} \sin \theta_i \frac{\partial}{\partial \theta_i} + \frac{1}{\sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2}. \quad (31)$$

The corresponding classical functions are given in terms of the conjugated momenta p_{x_i} , p_{θ_i} , p_{φ_i} :

$$T = (2m)^{-1} \sum_i (p_{x_i}^2 + \mathbf{l}_i^2/x_i^2), \quad (32)$$

$$\mathbf{l}_i^2 = p_{\theta_i}^2 + p_{\varphi_i}^2/\sin^2 \theta_i. \quad (33)$$

The only rigorously conserved quantity is the total angular momentum $\mathbf{J} = \sum_i \mathbf{l}_i$, which can be shown to be independent of kinematic rotations.

However, the full many body problem arising in chemical dynamics will most likely be unmanageable either in quantum or in classical mechanics. The possibility of con-

structing vectors which mimic the local character of bond vibrations can be exploited by a full or partial freezing of angular momenta. A vibrational analysis based on such localized orthogonal coordinates such as those introduced in Sec. IV should start by considering small stretchings of the vectors around the equilibrium position. To decide whether this approach will turn out to be useful also for dealing with large amplitude vibrations requires the investigation of specific systems, which are currently being considered.

A further area of interest is in elementary chemical reactions: this is not unexpected, because it is for dealing with problems in chemical kinetics that Smith⁵ focused the attention on the concept of kinematic rotations. Actually, this originated as an extension and generalization of the concept of reaction skewing angle, introduced in the 30's by Polanyi, Eyring, and Wigner.¹⁵ The role of kinematic rotations and its relationship with the reaction skewing angle will be further discussed within the hyperspherical framework in the following paper.²

APPENDIX: THE ANGLES OF KINEMATIC ROTATIONS AS COORDINATES

In the main text, we have constructed $N - 1$ vectors for the N -particle problem by using the Jacobi procedure and exploiting the possibilities which arise when these vectors undergo kinematic rotations. These kinematic rotations are described by orthogonal matrices, which depend on parameters containing only ratios of masses. Although the $D \times (N - 1)$ Cartesian components of these vectors are obvious orthogonal coordinates for the description of motion in a $D \times (N - 1)$ Euclidean space, these vectors are in general not orthogonal in the physical D dimension. Attempts at their orthogonalization, specifically by the Gram-Schmidt procedure, suggests a way to alternative representations, leading to non-Jacobi vectors. In line with the point of view stressed in this paper, we will outline how these vectors can be obtained by introducing explicitly as variables the parameters which describe the kinematic rotations.

In this Appendix, we will neglect the center-of-mass vector, so that all the indices and sums will run from 1 to $N - 1$. Also, we will omit from the notation the explicit indication of the dimension of matrices. Consider then a set of the $N - 1$ vectors \mathbf{x}_k and form the $(N - 1) \times (N - 1)$ matrix \mathbf{X} , whose elements are obtained taking their scalar products $\mathbf{X} = \tilde{\mathbf{x}} \mathbf{x}$, i.e.,

$$X_{kk'} = X_{k'k} = \mathbf{x}_k \cdot \mathbf{x}_{k'}. \quad (\text{A1})$$

These elements appear in the formulas for the square distances, Eq. (6'). The matrix \mathbf{X} is invariant with respect to any rotation of vectors \mathbf{x}_k in the D -dimensional space. Such a rotation, represented by an $SO(D)$ matrix, say \mathcal{D} , can be parametrized by $D \times (D - 1)/2$ parameters, e.g., Euler angles (external coordinates). Therefore, although the \mathbf{x} matrices contain $D \times (N - 1)$ elements, only

$$D \times (N - 1) - D \times (D - 1)/2 \quad (\text{A2})$$

coordinates will be sufficient in general for parametrizing the \mathbf{X} matrix (internal coordinates). The number of distances between particles is instead $N(N - 1)/2$.

The determinant of the \mathbf{X} matrix, known as the Gra-

mian determinant, is different from zero only when the vectors are linearly independent, i.e., when all its eigenvalues are different from zero. Let us compute then the eigenvalues of the \mathbf{X} matrix, which is symmetric and $(N-1) \times (N-1)$. These eigenvalues will be obtained using a kinematic rotation matrix, $\mathbf{K} \in SO(N-1)$,

$$\mathbf{K}\mathbf{X}\mathbf{K} = \text{diag}(\xi_1^2, \dots, \xi_{N-1}^2). \quad (\text{A3})$$

Consider now that the scalar product be taken in the kinematic $N-1$ dimensional space, rather than in the physical D -dimensional space. We would then define a $D \times D$ matrix $\mathbf{Z} = \mathbf{x} \bar{\mathbf{x}}$, to be diagonalized by the $SO(D)$ matrix \mathcal{D} ,

$$\mathcal{D} \mathbf{Z} \mathcal{D} = \text{diag}(\xi_1^2, \dots, \xi_D^2) \quad (\text{A4})$$

but parametrize the $D \times (N-1)$ matrix as follows:

$$\mathbf{x} = \mathcal{D} \mathbf{A} \mathbf{K}, \quad (\text{A5})$$

where \mathbf{A} has D rows and $N-1$ columns, but only its diagonal elements are possibly different from zero. From Eq. (A5), one has also

$$\bar{\mathbf{x}} = \tilde{\mathbf{K}} \tilde{\mathbf{A}} \tilde{\mathcal{D}}. \quad (\text{A6})$$

Obviously, three different cases arise:

(1) When $D = N-1$ (e.g., three particles on a plane, four particles in space) \mathbf{A} is a diagonal square matrix, and $\mathbf{A} = \tilde{\mathbf{A}}$. Inserting Eqs. (A5) and (A6) into Eq. (A3), one finds that the elements of \mathbf{A} are square roots of the eigenvalues $\xi_1^2, \dots, \xi_{N-1}^2$ of \mathbf{X} . Similarly, inserting Eqs. (A5) and (A6) into Eq. (A4), one finds that the elements of \mathbf{A} are also square roots of the eigenvalues ξ_i^2 of \mathbf{Z} . Therefore the eigenvalues of \mathbf{X} and \mathbf{Z} can be ordered so to coincide. These non-zero elements of the \mathbf{A} matrix can be taken as the lengths of orthogonal vectors: they are $D = N-1$ in number, and are related to the principal axes of inertia of the body formed by the particles. Since the matrix \mathbf{K} requires $(N-1)(N-2)/2$ parameters, which are functions of the positions of particles, these parameters will provide the other effective internal coordinates needed to specify the problem, according to Eq. (A2).

(2) When $D < N-1$ (e.g., three particles on a line, four particles on a plane, more than four particles in space), the matrix \mathbf{A} will have D nonzero elements, and will have zero in its last $N-1-D$ columns. Therefore, the last $N-1-D$ rows of the \mathbf{K} matrix are not needed in the parametrization (A5). In this case, the \mathbf{X} matrix has D nonzero eigenvalues, which are easily shown to be the same as those of \mathbf{Z} , and its remaining $N-1-D$ eigenvalues will be zero. Therefore \mathbf{K} contributes with $(N-1)(N-2)/2 - (N-D-1)(N-D-2)/2$ parameters, rather than $(N-1) \times (N-2)/2$, since $N-1-D$ rows are not needed. The total number is thus $(N-1)D - D(D-1)/2$, as required by Eq. (A2) for the internal coordinates.

(3) When $D > N-1$ (three particles in the three-dimensional space) the situation is reversed, the matrix \mathbf{A} will now have $N-1$ nonzero elements, and its last $D-N+1$ rows will be zero. It is the last $D-N+1$ columns of the \mathcal{D} matrix that will now be not needed. The considerations made for the previous case here apply also, when the proper interchange is made between rows and columns, D and $N-1$, \mathbf{K} and \mathcal{D} matrices.

Since the \mathbf{Z} matrix is related to the inertia tensor \mathbf{I} ,

$$\mathbf{I} = \mathbf{1} \text{tr} \mathbf{Z} - \mathbf{Z} \quad (\text{A7})$$

the procedure outlined, based on diagonalization of \mathbf{Z} by spatial rotation, leads to a diagonal inertia tensor. The basic quantity

$$\text{tr} \mathbf{Z} = \text{tr} \mathbf{X} = \rho^2 \quad (\text{A8})$$

(with ρ being the hyperradius) will play a role in further developments, outlined in the next paper: all three cases above occur when considering three particles on a line, a plane, and in space. For three particles in a plane or in space, one obtains the so-called symmetric parametrization by Smith.^{16,2} For four particles in space case 1 applies: it was considered by Zickendraht¹⁷ (see also Ref. 7). The case (2) for more than four particles in space has also been treated by Zickendraht,¹⁸ and taken as the basis for the discussion of collective modes in systems of many particles.¹⁹

In general, these parametrizations lead to nonorthogonal coordinates. For them, it is not always possible to obtain separate wave functions for the kinetic energy operator, nor to write down explicitly wave functions of definite angular momentum. However, for three particles on a plane or for three particles in space with zero total angular momentum, the separation can be done, and this will lead to drastic simplifications for these problems, as will be shown in the next paper.²

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