Optimization of vibrational coordinates

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The enormous progress made in recent years in the techniques for detecting and analysing highly excited vibrational states of polyatomic molecules has prompted development of theoretical quantum mechanical methods to determine and characterize these states. A number of techniques, both approximate and exact, have been proposed for solving the vibrational Schrödinger equation and special attention has been paid to the coordinate system used for describing the vibrational motions of the molecule. The use of good coordinate systems that give the best possible degree of separability of vibrational motions enables us to understand molecular dynamics better and substantially reduces the computational effort required to determine excited vibrational states. A number of coordinate systems have been used for triatomic molecules, ranging from the classical rectilinear normal modes to more elaborate curvilinear systems such as valence, Jacobi, Radau *etc.* The quality of these systems can be improved considerably by making coordinate transformations depending on a certain number of parameters to be optimized. The present study reviews the different techniques proposed for parametrizing and optimizing vibrational coordinates for triatomic molecules and gives specific examples to show their efficiency in determining highly excited vibrational states.

1   Introduction

Highly excited vibrational states in polyatomic molecules play an active part in numerous areas of molecular spectroscopy and dynamics, such as elementary reaction kinetics,[1] relaxation phenomena of highly excited molecules,[2] stimulated emission spectroscopy,[3] selective chemistry processes[4] and collision energy transfer.[5] The experimental progress made in these areas in recent years, basically due to the development of laser radiation sources, has clearly revealed the invalidity of the normal mode approximation for describing theoretically highly excited vibrational states. The classical normal mode theory[6] is adequate for small-amplitude vibrational motions. An increase in excitation causes large-amplitude coupled motions, the physical description of which requires the use of a system of more general curvilinear coordinates that better adapt to this type of motion.

The search for optimal coordinate systems to describe highly excited states of polyatomic molecules is not a simple task.[7–12] Much of the difficulty lies in the great diversity of molecular vibrational dynamics, ranging from the quasi-rigid vibrational motions that take place in strongly bonded molecules to the far more extended and floppy motions that occur in clusters bound by weak van der Waals interactions. Practical problems also arise when it comes to selecting a good coordinate system, since the most separable of all may be the most complicated to use. For a given molecule the best coordinates can generally be defined as those that suitably combine mathematical simplicity with the highest possible degree of separability. Unfortunately, there is no systematic way of achieving this, although various criteria have been proposed to facilitate the search for good coordinate systems.[7,8,10,13] All essentially touch upon the reduction of the number of coupling terms present both in the kinetic-energy operator, by choosing for example orthogonal coordinate systems which do not contain differential cross-terms, and in the potential-energy operator, by using for example normal coordinates for which the second-order potential couplings are cancelled out. Considerations arising from the types of motions which can intuitively be expected in the molecule also prove useful. It is also convenient for the optimal coordinates to take as much advantage as possible of the symmetry of the molecule.

The success of a given vibrational coordinate system also depends largely on the method used to solve the Schrödinger equation. The variational method guarantees accurate results for any coordinate system, which, in principle, seems to minimize the role the coordinates play in solving the problem. In fact the opposite occurs, since the efficiency of the variational method depends, as a last resort, on the number of basic functions needed to reach convergence in the energy eigenvalues and wavefunctions, and this number in turn depends strongly on the degree of separability of the coordinate system used. The weaker the couplings the faster the convergence and the smaller the number of basis functions required in the variational calculation. The choice of an optimal coordinate system not only facilitates the solution of the vibrational Schrödinger equation but also enables us to understand and interpret the vibrational dynamics of the molecule more clearly and simply. In situations where the use of the variational method is prohibitive, for example when the number of degrees of freedom increases sufficiently, one must resort to approximate methods such as those based on perturbation theory[14–19] or those in which the wavefunction is written as a product of one-dimensional wavefunctions, *e.g.* self-consistent field (SCF)[8,20,21] and adiabatic[13,22–24] treatments. Approximate methods are still more sensitive to the choice of coordinate systems than variational methods, and finding optimal coordinates in this case, therefore, becomes more difficult.

Triatomic molecules constitute an excellent model to test different strategies in order to optimize vibrational coordinates. A number of coordinate systems have been used to describe the vibrational motions of triatomic molecules, ranging from rectilinear normal coordinates[25–29] to curvilinear systems such as valence,[30–36] internuclear,[37–39] Jacobi,[7,40–45] Radau,[13,46–50] hyperspherical[51–60] and ellipsoidal[53,61–63] coordinates. Efficient algebraical methods have also been developed to derive kinetic-energy operators for rovibrational coordinate systems.[12,64,65]

The quality of coordinate systems can be improved by using coordinate transformations depending on one or more optimization parameters. A well known example of this type of transformation is the rotation of coordinates, which has been applied with success to various vibrational problems.[66–75] Another type of rotation, the so-called kinematic rotation,[76–79] relates the coordinates corresponding to the differ-

ent Jacobi and Radau arrangements. By varying the kinematic angle, one can obtain all the orthogonal coordinate systems associated with two arbitrary internal vectors and the angle between them for a triatomic molecule. The kinematic coordinates, in turn, are included in an even larger set of nonorthogonal coordinate systems made up of all the possible orientations that the internal vectors of the molecule may have.[80–83] All these systems of generalized internal coordinates can be generated by varying two parameters, and have a common kinetic-energy operator in which the reduced masses depend explicitly on them. Other transformations, apart from coordinate rotation, have also been used to parametrize vibrational coordinate systems. Bačic et al.[61] developed a system of generalized ellipsoid coordinates to describe the vibrational motions of the hydrogen atom around the CN fragment in the HCN molecule, in which the interfocal distance acts as an optimization parameter. Sibert and co-workers[9,84] introduced a special type of curvilinear vibrational coordinates parametrized by their curvature and studied their separability in different types of stretch–bend interactions. Along the same lines, Requena et al. developed a system of generalized hyperspherical coordinates, derived from orthogonal kinematic coordinates, which depends on two displacement parameters that specify their orientation and curvature.[85–88]

The present paper reviews the methods for optimizing vibrational coordinate systems for triatomic molecules. In particular, a systematic study is made of the coordinate systems consisting of two distances and one angle, and of the various techniques for parametrizing these systems, in order to describe the excited vibrational states of triatomic molecules. We begin, in Section 2, by analysing the generalized internal coordinates, which are generated by making arbitrary linear combinations of the internal vectors depending on two optimization parameters. In Section 3, we consider the possibility of these systems being orthogonal, such that the kinetic-energy operator does not contain differential cross-coupling terms. These systems are parametrized by the kinematic rotation angle and contain, as special cases, the Jacobi and Radau coordinate systems. The simple way in which the kinetic-energy operator is expressed for the orthogonal systems facilitates further transformations that improve their quality, such as rotation of the stretch variables and transformation of these to hyperspherical coordinates. Both transformations, which include additional optimization parameters, are discussed and illustrated in Sections 4 and 5, respectively. In Section 6 we describe how confocal elliptic coordinates are optimized by varying the interfocal distance, which is defined as the equilibrium distance between the two heaviest atoms of the triatomic molecule. Finally, in Section 7, we set out the conclusions drawn from this study.

2 Generalized internal coordinates

The vibrational coordinates which most connect with the physical picture of the bonds in a molecule are valence or internal coordinates. For a triatomic molecule, these coordinates are defined as the magnitudes of the vectors r_1 and r_2 joining the end atoms to the central atom and the angle they form. Valence coordinates appear from the beginning in the quantum theories of molecular vibrations to characterize the vibrational force field of the molecule, although their use remains closely tied to the normal coordinates which, due to their simplicity, are those employed to solve the vibrational Schrödinger equation. The development of local mode models[30,31,89–95] to describe molecular bonds between light atoms, such as hydrogen, and heavy atoms, or groups thereof, gives valence coordinates with their own physical identity. Local modes contrast the localization of vibrational motions in specific bonds with the collective nature implicit in the

description of normal modes. The derivation of the exact vibrational Hamiltonian valence coordinates[96–98] and the development of highly efficient techniques to solve the corresponding Schrödinger equation[99] have led to the practically systematic use of these coordinates to describe the excited vibrational states of triatomic molecules.[32–36]

Internal coordinates can be generalized by making arbitrary linear combinations of the internal vectors r_1 and r_2. This idea was originally proposed by Sutcliffe and Tennyson to relate, by means of one parameter, the dispersion, or Jacobi, coordinates to the valence coordinates.[80] These authors[81] and also Makarewicz,[82] later, introduced more general definitions of generalized internal coordinates, depending on two parameters; derived the rovibrational Hamiltonian for them; and discussed their utility in determining vibrational energy levels and wavefunctions. The generalized internal vectors t_1 and t_2 (Fig. 1) can be defined as follows[83]

$$t_1 = \frac{1}{(1-ab)^{1/2}}(r_1 + ar_2) \tag{1}$$

$$t_2 = \frac{1}{(1-ab)^{1/2}}(br_1 + r_2) \tag{2}$$

where a and b are the parameters which specify the orientation of the vectors and where the scaling factor $1/(1-ab)^{1/2}$ is introduced to make the Jacobian of the transformation equal to unity. This definition is slightly different from those proposed by Sutcliffe and Tennyson and Makarewicz, but totally equivalent to them.

Generalized internal vibrational coordinates are defined as the magnitudes of the vectors t_1 and t_2 and the angle θ between them, and the vibrational ($J = 0$) Hamiltonian is given by[81]

$$\begin{aligned}
\hat{H}(t_1, t_2, \theta) = &-\frac{\hbar^2}{2}\left[\frac{1}{\mu_{11}}\frac{\partial^2}{\partial t_1^2} + \frac{1}{\mu_{22}}\frac{\partial^2}{\partial t_2^2}\right.\\
&+ \left(\frac{1}{\mu_{11}t_1^2} + \frac{1}{\mu_{22}t_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]\\
&+ \frac{\hbar^2}{\mu_{12}}\left[-\cos\theta\frac{\partial^2}{\partial t_1\,\partial t_2}\right.\\
&+ \frac{\cos\theta}{t_1 t_2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\\
&+ \left.\left(\frac{1}{t_1}\frac{\partial}{\partial t_2} + \frac{1}{t_2}\frac{\partial}{\partial t_1} - \frac{1}{t_1 t_2}\right)\left(\sin\theta\frac{\partial}{\partial\theta} + \cos\theta\right)\right]\\
&+ \hat{V}(t_1, t_2, \theta)
\end{aligned} \tag{3}$$

where the volume element is $d\tau = \sin\theta\,dt_1\,dt_2\,d\theta$ and where the reduced masses depend on the optimization parameters a and b.[81–83] The vibrational Schrödinger equation for these coordinates can be solved in general terms as a function of the external parameters a and b.

By giving specific values to a and b, we get a number of known vibrational coordinate systems. The most immediate
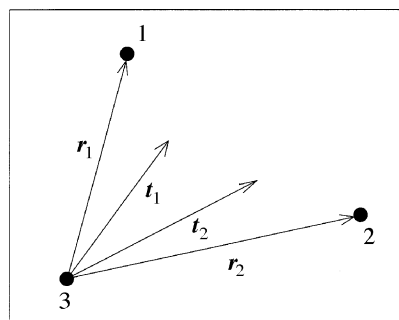

Fig. 1 Generalized internal vectors t_1 and t_2 for a triatomic molecule

ones are the valence coordinates for which $a = b = 0$. The generalized internal coordinates can be also chosen to be orthogonal by imposing the following condition on the parameters a and b[81–83]

$$\frac{1}{\mu_{12}} = \frac{1}{1 - ab}\left(\frac{b}{m_1} + \frac{a}{m_2} + \frac{(1 + a)(1 + b)}{m_3}\right) = 0 \qquad (4)$$

Thus we obtain a family of orthogonal coordinate systems depending on one parameter that, as we will see in the next section, can be redefined in a more convenient way as a kinematic rotation angle. Jacobi and Radau coordinates belong to this family of orthogonal systems.

The vibrational couplings in the potential-energy function also depend clearly on the parameters a and b. These couplings can be quantified by the non-diagonal force constants, *i.e.* the mixed partial derivatives of the potential-energy function evaluated at the equilibrium point. For linear triatomic molecules, the potential function is symmetrical in the angular coordinate θ with respect to the equilibrium geometry and therefore, the non-diagonal force constants corresponding to odd powers in this coordinate are cancelled out. As a consequence the angular coordinate is quadratically decoupled from the stretching coordinates t_1 and t_2, thus representing a bending normal mode. The radial coordinates remain coupled and describe combinations of the two stretching normal modes. This coupling, however, is removed when the parameters a and b satisfy the condition[83]

$$G_{12} = \frac{[aF_{11} + (1 + ab)F_{12} + bF_{22}]}{(1 - ab)} = 0 \qquad (5)$$

where F and G are second-order force constants for valence and generalized internal coordinates, respectively.

The separability of the vibrational motions of the molecule as described by generalized internal coordinates can be investigated by continuously varying the parameters a and b. Determining their optimal values partially depends on the method used to solve the Schrödinger equation. The method we habitually use is a variational optimization technique which consists of performing variational calculations of the vibrational energies using reduced sets of basis functions, which are built up as products of the anharmonic wavefunctions extracted from one-dimensional cuts of the Hamiltonian at the equilibrium point. The basis sets used are small enough so as not to reach convergence in the vibrational energies, and their variations with the parameters a and b enable us to find their optimal values as those which minimize the unconverged energies.

In order to illustrate the optimization of generalized internal coordinates Fig. 2 shows the average percentage error obtained for the first 22 vibrational energy levels of the CO_2 molecule computed variationally using generalized internal coordinates with basis sets of 50 anharmonic product-type functions, *versus* the parameters a and b, which are given the same value to take advantage of the symmetry of the molecule. The percentage errors corresponding to the valence ($a = b = 0$), Radau ($a = b = -0.31$), normal ($a = b = -0.04$) and optimal internal ($a = b = -0.18$) vibrational coordinates are represented by dots. The valence coordinates have the greatest uncertainty, followed by Radau and normal, which have similar percentage errors. The optimal generalized internal coordinates remarkably improve the descriptions offered by the other coordinate systems, with a practically negligible percentage error. Table 1 displays the vibrational energies obtained using the optimal coordinates together with the exact energies; the differences observed are very small.

The internal coordinates (r_1, r_2, θ) can be transformed into internuclear coordinates (r_1, r_2, r_3) by using the cosine rule. These coordinates are particularly attractive for describing the vibrational motions of molecules with three identical atoms
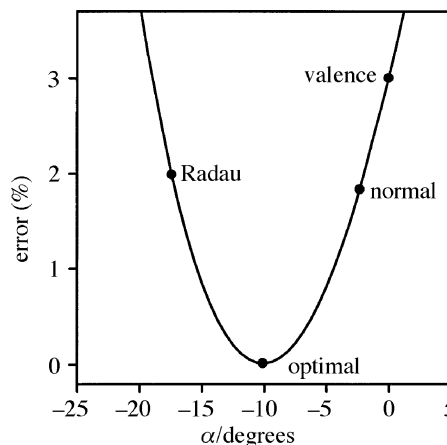

Fig. 2 Mean percentage error for the first 22 vibrational energy levels of the CO_2 molecule computed using generalized internal coordinates with $a = b$ ($\alpha = \arctan a$)

and an equilateral equilibrium geometry, since they suitably account for the high degree of symmetry of these molecules. Spirko *et al.*[37] and, more recently, Watson,[38] have used internuclear coordinates to compute rovibrational energies of the H_3^+ molecular ion and its isotopes. From the coordinate optimization perspective to which this paper refers, Sutcliffe[100] recently proposed generalizing the internuclear coordinates by defining them from the generalized internal coordinates. The third internuclear distance t_3 is then given by

$$t_3^2 = t_1^2 + t_2^2 - 2t_1t_2 \cos \theta \qquad (6)$$

The generalized internuclear coordinates (t_1, t_2, t_3) thus depend implicitly on the optimization parameters a and b. As far as we know, no numerical applications of these coordinates have been made. Sutcliffe has also suggested further

Table 1 Vibrational energy levels (in cm^{-1}) of the CO_2 molecule computed using optimal generalized internal coordinates

v_1, v_2, v_3 [a]	optimal[b]	exact[c]
0, 0, 0	2533.0	2533.0
1, 0, 0	3818.0	3818.0
0, 2, 0	3921.1	3921.1
0, 0, 1	4882.3	4882.3
2, 0, 0	5080.9	5080.9
1, 2, 0	5203.9	5203.9
0, 4, 0	5330.1	5330.1
1, 0, 1	6145.6	6145.6
0, 2, 1	6248.7	6248.7
3, 0, 0	6326.2	6325.7
2, 2, 0	6476.0	6475.4
1, 4, 0	6597.6	6597.2
0, 6, 0	6758.6	6758.4
0, 0, 2	7213.6	7213.5
2, 0, 1	7386.7	7386.3
1, 2, 1	7512.2	7511.8
0, 4, 1	7561.9	7556.3
4, 0, 0	7635.2	7634.8
3, 2, 0	7735.5	7730.6
2, 4, 0	7868.2	7862.6
1, 6, 0	8011.6	8008.6
0, 8, 0	8203.8	8201.4

[a] The quantum numbers correspond to the symmetrical stretching (v_1), bending (v_2) and asymmetrical stretching (v_3) normal modes.
[b] Results obtained using 50 anharmonic basis set functions (see text).
[c] Results obtained using a number of anharmonic basis set functions large enough to reach convergence in all the levels included in this Table.

transformtion of generalized internal coordinates into perimetric coordinates (z_1, z_2, z_3) which are defined as follows

$$z_1 = \tfrac{1}{2}(r_2 + r_3 - r_1) \tag{7}$$

$$z_2 = \tfrac{1}{2}(r_3 + r_1 - r_2) \tag{8}$$

$$z_3 = \tfrac{1}{2}(r_1 + r_2 - r_3) \tag{9}$$

in order to avoid the computational problems caused by the interdependence of the ranges of the internuclear variables due to the triangular relation existing between them.

3 Jacobi, Radau and kinematic coordinates

The Jacobi vectors for an ABC triatomic molecule are defined as the position vector $\boldsymbol{R}_\tau$ of one of the atoms $\tau (\tau = A, B, C)$ with respect to the centre of mass of the left diatom and the internuclear position vector $\boldsymbol{r}_\tau$ of the same. There are, therefore, three different Jacobi coordinate systems corresponding to the three possible atom–diatom arrangements as shown in Fig. 3. Jacobi vectors can be scaled as follows

$$\boldsymbol{S}_\tau = d_\tau \boldsymbol{R}_\tau \tag{10}$$

$$\boldsymbol{s}_\tau = d_\tau^{-1} \boldsymbol{r}_\tau \tag{11}$$

where d_τ is a given dimensionless mass-dependent factor.[76,101-104] The three different Jacobi coordinate systems are related to each other by means of kinematic rotations[76,79,101]

$$\begin{pmatrix} \boldsymbol{S}_\xi \\ \boldsymbol{s}_\xi \end{pmatrix} = \begin{pmatrix} \cos \chi_{\xi,\tau} & \sin \chi_{\xi,\tau} \\ -\sin \chi_{\xi,\tau} & \cos \chi_{\xi,\tau} \end{pmatrix} \begin{pmatrix} \boldsymbol{S}_\tau \\ \boldsymbol{s}_\tau \end{pmatrix} \tag{12}$$

where the kinematic angles $\chi_{\xi,\tau}$ are those which satisfy the expression $\tan \chi_{\tau+1,\tau} = [m_{\tau+2}^2(m_A + m_B + m_C)/m_A m_B m_C]^{1/2}$.

Jacobi coordinates were originally introduced to describe atom–diatom collisions.[105] They were later used to compute rovibrational energy levels, both of molecules with a well defined atom–diatom structure which undergo large amplitude vibrations that give rise to molecular redistributions and isomerizations[7,40,42-45] and of strongly bounded triatomic molecules.[41] For AB_2 symmetrical triatomic molecules with C_{2v} symmetry the angular Jacobi coordinate corresponding to the $A–B_2$ arrangement is quadratically decoupled in the potential function from the radial coordinates and represents an asymmetrical stretching normal mode.[69] If the molecule has a linear equilibrium geometry the two stretching coordinates are also decoupled, and the $A–B_2$ Jacobi coordinates become normal.[106] For ABC triatomic molecules with a much heavier central atom than the end atoms, like for instance H_2O, the A–BC Jacobi coordinates closely resemble valence coordinates.

Another system of orthogonal coordinates which has regained special interest over the last few years is the Radau system. These coordinates were proposed by Radau more than a century ago to study astronomical problems[107] and have been recently considered for application to molecular systems.[13,46-50,77,78,108,109] The orthogonal Radau vectors (Fig. 4), also called displaced heliocentric or baricentric, are
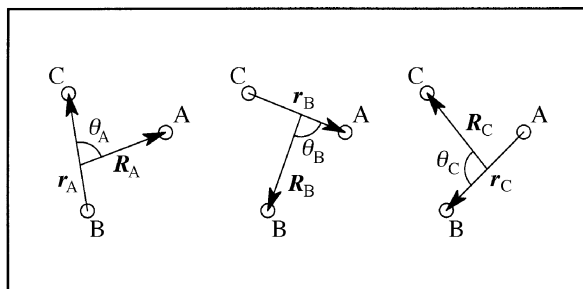
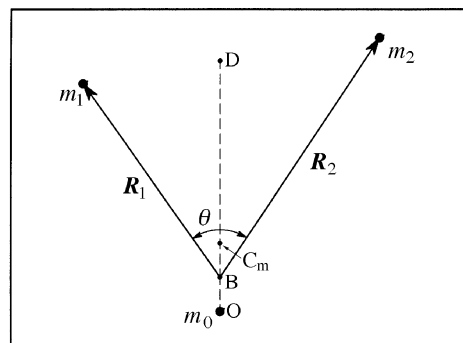**Fig. 3** Jacobi coordinates for a triatomic molecule

Fig. 4 Radau coordinates for a triatomic molecule

built by choosing one of the atoms as a planetary centre of the system, O, and defining a new centre, B, located between this atom and the centre of mass of the molecule, C_m, at a distance from the centre of mass of the two satellite atoms, D, equal to the geometrical mean of the distances $\overline{OD}$ and $\overline{C_mD}$. The Radau vectors are then those which join the new centre, called the canonical point, and the satellite atoms and can be labelled $\boldsymbol{R}_{\tau,\tau+1}$ where the first subscript indicates the atom chosen as the heliocentre, and the second the atom towards which the vector points. The scaled Radau vectors are given by

$$\boldsymbol{S}_{\tau,\tau+1} = d_\tau \boldsymbol{R}_{\tau,\tau+1} \tag{13}$$

$$\boldsymbol{S}_{\tau,\tau+2} = d_\tau^{-1} \boldsymbol{R}_{\tau,\tau+2} \tag{14}$$

where d_τ is the corresponding adimensional mass-dependent scaling factor.[78,83] The three possible Radau coordinate systems for a triatomic molecule can be derived from Jacobi coordinates by means of the kinematic rotation[78]

$$\begin{pmatrix} \boldsymbol{S}_{\tau,\tau+2} \\ \boldsymbol{S}_{\tau,\tau+1} \end{pmatrix} = \begin{pmatrix} \cos \chi_\tau & \sin \chi_\tau \\ -\sin \chi_\tau & \cos \chi_\tau \end{pmatrix} \begin{pmatrix} \boldsymbol{S}_\tau \\ \boldsymbol{s}_\tau \end{pmatrix} \tag{15}$$

where $\tan \chi_\tau = -(m_{\tau+1}/m_{\tau+2})^{1/2}$.

Radau coordinates have practically replaced valence coordinates in describing the vibrational motions of triatomic molecules in which the central atom is much heavier than the end atoms. For this type of molecule, the prototype of which is water, both systems are very similar, the former having the advantage of being orthogonal, which simplifies the solution of the vibrational Schrödinger equation. The success of Radau coordinates in accounting for excited rovibrational states of H_2O has led to its practically generalized use in fitting the potential-energy function of this molecule from the observed spectroscopic data.[48]

Kinematic rotation provides a mechanism to generate different systems of orthogonal coordinates when defined in general as follows[78,87]

$$\begin{pmatrix} \boldsymbol{S} \\ \boldsymbol{s} \end{pmatrix} = \begin{pmatrix} \cos \chi & \sin \chi \\ -\sin \chi & \cos \chi \end{pmatrix} \begin{pmatrix} \boldsymbol{S}_0 \\ \boldsymbol{s}_0 \end{pmatrix} \tag{16}$$

where the kinematic rotation angle χ is assumed to have continuous values, and where $\boldsymbol{S}_0$ and $\boldsymbol{s}_0$ is an arbitrary set of initial orthogonal vectors. The vibrational ($J = 0$) Hamiltonian operator for kinematic coordinates (S, s, θ) is given by[87]

$$\hat{H}(S, s, \theta) = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial S^2} + \frac{\partial^2}{\partial s^2} \right.$$
$$\left. + \left(\frac{1}{S^2} + \frac{1}{s^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right] + V(S, s, \theta) \tag{17}$$

where $\mu = [m_A m_B m_C/(m_A + m_B + m_C)]^{1/2}$ and where the volume element is $d\tau = \sin \theta \, dS \, ds \, d\theta$. Except for the way the parameter on which they depend is defined, kinematic coordi-
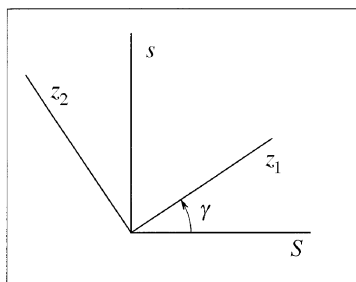
Fig. 5 Definition of rotated kinematic coordinates

nates are totally equivalent to orthogonal generalized internal coordinates, *i.e.* those satisfying equation (4). For linear triatomic molecules, the angular kinematic coordinate, θ, is, therefore, quadratically decoupled from the radial kinematic coordinates S and s in the potential-energy function, and these in turn are decoupled each other for the value of the kinematic angle[87]

$$\chi_n = \frac{1}{2} \arctan\left(\frac{2J_{Ss}}{J_{SS} - J_{ss}}\right) \quad (18)$$

where J represents the second-order force constants for the initial kinematic coordinates (S_0, s_0, θ_0). A coordinate system which is both normal and orthogonal is thus obtained for linear triatomic molecules.

4 Rotated coordinates

Kinematic vibrational coordinates are parametrized by the kinematic rotation angle χ. These coordinates can be used further as a starting point to derive new coordinate systems that include additional optimization parameters. This is the case of the coordinate transformations which leads to rotated and hyperspherical coordinate systems.

The rotation of vibrational coordinates as an optimization technique first appears in the framework of the self-consistent-field (SCF) approach to solve vibrational problems.[66–68] Thompson and Truhlar[66] applied it to compute vibrational energy levels of water by rotating the symmetrical stretching and bending normal coordinates. Their study clearly shows that optical coordinates are state dependent. The optimal values of the rotation angle which minimizes the SCF energies vary considerably from one state to another, and a certain

average value is needed to determine a single optimal coordinate system able to account for a given set of vibrational states overall. Lefebvre[67] employed the orthogonal rotation to build up symmetry-constrained non-stationary states for a model of coupled oscillators presenting dynamic tunnelling. These states are shown to progressively line up along the dissociative channels as the energy excitation increases. Almost simultaneously Moiseyev[68] carried out a study on the analytical determination of the optimal values of the rotation angle for several coupled oscillator models using the SCF method.

Rotated kinematic coordinates (z_1, z_2) are obtained by performing an orthogonal rotation of the radial kinematic coordinates S and s (Fig. 5), *i.e.*

$$\begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \begin{pmatrix} \cos \gamma & \sin \gamma \\ -\sin \gamma & \cos \gamma \end{pmatrix} \begin{pmatrix} S \\ s \end{pmatrix} \quad (19)$$

The vibrational Hamiltonian operator for these coordinates is given by[69]

$$\hat{H}(z_1, z_2, \theta) = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2} \right.$$
$$\left. + \frac{z_1^2 + z_2^2}{[z_1 z_2 \cos 2\gamma + \frac{1}{2}(z_1^2 - z_2^2)\sin 2\gamma]^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right]$$
$$+ V(z_1, z_2, \theta) \quad (20)$$

Two consecutive orthogonal rotations are therefore involved in this transformation, the first (the kinematic) being that of the internal vectors, and the second (defined above) that of the magnitudes of these vectors.

The value of the angle γ can be determined by minimizing the vibrational energies computed variationally using reduced basis sets, or else can be fixed by using some criterion of separability of the vibrational modes. In this second case, for example, we can choose the value of the angle as that for which the second-order force constant coupling the rotated coordinates z_1 and z_2 is cancelled out, which is given by[69]

$$\gamma = \frac{1}{2} \arctan\left(\frac{2K_{Ss}}{K_{SS} - K_{ss}}\right) \quad (21)$$

where K represents the second-order kinematic force constants. For bent AB_2 symmetrical molecules the angular coordinate corresponding to the A–B_2 Jacobi arrangement represents, as mentioned above, an asymmetrical stretching normal mode. Use of eqn. (21) enables us then to decouple the left radial Jacobi coordinates to second order in the potential providing a normal coordinate system for these type of molecules. Bowman *et al.*[69] applied the rotated A–B_2 Jacobi coordinates to the H_2O molecule, showing that their variational optimization leads precisely to the corresponding normal rotated coordinates, and Zúñiga *et al.*[70] extended this study to the molecules of SO_2 and O_3.

The angular kinematic coordinate is also quadratically decoupled from the radial coordinates for linear triatomic molecules, and eqn. (21) provides a set of normal rotated coordinates which are parametrized by the kinematic rotation angle. These coordinates have been used by Bowman and co-workers[71,72] to compute vibrational energy levels of the HCN and HCO molecules using the H—CN and H—CO Jacobi arrangements, respectively, *i.e.* those in which the lighter hydrogen atom orbits the heavier diatom. These arrangements are, in principle, the most natural for describing isomerization vibrational motions as those that occur in the HCN–HNC molecular system. For vibrational states located around one of the potential wells, however, other arrangements may prove more suitable in this respect. This is precisely what happens for the HCN–HNC system, for which the optimal rotated Jacobi coordinates corresponding to the HCN potential well are, as shown in Table 2, those derived from the N—CH

Table 2 Vibrational energy levels (in cm^{-1}) of the HCN molecule computed using rotated Jacobi coordinates. The excited-state energies are relative to the ground-state energy.

v_1, v_2, v_3 [a]	C—NH	H—CN	N—CH	exact[b]
0, 0, 0	3483.77	3483.62	3483.30	3483.10
0, 2, 0	1439.46	1425.70	1418.31	1418.30
1, 0, 0	2098.23	2097.26	2097.02	2096.87
0, 4, 0	2958.91	2871.78	2807.41	2806.54
0, 0, 1	3321.70	3324.65	3321.00	3318.53
1, 2, 0	3561.18	3528.30	3510.44	3508.60
0, 6, 0	4631.71	4402.57	4163.03	4161.07
2, 0, 0	4181.02	4178.34	4176.13	4172.85
0, 2, 1	4813.54	4759.86	4709.68	4706.89
1, 4, 0	5177.67	5002.36	4893.69	4890.58
1, 0, 1	5418.39	5412.54	5407.26	5400.71
0, 8, 0	6659.48	6025.77	5488.13	5477.53

[a] The quantum numbers correspond to the lowest-frequency stretching (v_1), bending (v_2) and highest-frequency stretching (v_3) normal modes. [b] Results obtained using a number of anharmonic basis set functions large enough to reach convergence in all the levels included in this Table.

arrangement.[73] Because of the close proximity of the centre of mass of the CH diatom to the carbon atom, these coordinates turn out to be very close to the valence coordinates, which were successfully used by Handy and co-workers[35] to fit the potential surface of HCN from the experimental frequencies.

5 Hyperspherical coordinates

Hyperspherical coordinates were introduced in the late 1950s to describe reactive scattering molecular processes.[76,103,105] More recently, they have been used to compute vibration–rotation energy levels for both strongly bounded triatomic molecules[51,52] and systems undergoing large amplitude vibrational motions.[53-60] The simplest way, but not the only one, of obtaining a set of hyperspherical coordinates consists of transforming the radial kinematic coordinates S and s into polar coordinates ρ and ϕ, in the usual manner[103]

$$\rho = \sqrt{(S^2 + s^2)} \qquad (22)$$

$$\phi = \arctan\left(\frac{s}{S}\right) \qquad (23)$$

This hyperspherical transformation leaves the angular coordinate θ unchanged and generates a hyperspherical coordinate system (ρ, ϕ, θ) which depends implicitly on the kinematic rotation angle χ. These coordinates can be additionally parametrized by arbitrarily choosing the origin (a, b) of the polar transformation,[84-88] as shown in Fig. 6. A set of generalized hyperspherical coordinates (P, Φ, θ) is thus derived, which are related to the kinematic coordinates (S, s, θ) by the expressions

$$P = \sqrt{[(S - a)^2 + (s - b)^2]} \qquad (24)$$

$$\Phi = \arctan\left(\frac{s - b}{S - a}\right) \qquad (25)$$

The vibrational Hamiltonian operator for the generalized hyperspherical coordinates is given by

$$\hat{H}(P, \Phi, \theta) = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial P^2} + \frac{1}{4P^2} + \frac{1}{P^2} \frac{\partial^2}{\partial \Phi^2} \right.$$
$$+ \left(\frac{1}{(P \cos \Phi + a)^2} + \frac{1}{(P \sin \Phi + b)^2} \right)$$
$$\left. \times \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right] + V(P, \Phi, \theta) \qquad (26)$$

where the volume element is $d\tau = \sin \theta \, dP \, d\Phi \, d\theta$.

There are, therefore, three parameters to be specified in order to apply the generalized hyperspherical coordinates: the kinematic angle χ and the two displacement parameters a and
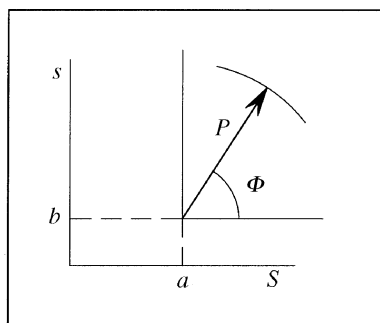

Fig. 6 Definition of generalized hyperspherical coordinates

b, which fix the orientation and curvature of the polar variables. The quadratic potential coupling between these two variables vanishes when the displacement parameters satisfy the following relationship[85-87]

$$\tan \Phi_e = \frac{s_e - b}{(S_e - a)}$$
$$= \frac{K_{ss} - K_{SS}}{2K_{Ss}} \pm \left[\left(\frac{K_{ss} - K_{SS}}{2K_{Ss}} \right)^2 + 1 \right]^{1/2} \qquad (27)$$

If the triatomic molecule has a linear equilibrium geometry, the angle θ is, as we already know, uncoupled from the polar coordinates P and Φ and up to second order in the potential, and eqn. (27) provides a family of normal hyperspherical kinematic systems with their origins (a, b) located along two perpendicular straight lines which intersect at the equilibrium point. All these normal coordinate systems, therefore, have a common fixed orientation and a variable curvature.

The polar coordinate parametrization by arbitrarily choosing the origin of coordinates was originally proposed by Johnson[110] to treat collinear reactive collisions. Much more recently, Colbert and Sibert[84] introduced the so-called variable curvature coordinates to describe vibrational bound states which are constructed by displacing the origin along one of the axes with respect to which the polar coordinates are defined. These authors analysed in detail how the curvature affects the separability of the vibrational modes in various two-dimensional problems. Mayrhofer and Sibert[9] extended this study to the SO_2 and H_2O triatomic molecules, considering the effect that different independent-mode models to describe highly excited vibrational states has on the curvature of the coordinate system.

We have investigated the optimization of generalized hyperspherical coordinates for a number of molecular systems.[83,85-88] In so doing, we showed the versatility of these coordinates in describing both normal and local vibrational-type motions in two non-bending models corresponding to the molecules of CO_2 and H_2O.[85] We carried out the combined variational optimization of the kinematic angle and the orientation and curvature of the polar coordinates for the linear triatomic molecules of CO_2, N_2O and OCS.[83,86,87] The optimal values of the kinematic angle, found for CO_2 and N_2O, are those corresponding to Radau coordinates with the central atom taken as the heliocentre, and for OCS it is that corresponding to the S—OC Jacobi arrangement. The optimal orientation of the hyperspherical coordinates is, for the three molecules, that which satisfies condition (27) for the system to be normal, and the optimal curvature adapts, for each of them, to the nodal structure of the vibrational wavefunctions. Normal hyperspherical coordinates are, moreover, better than normal rotated coordinates, with the kinematic arrangement being the same.[83,86] Fig. 7 shows the percentage errors for the first 23 vibrational energy levels of OCS variationally computed using the optimal normal rotated and hyperspherical coordinates with reduced basis sets. As observed, the hyperspherical transformation provides energies which are closer to the exact energies for all the levels considered. The more noticeable improvements occur, as expected, in the overtones and combination bands corresponding to the stretching normal modes, since the polar transformation acts on these modes complementing the optimization provided by the kinematic rotation, which mainly affects the couplings between the bending and the stretching modes.

The application of generalized hyperspherical coordinates to characterize the so-called horseshoe vibrational states of the $H_3{}^+$ molecular ion very clearly illustrates their optimization and utility in dealing with excited vibrational states.[88] The $H_3{}^+$ ion undergoes very rich vibrational dynamics, in which strongly anharmonic and coupled vibrational motions take place that lead the molecule to regions far
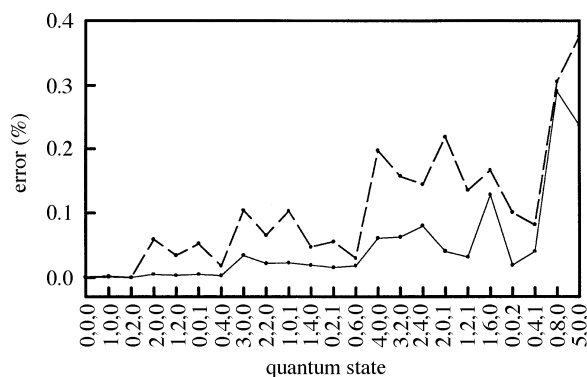
Fig. 7 Percentage errors for vibrational energy levels of the OCS molecule computed using normal rotated S–OC Jacobi coordinates (– – –) and normal hyperspherical coordinates (——)

Table 3 Vibrational energy levels (in cm^{-1}) for the H_3^+ molecule computed using generalized hyperspherical coordinates

b	$E_{0,4}$	$\Delta E_{0,4}$	$E_{0,6}$	$\Delta E_{0,6}$
0	12102.5	43.0	15605.1	272.6
0.122	12078.1	18.6	15530.2	197.7
0.244	12066.7	7.2	15526.3	193.8
0.366	12068.5	9.0	15464.7	132.2
0.488	12088.4	28.9	15399.6	67.1
0.610	12128.7	69.2	15457.1	124.6
0.732	12168.3	108.8	15561.7	229.2

removed from the equilateral equilibrium geometry at relatively low excitation energies.[44] The horseshoe states, which are thought to play an important role in the dissociation spectrum of this molecule, describe perpendicular motions of one of the hydrogen atoms towards the internuclear axis of the H_2 diatom, which stretches out to allow access of the molecule to the linear configuration. Fig. 8 shows the wavefunctions of four horseshoe states superposed over the contour plots of the potential-energy function in Jacobi coordinates. The bent geometry of the nodal lines for these states clearly suggests the use of generalized polar coordinates to improve their description. It is also convenient to optimize the displacement parameters in this case by moving the origin of the polar coordinates along the axis r, $i.e.$ keeping $a = 0$, in order to take advantage of the symmetry of these states with respect to the linear configuration ($R = 0$). Table 3 displays the differences between the vibrational energies for the (0, 4) and (0, 6) horseshoe states computed variationally using reduced basis sets and the exact energies for different values of b. As observed, the improvements gained in the energies when the coordinates are optimized are noticeable and the optimal values of the parameter b, which correspond to the lowest energy differences, increase with the excitation of the state. Fig. 9 shows the (0, 6) horseshoe wavefunction as plotted in Jacobi coordinates and generalized hyperspherical coordinates for three different values of b. The wavefunction clearly lines up along the polar gener-
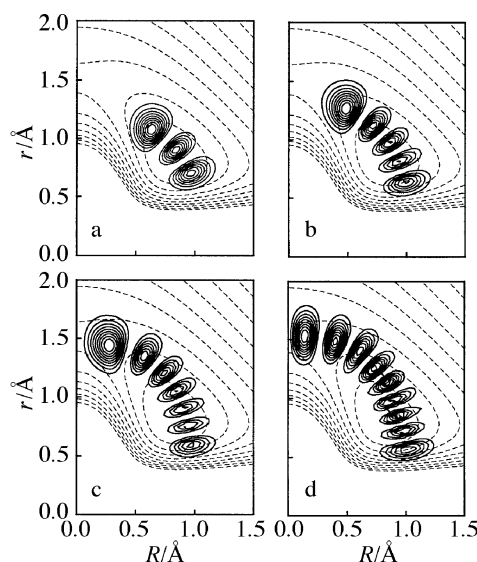
alized coordinate Φ as the displacement parameter b tends towards its optimal value.

A different hyperspherical coordinate system can be constructed by following the indications given by Pack and Parker.[79] These authors introduce the so-called APH hyperspherical coordinates APH (ρ, θ, χ) defined as

$$\rho^2 = S_\tau^2 + s_\tau^2 \tag{28}$$

$$\tan\frac{\theta}{2} = \frac{[(S_\tau^2 - s_\tau^2)^2 + (2S_\tau s_\tau \cos\varphi_\tau)^2]^{1/2}}{2S_\tau s_\tau \sin\varphi_\tau} \tag{29}$$

$$\sin(2\chi) = \frac{2S_\tau s_\tau \cos\varphi_\tau}{[(S_\tau^2 - s_\tau^2)^2 + (2S_\tau s_\tau \cos\varphi_\tau)^2]^{1/2}} \tag{30}$$

$$\cos(2\chi) = \frac{(S_\tau^2 - s_\tau^2)}{[(S_\tau^2 - s_\tau^2)^2 + (2S_\tau s_\tau \cos\varphi_\tau)^2]^{1/2}} \tag{31}$$

where (S_τ, s_τ, φ_τ) are the mass-scaled Jacobi coordinates for a given arrangement τ. As noted, in these hyperspherical coordinates the kinematic rotation angle χ does not play the role of a parameter, as it does in the hyperspherical kinematic coordinates, but that of a coordinate. The APH hyperspherical coordinates have been used to determine vibrational energy levels and wavefunctions of a number of triatomic molecules,[7,55-60] although no treatment has been developed to parametrize and optimize them in similar terms to the hyperspherical kinematic coordinates.

6 Confocal elliptic coordinates

Let us finally consider the use of confocal elliptic coordinates, also referred to as prolate spheroidal coordinates, to describe
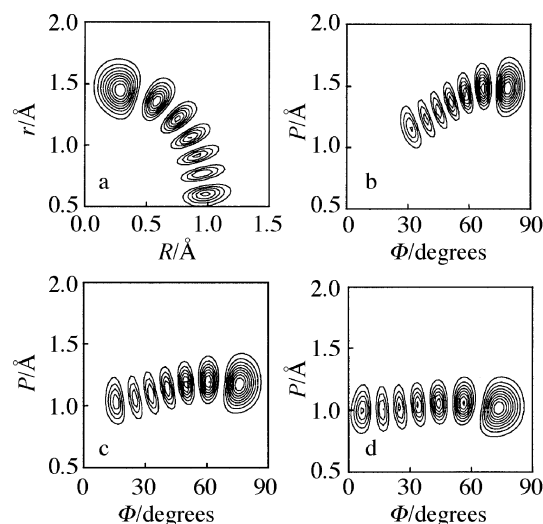

Fig. 8 Contour plots of the H_3^+ horseshoe wavefunctions corresponding to states (0,2) (a), (0,4) (b), (0,6) (c) and (0,8) (d)

Fig. 9 Contour plots of the H_3^+ horseshoe wavefunction corresponding to state (0,6) in Jacobi (a) and hyperspherical coordinates with $b = 0$ (b), $b = 0.325$ (c) and $b = 0.488$ (d)

vibrational motions in triatomic molecules.[53,61–63] These coordinates adapt well to molecules in which one of the atoms, much ligher than the other two, undergoes large amplitude vibrational motions around the strongly bonded remaining diatom. Jacobi coordinates are therefore the starting point to derive confocal elliptic coordinates. For an ABC triatomic molecule the vibrational Hamiltonian in Jacobi coordinates is given by

$$
\hat{H}(R, r, \theta, \phi) = -\frac{\hbar^2}{2\mu_{A, BC}}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r^2}
$$
$$
- \frac{\hbar^2}{2}\left(\frac{1}{\mu_{A, BC} R^2} + \frac{1}{\mu_{BC} r^2}\right)
$$
$$
\times \left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)
$$
$$
+ V(R, r, \theta) \tag{32}
$$

where ϕ is the rotation angle of atom A about the BC internuclear axis and where the reduced masses are $\mu_{A, BC} = m_A(m_B + m_C)/(m_A + m_B + m_C)$ and $\mu_{BC} = m_B m_C/(m_B + m_C)$. If the mass of the orbiting atom A is much smaller than the masses of the atoms forming the diatom BC, i.e. if $m_B, m_C \gg m_A$, then $\mu_{BC} \gg \mu_{A, BC} \approx m_A$ and the term $1/(2\mu_{BC} r^2)$ can be neglected compared with $1/(2\mu_{A, BC} R^2)$ in Hamiltonian (32), which is equivalent to removing the rotational energy of the diatom BC.[61] The vibrational Hamiltonian thus becomes

$$
\hat{H}(R, r, \theta, \phi) = -\frac{\hbar^2}{2\mu_{A, BC}}\left[\frac{\partial}{\partial R^2}\right.
$$
$$
\left. + \frac{1}{R^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right]
$$
$$
- \frac{\hbar^2}{2\mu_{BC}}\frac{\partial}{\partial r^2} + V(R, r, \theta) \tag{33}
$$

The confocal elliptic coordinates ξ, η are then defined by[61–63,111]

$$
\xi = \frac{r_1 + r_2}{r_e} \tag{34}
$$

$$
\eta = \frac{r_1 - r_2}{r_e} \tag{35}
$$

where r_1 and r_2 are the internuclear distances r_{AC} and r_{AB}, respectively, and where the internuclear distance of the diatom is assumed to be frozen at its equilibrium value in the coordinate transformation. The vibrational Hamiltonian in elliptic coordinates is thus given by[111]

$$
\hat{H}(\xi, \eta, r, \phi) = -\frac{\hbar^2}{2\mu_{A, BC}}\frac{1}{a(\xi^2 - \eta^2)}
$$
$$
\times \left[(\xi^2 - 1)\frac{\partial^2}{\partial\xi^2} + 2\xi\frac{\partial}{\partial\xi} + (1 - \eta^2)\frac{\partial^2}{\partial\eta^2}\right.
$$
$$
\left. - 2\eta\frac{\partial}{\partial\eta} + \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2}\right)\frac{\partial^2}{\partial\phi^2}\right]
$$
$$
- \frac{\hbar^2}{2\mu_{BC}}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + V(\xi, \eta, r) \tag{36}
$$

where $a = r_e/2$ and the volume element is $d\tau = -a^3(\xi^2 - \eta^2)r^2\,d\xi\,d\eta\,dr\,d\phi$.

Confocal elliptic coordinates are well known in quantum chemistry because they factorize the electronic Schrödinger equation for the H_2^+ molecule, decoupling the Coulomb interactions between the electron and the two nuclei.[112]

Accordingly, these coordinates have been used extensively in electronic structure problems of diatomic molecules.[113] Their applications to molecular problems have been more limited, although they have provided one of the finest illustrations of parametric optimization of vibrational coordinates. This is the case of the Bačic et al.[61] application of elliptic coordinates to describe large-amplitude vibrational motions of the hydrogen atom, in the HCN molecule, around the diatom CN with the internuclear distance frozen at the equilibrium value. The choice of these coordinates was dictated by physical intuition, since the minimum-energy path taking the hydrogen atom from one isomer to the other is practically elliptical. On these grounds, Bačic et al.[61] interpret the interfocal distance $2a$ as an optimization parameter and compute its optimal values for the different vibrational states by minimizing the corresponding SCF energies. The improvements obtained in these energies, for vibrational states excited in the bending mode, are so remarkable that they completely invalidate the starting coordinate system. It is also observed that, the higher the bending excitation, the greater the optimal values of the interfocal distance. In this way the corresponding ellipses fit increasingly bigger portions of the minimum-energy path. These portions span regions that are closer and closer to the transition state and over which the bending overtones extend. These results confirm both the suitability of elliptic coordinates for this problem and the success in the choice of the interfocal distance as an optimization parameter.

Confocal elliptic coordinates have been also used to describe vibrational motions in $I_2 \cdots X$ (X = He, Ne) van der Waals clusters.[53,62] In particular, Horn et al.[53] carried out an SCF study of the vibrational dynamics of the I_2He complex, showing that elliptic coordinates are better than Jacobi coordinates to account for the excited bending states of the complex, and García-Vela et al.[62] used elliptic coordinates to compute vibrational bound states of the I_2He and I_2Ne clusters by performing an adiabatic separation of the stretching and bending elliptical motion. Another application of confocal elliptic coordinates was performed by Thorson et al.[63] to study the vibrational states of the bifluoride anion FHF⁻. None of these studies included, however, the optimization of the interfocal distance.

7 Conclusions

The use of optimal coordinate systems to describe excited vibrational motions in polyatomic molecules largely simplifies, both physically and computationally, the analysis and understanding of their vibrational structure and dynamics. The great variety of existing vibrational interactions and of different coordinate systems to be used frequently make it difficult to choose the optimal coordinate system for a given vibrational problem. Thus, it is convenient to accompany the physical intuition needed to find the proper coordinate system with systematic techniques able to improve efficiently the separability of the vibrational motions. One of the most promising and effective methods in this respect consists of using coordinate systems that include a certain number of parameters to be optimized.

In this paper we have reviewed different parametrization and optimization techniques of vibrational coordinate systems for triatomic molecules. We illustrated both the dependence of optimal coordinates on individual vibrational states and the possibility of deriving optimal coordinate systems that account for a given set of states overall. Global optimal systems are very useful, for example, for numerically fitting potential-energy surfaces from experimental data, whereby the computational volume needed to determine the potential parameters to be fitted increases very rapidly with the number of such parameters. Moreover, all the experience acquired in the search of optimal vibrational coordinates for triatomic

molecules is essential for undertaking the optimization of vibrational coordinates in molecules with four or more atoms, for which the computational restrictions to determine excited vibrational states are much more severe.[114–117]

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