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Hyperquantization algorithm. I. Theory for triatomic systems

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In this paper we present the theoretical concepts and methodology of the hyperquantization algorithm for the three body quantum mechanical problem. Within the framework of the hyperspherical approach to reaction dynamics, we use angular momentum algebra (or its generalization, e.g., including Hahn coefficients which are orthonormal polynomials on a set of grid points which span the interaction region) to compute matrix elements of the Hamiltonian operator parametrically in the hyperradius. The particularly advantageous aspects of the method proposed here is that no integrals are required and the construction of the kinetic energy matrix is simple and universal: salient features are the block tridiagonal structure of the Hamiltonian matrix and a number of symmetry properties. The extremely sparse structure is a further advantage for the diagonalization required to evaluate the adiabatic hyperspherical states as a function of the hyperradius. Numerical implementation is illustrated in the following paper by a specific example. © 1998 American Institute of Physics. [S0021-9606(98)01734-6]

I. INTRODUCTION

The hyperspherical approach to the dynamics of three atoms and in particular to reactive scattering¹⁻³ has seen considerable progress recently. In hyperspherical coordinates the complete description of a three body problem is accomplished by solving first a quantization problem on S^5 (the surface of a sphere in a six-dimensional space) at fixed values of the hyperradius and then either coupled-channel equations are integrated applying a propagator technique⁴ or a (reduced) algebraic problem is solved. The calculation of the hyperspherical adiabatic states containing information on the structure, rotations and all the internal modes (except that along the hyperradius) is typically most demanding from a computational viewpoint. Currently, there is no state-of-the-art algorithm prevailing over the others for generic values of the hyperradius and for all systems, the key problem being the high number of states one has to deal with in the general case. Except for some specific examples, systems having total angular momentum different from zero and more than two open rearrangement channels are currently very hard to cope with, although there have been some successful applications on triatomic systems with near collinear transition state. Reactions involving more than one atom different from H are also practically out reach of exact approaches, although progress is recorded for $\text{Li} + \text{HF}$ ⁵ and $\text{O} + \text{HCl}$.⁶ Also, all calculations have been carried out only on a single potential energy surface and it is desirable to develop a theory for an accurate treatment of the dynamics of three atoms systems including excited electronic states and fine structure, of paramount relevance for reactivity. The following paper (Part II)⁷ deals with these aspects.

The hyperradius is a natural reaction coordinate. At small values it corresponds to the region of strong triatomic interaction while at large values it describes the asymptotic

rearrangement regions of the reactants and products. The other five variable “angles” are divided into three “external” coordinates, which do not appear in the interaction potential function, and two “internal” angles, which describe the triatomic geometry. For external coordinates it is natural to use three Euler angles which define, appropriately, a rotating body frame. Two basic choices are possible to define the other two internal angles needed to complete the parametrization of the problem on the surface of a hypersphere. We refer to them as *asymmetric* and *symmetric* hyperspherical parametrizations, corresponding to the two basic different choices available to span a two-dimensional section on the surface of the hypersphere.⁸ Other coordinate systems can be trivially related to these two essentially different parametrizations by a constant phase factor that scales the original angles (for a list of alternatives and connection among them see Ref. 9). Basically, in the *asymmetric* parametrization, the choice is, for example, the quantization axis along the Jacobi vector joining the atom to the center of mass of the diatom; in the *symmetric* case the choice is instead along the axis of least or maximum inertia, so to diagonalize the inertia tensor. We use the original definition of hyperangles as given by Smith in the symmetric case and of Fock for the asymmetric one, adhering to the notation described in Refs. 8 and 9.

We have developed and implemented a new method that we have called *hyperquantization algorithm*¹⁰ which will be shown to be useful for solving quantization problems on a surface of a multidimensional sphere, both in the symmetric and asymmetric parametrization of hyperangles.¹¹

The most important ingredients of this algorithm are generalized $3j$ symbols or Hahn polynomials¹² which are the discrete analogs of hyperspherical harmonics on a discrete grid of points. Using these quantities we build up an algebraic representation of the eigenvalue problem with very attractive characteristics from a computational viewpoint. In particular the Hamiltonian matrix has many symmetries and is very sparse. This novel treatment of the five-dimensional

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problem at fixed values of the hyperradius is presented in two papers. The first one concentrates on the theoretical concepts and methodology while in the second one we focus on the numerical aspects and on the application to the $F+H_2$ reaction including spin orbit and electronic effects.

In Sec. II, the treatment of the motion of three atoms in space is reviewed in both the symmetric and asymmetric hyperspherical coordinates. Explicit expansions in hyperspherical harmonics are developed to obtain a continuum basis representation of the fixed hyperradius problem. Section III is concerned with the description of the hyperquantization algorithm, where a continuum basis is transformed into a discrete one. In Sec. III A the discrete analogs of hyperspherical harmonics, i.e., Hahn coefficients,¹² are introduced and some important properties used to develop our algorithm are reviewed. Section III B specializes the hyperquantization algorithm to the symmetric hyperangular parametrization when the total angular momentum is equal to zero. The asymmetric hyperangular parametrization is discussed in Sec. III C and the treatment is generalized to any value of the total angular momentum. The symmetry properties of both representations are derived from those of Hahn coefficients, and the structure of the Hamiltonian matrix is given. In Sec. IV we give explicit formulas for the overlap and the interaction matrices needed for the solution of the coupled-channel equations, and also in the case where two different grids or two different parametrizations are employed. The conclusions and some perspectives about the potentialities of this method are presented in Sec. V.

II. HYPERSPHERICAL COORDINATES AND HARMONICS FOR A THREE PARTICLE SYSTEM

In the laboratory reference frame the motion of three particles depends on nine variables, three of which define the position of the center-of-mass while the other six describe the internal (e.g., rotational and vibrational) modes. The center-of-mass, or translational, degrees of freedom are separated out introducing two tridimensional vectors, \mathbf{r}_{ij} and $\mathbf{R}_{k,ij}$ which denote the vector from atom i to j and the vector from the center-of-mass of the pair ij to the atom k , respectively. The choice of these Jacobi vectors is not unique: explicitly, for the reaction of an atom A with a molecule BC a suitable set for describing the reactants' channel $A+BC$, corresponds to the vectors \mathbf{r}_{BC} and $\mathbf{R}_{A,BC}$. Alternatively, two other sets of vectors, \mathbf{r}_{AB} and $\mathbf{R}_{C,AB}$ or \mathbf{r}_{AC} and $\mathbf{R}_{B,AC}$ are more appropriate for describing the products' channels $AB+C$ or $AC+B$. Under proper mass scaling (see below) these three sets of vectors can be related to each other by a planar rotation of an angle which depends only on the masses of A, B and C atoms⁹ and is an extension of the so-called skewing angle concept introduced in the 1930s in chemical kinetics. In a previous paper,¹³ we have shown that alternative coordinate systems such as the Radau-Smith vectors¹⁴ can be obtained from the Jacobi ones by a sequence of *kinematic rotations* and we have given the explicit expressions of the (mass-dependent-only) rotation angles.⁹ It is also possible to use arbitrary kinematic rotations of the Jacobi vectors keeping the kinematic angles as variables. For each set k (or i or j) of the two Jacobi vectors the normalization can be written

$$\mathbf{x}_k = \left(\frac{\mu_{ij}}{\mu} \right)^{1/2} \mathbf{r}_{ij}, \quad \mathbf{X}_k = \left(\frac{\mu}{\mu_{ij}} \right)^{1/2} \mathbf{R}_{k,ij}, \quad (1)$$

where μ_{ij} is the two-body reduced mass for the ij couple. The Cartesian components of the vectors \mathbf{x}_k and \mathbf{X}_k along the center-of-mass reference frame can be viewed as the rectangular coordinates which define the position of a body of mass μ in a six-dimensional space. Such a mass is conveniently identified with the three-body reduced mass $\mu = \sqrt{m_i m_j m_k / (m_i + m_j + m_k)}$, where m_i , m_j and m_k are the masses of the three particles. In this multidimensional space hyperspherical coordinate systems (i.e., one radius and five angles) can be introduced. The *hyperradius* is defined as:

$$\rho^2 = |\mathbf{x}_k|^2 + |\mathbf{X}_k|^2 \quad (2)$$

and enjoys the important property of being independent on the particular choice k , or i , or j . Being invariant under kinematic rotations, it is referred to as a variable *democratic* with respect to all reactant and product channels.

In hyperspherical coordinates, the kinematic of three particles is reduced to that of the motion of one body of mass μ on a five-dimensional surface, that of a six-dimensional sphere whose variable radius is ρ . The kinetic energy operator takes the following form:

$$T = -\frac{1}{2\mu} \left(\rho^{-5} \frac{\partial}{\partial \rho} \rho^5 \frac{\partial}{\partial \rho} - \frac{\Lambda^2(\omega_5)}{\rho^2} \right), \quad (3)$$

where Λ^2 is mathematically related to the quadratic Casimir's operator of the six-dimensional rotation group and physically is interpreted as the generalized or grand orbital angular momentum operator.¹⁵ Its eigenvalues, as labeled by a quantum number λ (see below), are $\lambda(\lambda+4)$ and its eigenfunctions (hyperspherical harmonics⁸), when available in closed form, will be used as expansion basis sets for the algebraic solution of the hyperangular part of the problem. The set of five angles that define the orientation of a point on the surface of the six-dimensional sphere is denoted by ω_5 .

Each of the alternative ways available for choosing the angular variables offer advantages whose exploitations make the hyperspherical approach extremely flexible and powerful. Each parametrization leads to an alternative coupling scheme of angular momenta and, as a consequence, to an alternative representation of the Schrödinger equation for the three particles. We have given a classification of these parametrizations,⁸ where, as also experienced by the vast literature on three-body problems, it is basic to separately consider the two classes, which we will call here *asymmetric*¹⁶ and *symmetric*¹⁷ hyperangular parametrizations. The choice of the reference frame is also important. In the following, the asymmetric and the symmetric hyperspherical coordinates are referred to as the center-of-mass and to the inertia principal axes frames, respectively.

Within the hyperspherical coordinates approach, the quantum mechanical three-body problem is often conveniently tackled by first studying the dynamics on a family of effective potentials parametrically dependent on ρ , and treating the ρ dependence on a second (the propagation) step. So,

one has first to solve the following quantization problem on the surface of a hypersphere at given fixed values of the hyperradius:

$$\left(\frac{1}{2\mu\rho^2} \Lambda^2(\omega_5) + V(\rho, \omega_{\text{int}}) \right) \Psi_i = \varepsilon_i(\rho) \Psi_i, \quad (4)$$

where in the absence of external forces the three-body interaction potential V depends only on ρ and two internal angles, denoted as ω_{int} . The resulting sets of eigenvalues $\varepsilon_i(\rho)$ and wave functions Ψ_i contain information on the structure and on all rotational and internal modes, except the motion along the reaction radius, ρ .

The proposed algorithm for solving Eq. (4) exploits the discrete analogs of hyperspherical harmonics as an expansion basis for the unknown functions Ψ_i . The following presentation will consider separately the cases of symmetric and asymmetric hyperangular parametrizations.

A. The symmetric hyperangular parametrization

The symmetric parametrization of hyperangles first introduced by Smith,¹⁷ has been employed successfully by many for reaction scattering problems.^{2,3,5,6} Three of the five angles ω_5 are the Euler angles orienting the principal-axis frame with respect to the center-of-mass frame. Of the two ‘‘internal’’ angles, Θ —which is related to the area of the triangle formed by the three atoms—varies between 0 and $\pi/4$, and Φ —which distinguishes the different shapes of all triangles with the same moments of inertia—varies cyclically between 0 and 2π and is defined within a phase factor which depends only on masses and specifies the particular choice of Jacobi’s vectors. The angle Θ enjoys the same property of ρ of being invariant with respect to particle permutations. The *kinematic rotation* angle Φ , a continuous generalization of the reaction skewing angle concept, is defined within a phase factor⁹ which identifies the rearrangement channel.

In these coordinates, the grand orbital angular momentum operator reads:^{2,3,18,19}

$$\Lambda^2 = -\frac{1}{\sin 4\Theta} \frac{\partial}{\partial \Theta} \sin 4\Theta \frac{\partial}{\partial \Theta} - \frac{1}{\cos^2 2\Theta} \times \left(\frac{\partial^2}{\partial \Phi^2} - J_3^2 - 2i \sin 2\Theta J_3 \frac{\partial}{\partial \Phi} \right) + \frac{J_1^2}{\sin^2 \Theta} + \frac{J_2^2}{\cos^2 \Theta}, \quad (5)$$

where J_1 , J_2 and J_3 are the components of the total angular momentum operators in the principal axes reference frame and depend on the three Euler angles. The quantization axis points along the minimum or maximum inertia axis when J_2 or J_3 is chosen as the component which commutes with both J^2 and the Hamiltonian. The representation of the Coriolis term, $J_3(\partial/\partial\Phi)$, which couples the external rotational modes to the internal angle Φ , depends on the choice of the quantization axis: when the latter points along the maximum inertia axis the operator J_3 is diagonal, otherwise it has to be given in terms of ladder operators. Since in this parametrization hyperspherical harmonics, i.e., eigenfunctions of Λ^2 (see below), are known explicitly only for selected values of the total angular momentum,²⁰ in the general case the singularities of the kinetic energy operator cannot be removed by

harmonic expansions. For reactions with collinear transition state, a reference Hamiltonian which conserves the body frame projection J_2 and washes out the singularities for linear configurations has been used,² the residual part of the rotational energy diverging only for the symmetric top configurations ($\Theta = \pi/4$). Some calculations on this reference Hamiltonian have been carried out successfully to test the reliability of the hyperquantization algorithm for the $J > 0$ case. The explicit treatment of the general case and the relative numerical results will be presented in the future, and it will be shown that along a similar line alternative reference Hamiltonians can be defined, and a partition of Λ^2 introduced, where the singularity at $\Theta = \pi/4$ is removed, this being relevant for the study of reactions with bent transition state.

Accordingly, we will only focus on the case of total angular momentum equal to zero, where the operator in Eq. (5) simplifies to

$$\Lambda_0^2 = -\frac{1}{\sin 4\Theta} \frac{\partial}{\partial \Theta} \sin 4\Theta \frac{\partial}{\partial \Theta} - \frac{1}{\cos^2 2\Theta} \frac{\partial^2}{\partial \Phi^2}, \quad (6)$$

whose orthonormalized solutions are the functions:¹⁹

$$Y_{\lambda/2, \sigma/2, 0}(4\Theta, 2\Phi) = \left(\frac{\lambda+2}{4\pi} \right)^{1/2} \times \exp(-i\sigma\Phi) d_{\sigma/4, \sigma/4}^{\lambda/4}(4\Theta), \quad (7)$$

where $\sqrt{(\lambda+2)/4\pi}$ is the normalization factor. The quantum number λ takes the values 0, 2, 4, ... and the quantum number σ takes positive and negative values, $\sigma = -\lambda, -\lambda+4, \dots, \lambda-4, \lambda$. The reduced Wigner d functions are particular cases of Jacobi polynomials.²¹ Actually in the applications, the real linear combinations of the functions $\exp(-i\sigma\Phi)$ are taken into account, i.e., the trigonometric functions $\cos \sigma\Phi$ and $\sin \sigma\Phi$, and only positive values of σ are included. Solutions of the eigenvalue equation (4) are searched through the following expansion of the adiabatic channel wave functions Ψ_i :

$$\Psi_i = \rho^{-5/2} \sum_{\lambda\sigma} t_{i\lambda\sigma}(\rho) \left(\frac{(\lambda+2)(2-\delta_{\sigma 0})}{4\pi} \right)^{1/2} \times d_{\sigma/4, \sigma/4}^{\lambda/4}(4\Theta) \begin{cases} \cos \sigma\Phi \\ \sin \sigma\Phi \end{cases} \quad (8)$$

When two of the three atoms are equal (as in the example worked out in Part II⁷), the cosine or sine functions serve to describe symmetrical or antisymmetrical behavior with respect to the exchange of the equal atoms. When the molecule is homonuclear in the *ortho* form only the cosine functions are included in (8), while only the sine functions are taken when it is in the *para* form. Introducing this expansion in Eq. (4) the following algebraic problem is obtained:

$$\sum_{\lambda'\sigma'} \left\{ \frac{\lambda'(\lambda'+4)+15/4}{2\mu\rho^2} \delta_{\lambda\lambda'} \delta_{\sigma\sigma'} + V_{\lambda\sigma, \lambda'\sigma'}(\rho) \right\} t_{i\lambda'\sigma'}(\rho) = \varepsilon_i(\rho) t_{i\lambda\sigma}(\rho), \quad (9)$$

where the kinetic energy matrix is diagonal and the potential energy matrix is a full matrix whose elements are

$$V_{\lambda\sigma,\lambda'\sigma'}(\rho) = \int d^{\lambda/4}_{\sigma/4,\sigma'/4}(4\Theta)\cos\sigma\Phi V(\rho,\Theta,\Phi) \\ \times d^{\lambda'/4}_{\sigma'/4,\sigma'/4}(4\Theta)\cos\sigma'\Phi d\cos4\Theta d2\Phi. \quad (10)$$

In Sec. II B discrete counterparts of the harmonics in Eq. (7) are introduced to obtain a novel representation of (9) to generate eigenvalues $\varepsilon_i(\rho)$ through an orthogonal transformation on the eigenvectors $t_{i\lambda\sigma}$.

B. The asymmetric hyperangular parametrization

The asymmetric hyperangular parametrization has been used since the early days of quantum mechanics, and notably by Fock:¹⁶ the set of the angular variables ω_5 includes the hyperangle χ_k

$$\chi_k = \arctan \frac{|\mathbf{X}_k|}{|\mathbf{x}_k|} \quad (11)$$

as well as the polar angles θ_{x_k} , ϕ_{x_k} and θ_{X_k} , ϕ_{X_k} which define the orientations $\hat{\mathbf{x}}_k$ and $\hat{\mathbf{X}}_k$ of the Jacobi vectors in the center-of-mass reference frame.

The potential energy acts on a reduced manifold, and it depends only on the internal hyperspherical coordinates: the hyperradius and two hyperangles ω_{int} , which are $2\chi_k$ and the angle ϑ_k between the two Jacobi vectors ($\cos\vartheta_k = \hat{\mathbf{x}}_k \cdot \hat{\mathbf{X}}_k$). The angle χ_k varies between 0 and $\pi/2$. For the three-body problem these two angles define a hyperplane of a unit four-dimensional sphere.^{8,22}

In the following, the subscript k is omitted for simplicity, but we remark that all five angles (and ϑ_k) depend on the choice for Jacobi vectors. In this coordinate system the grand orbital angular momentum operator takes the form:

$$\Lambda^2 = -\frac{1}{\sin^2\chi \cos^2\chi} \frac{d}{d\chi} \sin^2\chi \cos^2\chi \frac{d}{d\chi} \\ + \frac{j^2}{\cos^2\chi} + \frac{\ell^2}{\sin^2\chi}, \quad (12)$$

where j^2 and ℓ^2 denote the rotational and centrifugal angular momentum operators.

The eigenfunctions of Λ^2 are the hyperspherical harmonics which in this parametrization are available in closed form:⁸

$$\Lambda^2 Y_{\lambda j/m_j m_\ell}(\omega_5) = \lambda(\lambda+4) Y_{\lambda j/m_j m_\ell}(\omega_5), \quad (13)$$

where λ , j and ℓ indicate the grand orbital, rotational and orbital angular momentum quantum numbers, respectively, and m_j and m_ℓ are the projections of j and ℓ on the center-of-mass frame quantization axis. Their explicit expression in terms of classical orthogonal polynomials is:

$$Y_{\lambda j/m_j m_\ell} = H_{\lambda j/\ell}(\chi) Y_{jm_j}(\hat{\mathbf{x}}) Y_{\ell m_\ell}(\hat{\mathbf{X}}), \quad (14)$$

where Y_{jm_j} and $Y_{\ell m_\ell}$ are spherical harmonics²¹ and

$$H_{\lambda j/\ell}(\chi) = \mathcal{N}_{\lambda j/\ell} \cos^{j+1/2}\chi \sin^{\ell+1/2}\chi P_{(\lambda-j-\ell)/2}^{\ell+1/2,j+1/2}(\cos 2\chi). \quad (15)$$

Here $P_{(\lambda-j-\ell)/2}^{\ell+1/2,j+1/2}$ is a Jacobi polynomial and $\mathcal{N}_{\lambda j/\ell}$ is a normalization factor.²¹

Hyperspherical harmonics can be properly combined to be eigenfunctions of the total angular momentum J , of its projection M onto the space fixed axis and of definite parity, $\epsilon = \pm 1$, with respect to the inversion of the coordinates:

$$Y_{\lambda j/\ell}^{JM\epsilon}(\omega_5) = H_{\lambda j/\ell}(\chi) \sum_{m_j, m_\ell} \langle jm_j \ell m_\ell | JM \rangle Y_{jm_j}(\hat{\mathbf{x}}) Y_{\ell m_\ell}(\hat{\mathbf{X}}), \quad (16)$$

where $\langle jm_j \ell m_\ell | JM \rangle$ is a vector coupling coefficients of two angular momentum and λ is an even or odd number when $\epsilon = 1$ or $\epsilon = -1$. When there are identical nuclei the additional symmetry with respect to the exchange of particles has to be considered: for homonuclear diatomic molecules only even or odd j are included if we consider ortho or para forms.

Since we can solve the eigenvalue equation (4) for solutions of each J and ϵ separately, the hyperspherical harmonics in (16) are a natural basis set for the expansion of the adiabatic function Ψ_i :

$$\Psi_i = \rho^{-5/2} \sum_{\lambda j/\ell} t_{i\lambda j/\ell}(\rho) Y_{\lambda j/\ell}^{JM\epsilon}(\omega_5). \quad (17)$$

Inserting this expansion into Eq. (4) the following system of coupled equations is obtained:

$$\sum_{\lambda' j' \ell'} \left\{ \frac{\lambda'(\lambda'+4)+15/4}{2\mu\rho^2} \delta_{\lambda\lambda'} \delta_{\ell\ell'} \delta_{jj'} + V_{\lambda j/\ell, \lambda' j' \ell'}(\rho) \right\} \\ \times t_{i\lambda' \ell' j'}(\rho) = \varepsilon_i(\rho) t_{i\lambda j/\ell}(\rho), \quad (18)$$

where the factor 15/4 comes from the elimination of the first derivative in ρ . The kinetic energy matrix is diagonal and its elements are the eigenvalues of the grand orbital angular momentum operator. The potential energy matrix elements are the multidimensional integral:

$$V_{\lambda j/\ell, \lambda' j' \ell'}(\rho, \chi) = \int d\omega_5 Y_{\lambda j/\ell}^{JM\epsilon*} V(\rho, 2\chi, \vartheta) Y_{\lambda' j' \ell'}^{JM\epsilon}. \quad (19)$$

The dependence of this integral on ϑ can be made explicit if the hyperspherical harmonics in (16) are written in terms of a “body fixed” expansion basis:

$$Y_{\lambda j/\ell}^{JM\epsilon} = H_{\lambda j/\ell}(\chi) \sum_{\Omega} G_{j/\ell\Omega}^{J\epsilon} [D_{M\Omega}^J + \epsilon(-)^{J+\Omega} D_{M-\Omega}^J] \\ \times Y_{j\Omega}(\vartheta, 0), \quad (20)$$

where $Y_{j\Omega}(\vartheta, 0)$ is a spherical harmonic and $D_{M\Omega}^J$ is a symmetric top wave function. The latter depends on the Euler angles which specify the orientation of the center-of-mass reference frame with respect to a rotating frame whose quantization axis is chosen to be in the same direction as the Jacobi vector \mathbf{X}_k . The quantities $G_{j/\ell\Omega}^{J\epsilon}$ are the coefficients

for the transformation from the center-of-mass reference frame to the body frame²³ and are related to $3j$ symbols:

$$G_{j/\Omega}^{J\epsilon} = (-)^{J+\Omega} [(2\ell+1)(2-\delta_{\Omega 0})]^{1/2} \begin{pmatrix} j & J & \ell \\ \Omega & -\Omega & 0 \end{pmatrix}. \quad (21)$$

The body frame component Ω of the total angular momentum takes only non-negative values, and this encompasses the correct behavior under inversion of all coordinates.

When J is zero (and thus both $j=\ell$ and $\Omega=0$), the hyperspherical harmonics in Eq. (16) or (20) simplify to

$$Y_{\lambda/2,j,0}(2\chi, \vartheta, 0) = \mathcal{N}_{\lambda/2,j} \sin^{j+1/2} 2\chi C_{(\lambda/2)-j}^{j+(1/2)}(\cos 2\chi) P_j(\cos \vartheta), \quad (22)$$

where $C_{(\lambda/2)-j}^{j+(1/2)}$ is a Gegenbauer polynomial and P_j is a Legendre polynomial. The normalization factor $\mathcal{N}_{\lambda/2,j}$ ¹³ is referred to an integration over the volume element $d \cos 2\chi d \cos \vartheta$.

Inserting (20) into (19), the following alternative expression of the multidimensional integrals is obtained:

$$\begin{aligned} V_{\lambda j \ell, \lambda' j' \ell'}(\rho, \chi) &= \sum_{\Omega \Omega'} G_{j/\Omega}^{J\Omega} G_{j'/\Omega'}^{J'\Omega'} \delta_{\Omega \Omega'} \\ &\times \int_{-1}^1 d \cos 2\chi H_{\lambda j \ell}(\chi) H_{\lambda' j' \ell'}(\chi) \\ &\times \int_{-1}^1 d \cos \vartheta Y_{j/\Omega}^*(\vartheta, 0) V(\rho, 2\chi, \vartheta) \\ &\times Y_{j'/\Omega'}(\vartheta, 0). \end{aligned} \quad (23)$$

Here $\delta_{\Omega \Omega'}$ is the result of the integration over the Euler angles.

In the application of the formalism illustrated above two main problems arise: the calculation of the integrals in (23) and the slow convergence of the expansion (17). In order to produce results of quantitative accuracy very large matrices must be built, stored and diagonalized. In Sec. III C we propose a novel representation of the algebraic problem in Eq. (18) whose main feature is the sparseness of the Hamiltonian matrix to be diagonalized. This goal is achieved exploiting the discrete analogs of hyperspherical harmonics, as shown in the Sec. III. For the asymmetric hyperangular parametrization the hyperspherical harmonics are known in closed form [Eq. (14)] for any value of the total angular momentum,⁸ and the singularities in the kinetic energy operator can be eliminated for all configurations.

III. THE HYPERQUANTIZATION ALGORITHM

In the following we present a technique to solve the eigenvalue problem parametric in ρ in the two internal hyperangles, both in asymmetric and symmetric hyperangular parametrizations. The algorithm is based on the discrete analogs of hyperspherical harmonics, i.e., generalized vector coupling coefficients or Hahn polynomials, and allows us to obtain alternative representations of Eqs. (9) and (18) in which the potential energy matrix is diagonal and the couplings are transferred to the kinetic energy. Moreover, no

integrals have to be computed since the potential energy matrix elements are the values of the potential energy surface on a lattice of equally spaced points specified by the discrete values of $\cos 4\Theta$ and Φ or $\cos 2\chi$ and $\cos \vartheta$ for the symmetric and asymmetric hyperspherical representations, respectively.

A. The Hahn polynomials as discrete analogs of hyperspherical harmonics

In Sec. II we have illustrated how hyperspherical harmonics [see Eqs. (7) and (20)] can be used as expansion basis sets in the quantum mechanics of three bodies. It has been pointed out that both in the asymmetric and symmetric hyperangular parametrizations, they are related to classical orthonormal polynomials, whose more general class are the Jacobi polynomials. Here we define their discrete analogs as the product of functions orthonormal on a set of grid points expressed explicitly in terms of Hahn polynomials, which can be physically interpreted as generalized $3j$ coefficients.¹² The latter enjoy many properties, in particular recurrence equations with respect to the discrete variable, which simplify both the algebra and the explicit calculations.

The Jacobi polynomials $P_n^{\alpha, \beta}(\cos \theta)$ and their special cases (Gegenbauer and Legendre polynomials, Wigner d functions) are related to the Hahn polynomials $Q_n(\xi, \alpha, \beta, X)$,²⁴ i.e., functions of a discrete variable ξ orthonormal on a set of $X+1$ points, by the following limiting relation

$$\begin{aligned} \lim_{X \rightarrow \infty} \left(\frac{X+1}{2} \right)^{1/2} Q_{n, \xi}^{\alpha, \beta, X} \\ = \mathcal{N}_{n\alpha\beta} \cos^\beta \frac{\theta}{2} \sin^\alpha \frac{\theta}{2} P_n^{\alpha, \beta}(\cos \theta), \end{aligned} \quad (24)$$

where

$$Q_{n, \xi}^{\alpha, \beta, X} = \sqrt{w(\xi)} \pi_n Q_n(\xi, \alpha, \beta, X), \quad (25)$$

and

$$\cos \theta = \frac{X-2\xi}{X+1}, \quad (26)$$

where ξ is the discrete variable, n the degree of the polynomial and both vary in the range $0 \leq n, \xi \leq X$ (X being a positive integer). Both parameters α and β are greater than -1 . For the normalization factor in Eq. (24) see Ref. 22, for the weight function $w(\xi)$ and the norm π_n of Hahn polynomial in Eq. (25), see Ref. 12. For the important case of the Wigner d functions, extensively used in our applications, we illustrate in Fig. 1 how their discrete counterparts converge to them.

The Hahn coefficients defined above satisfy the following difference equation:²⁴

$$C(\xi) Q_{n, \xi-1}^{\alpha, \beta, X} + D(\xi) Q_{n, \xi}^{\alpha, \beta, X} + C(\xi+1) Q_{n, \xi+1}^{\alpha, \beta, X} = 0, \quad (27)$$

where

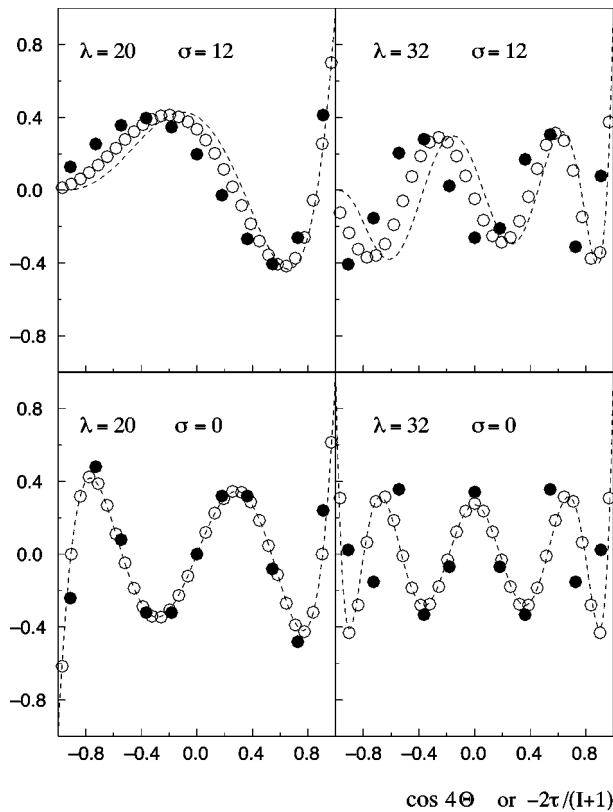


FIG. 1. Illustration of the relationship (36) between generalized vector coupling (or Hahn) coefficients and Wigner d functions. Dashed lines represent values of $d_{(\sigma/4)(\sigma/4)}^{(\lambda/4)}(4\Theta)$ [Eq. (4.1.15), p. 57 of Ref. 21] as a function of $\cos 4\Theta$. Closed and open circles correspond to Hahn coefficients $Q_{(\lambda-\sigma)/4,\tau}^{0,(\sigma/2),I}$ multiplied by $[2(I+1)/(\lambda+2)]^{1/2}$ for $I=10$ and 30 , respectively, as functions of $-2\tau/(I+1)$. The panels differ for the indicated values of λ and σ .

$$D(\xi) = n(n + \alpha + \beta + 1) - (\alpha + \xi + 1)(X - \xi) - \xi(X + \beta - \xi + 1), \quad (28)$$

$$C(\xi) = [\xi(\alpha + \xi)(X - \xi + 1)(X + \beta - \xi + 1)]^{1/2}, \quad (29)$$

and constitute an orthonormal set with respect to both ξ and n :

$$\sum_{\xi=0}^X Q_{n,\xi}^{\alpha,\beta,X} Q_{n',\xi}^{\alpha,\beta,X} = \delta_{nn'}, \quad (30)$$

and

$$\sum_{n=0}^X Q_{n,\xi}^{\alpha,\beta,X} Q_{n,\xi'}^{\alpha,\beta,X} = \delta_{\xi\xi'}. \quad (31)$$

The orthogonality and dual orthogonality properties, together with the recurrence relation (27), will be exploited in Sec. III B and are responsible for the sparseness of the Hamiltonian matrix to be diagonalized in the hyperquantization algorithm. Equations (30) and (31) define the discrete analogs of the orthogonality and completeness relations for hyperspherical harmonics.

In a previous paper¹² we have written explicitly on the relationship of Hahn coefficients with generalized angular momentum coupling coefficients:

$$\begin{pmatrix} n + \frac{\alpha + \beta}{2} & \frac{X}{2} + \frac{\alpha}{2} & \frac{X}{2} + \frac{\beta}{2} \\ \frac{\alpha + \beta}{2} & \frac{X}{2} - \frac{\alpha}{2} - \xi & -\frac{X}{2} - \frac{\beta}{2} + \xi \end{pmatrix} = \exp[i\pi(2n + \beta - \xi)](2n + \alpha + \beta + 1)^{-1/2} Q_{n,\xi}^{\alpha,\beta,X}. \quad (32)$$

This alternative form of writing the Hahn polynomials points out the link between (hyper)angular momentum theory and discrete orthogonal polynomials and serves to determine their symmetry properties. When α and β are integers the $3j$ symbol is an ordinary vector coupling coefficient, otherwise it is referred to as a “generalized” vector coupling coefficient.

When asymmetric hyperspherical coordinates are used, the potential energy depends on the two internal angles χ and ϑ . The grid points that span the interaction region are chosen so to have a lattice of equally spaced points in $\cos 2\chi$ and $\cos \vartheta$. A set of functions orthonormal with respect to such a grid is accomplished by specializing the limiting relation (24) to the Jacobi polynomials which explicitly define the hyperspherical harmonics in Eq. (20). For the polynomial $P_{(\lambda-j-\ell)/2}^{(\ell+1/2),j+(1/2)}(\cos 2\chi)$ the corresponding Hahn coefficient is established by setting $n = (\lambda - j - \ell)/2$, $\alpha = \ell + \frac{1}{2}$, $\beta = j + \frac{1}{2}$ and $X = I$ in Eq. (24):

$$\begin{aligned} \left(\frac{I+1}{2}\right)^{-1/2} H_{\lambda,j,\ell}(\chi) &\sim Q_{(\lambda-j-\ell)/2,\tau}^{\ell+1/2,j+1/2,I} \\ &= \exp\{i\pi[\tau - \lambda + j + (I+1)/2]\}(\lambda+2)^{1/2} \\ &\times \begin{pmatrix} \frac{\lambda}{2} + \frac{1}{2} & \frac{I}{2} + \frac{\ell}{2} + \frac{1}{4} & \frac{I}{2} + \frac{j}{2} + \frac{1}{4} \\ \frac{j+\ell}{2} + \frac{1}{2} & \tau - \frac{\ell}{2} - \frac{1}{4} & -\tau - \frac{j}{2} - \frac{1}{4} \end{pmatrix}, \quad (33) \end{aligned}$$

where $\tau = \xi - (I/2)$ denotes the discrete variable: according to this definition τ ranges in the interval $[-(I/2), (I/2)]$ and can be interpreted as the projection of an artificial angular momentum whose length is $(I+1)/2$ in the semiclassical limit, i.e., for I large.^{10,11} The τ values select the grid points for the angle χ .

Exploiting the relation connecting spherical harmonics $Y_{j\Omega}(\vartheta, 0)$ with Jacobi polynomials,²¹ from Eqs. (24) and (32) we identify the discrete analog of a spherical harmonic with a vector coupling coefficient:

$$\begin{aligned} \left(\frac{N+1}{2}\right)^{-1/2} Y_{j\Omega}(\vartheta, 0) &\sim Q_{j-\Omega,\nu}^{\Omega,\Omega,N} \\ &= (-)^{N/2-\nu-j-\Omega} (2j+1)^{1/2} \begin{pmatrix} \frac{N}{2} & \frac{N}{2} + \Omega & j \\ \nu & -\nu & 0 \end{pmatrix}, \quad (34) \end{aligned}$$

where $n = j - \Omega$, $\alpha = \beta = \Omega$ and $X = N$. In deriving the above equation use of a Regge symmetry for the $3j$ symbols has been made. The discrete variable is $\nu = \xi - (N/2)$ with $(-N + \Omega)/2 \leq \nu \leq (N - \Omega)/2$. The number of grid points in

the angle ϑ depend on the projection Ω of the total angular momentum along the quantization axis. The number ν has been interpreted as the steric quantum number.²⁵ For a given triatomic reaction, a stereodirected representation of the scattering matrix can be introduced where the number ν is defined so as to specify the orientation of the atom attacking the target molecule.²⁶

In the important case of total angular momentum equal to zero, discrete analogs of four-dimensional harmonics in Eq. (22) (see also Ref. 8) are obtained simply by taking $j=\ell$ in Eq. (33) and $\Omega=0$ in Eq. (34):

$$Y_{\lambda/2,j,0}(2\chi_\tau, \vartheta_\nu, 0) \sim [(N+1)(I+1)/4]^{1/2} Q_{(\lambda/2)-j,\tau}^{j+1/2,j+1/2,I} Q_{j\nu}^{00N}. \quad (35)$$

In Refs. 12 and 25, the discrete analogs of four-dimensional and spherical harmonics have been explicitly given and the validity of the relations (34) and (35) has been studied as a function of I and N . The Hahn coefficients in Eqs. (33)–(35) are used to derive the hyperquantization algorithm in the asymmetric hyperangular parametrization (see Sec. III C), and will serve to define the elements of the orthogonal transformation which will provide the discrete representation for the eigenvalue problem in Eq. (18).

In the following, we discuss the discretization of the hyperspherical harmonics $Y_{\lambda/2,\sigma/2,0}$ in Eq. (7), which are needed as the eigenfunctions of the kinetic energy operator for $J=0$, when symmetric hyperangular coordinates are employed, the lattice consisting of equally spaced points in $\cos 4\Theta$ and Φ . The function $d_{(\sigma/4)(\sigma/4)}^{\lambda/4}(4\Theta)$ in Eq. (7) is again a particular case of Jacobi polynomials,²¹ its discrete analog is obtained from the limit relation (24) by replacing $\alpha=|\sigma|/2$, $\beta=0$ and $n=(\lambda-|\sigma|)/4$

$$\begin{aligned} \left(\frac{I+1}{2}\right)^{-1/2} \left(\frac{\lambda}{2}+1\right)^{1/2} d_{(\sigma/4)(\sigma/4)}^{\lambda/4}(4\Theta_\tau) &\sim Q_{(\lambda-\sigma)/4,\tau}^{\sigma/2,0,I} \\ &= (-)^{I/2+\tau-\lambda/2} \left(\frac{\lambda}{2}+1\right)^{1/2} \begin{pmatrix} \frac{I}{2} & \frac{I}{2}+\frac{\sigma}{4} & \frac{\lambda}{4} \\ -\tau & \tau-\frac{\sigma}{4} & \frac{\sigma}{4} \end{pmatrix}. \end{aligned} \quad (36)$$

In Fig. 1 we give a graphical representation of the relation (36), we plot both the $d_{(\sigma/4)(\sigma/4)}^{\lambda/4}(4\Theta)$ functions and the Hahn coefficients as a function of $\cos 4\Theta$ at different values of I . From these plots we observe that when $\sigma \ll \lambda$ a small grid ($I=30$ in the figure) is sufficient to reproduce accurately the d functions. When σ increases the convergence is slower and large values of I are required.

In order to find the discrete counterparts of the functions $\exp i\sigma\Phi$, or of the real combinations $\cos \sigma\Phi$ and $\sin \sigma\Phi$ with σ an even non-negative integer (in the following σ is used in place of $|\sigma|$ to simplify the notation), a different procedure is required.²⁷ The kinematic angle varies in the range $0 \leq 2\Phi < 2\pi$. For reactions with two identical atoms, such as those involving a homonuclear molecule, the exchange symmetry allows to halve the interval and we divide the range of Φ into N equally spaced points:

$$\Phi_\nu = \frac{\pi\nu}{2N}; \quad \nu=0,\dots,N \quad (37)$$

and define the discrete analog of the cosine functions as follows:

$$f_{\sigma/2,\nu}^N = \left(\frac{2}{N(1+\delta_{\nu 0})(1+\delta_{\sigma/2,0})(1+\delta_{\nu N})(1+\delta_{\sigma/2,N})} \right)^{1/2} \times \cos \frac{\sigma\pi\nu}{2N} \quad (38)$$

with $\sigma/2=0,\dots,N$. The $f_{(\sigma/2)\nu}^N$ coefficients are orthonormal

$$\sum_{\nu=0}^N f_{\sigma/2,\nu}^N f_{\sigma'/2,\nu}^N = \delta_{\sigma\sigma'} \quad (39)$$

and moreover also enjoy a dual orthogonality property

$$\sum_{\sigma/2=0}^N f_{\sigma/2,\nu}^N f_{\sigma/2,\nu'}^N = \delta_{\nu\nu'} \quad (40)$$

Equations (36) and (38), needed in the hyperquantization algorithm to carry out reactive scattering calculations in symmetric hyperspherical coordinates, will be amply exploited in the Sec. III B where we show how to use the discrete analogs of the hyperspherical harmonics in Eq. (7) to put the quantization problem in Eq. (9) into a novel form suitable for numerical applications (see Part II⁷).

B. The symmetric hyperangular parametrization

The development of the hyperquantization algorithm in the symmetric hyperangular parametrization is based on the transformation of the eigenvectors $t_{in'\sigma'}$ in Eq. (9) so to obtain new eigenvectors $t_{i\tau'\nu'}$ labeled by the discrete variables τ' and ν' :

$$t_{in'\sigma'}(\rho) = \sum_{\tau'\nu'} Q_{n'\tau'}^{\sigma'/2,0,I} f_{\sigma/2,\nu'}^N t_{i\tau'\nu'}(\rho), \quad (41)$$

where $n'=(\lambda'-\sigma')/4$ denotes the degree of the Hahn polynomial and ranges from zero to I . The coefficients $Q_{n'\tau'}^{(\sigma'/2)0I}$ and $f_{(\sigma'/2)\nu'}^N$ have been defined in Eqs. (36) and (38). Through the use of discrete analogs of the harmonics in Eq. (7) we will obtain a very sparse and symmetric matrix representation for the kinetic energy while similarly to discrete variable representation²⁸ the potential energy matrix will be represented as a diagonal matrix.

When the transformation in (41) is inserted into (9), multiplying the left-hand side by $f_{(\sigma/2)\nu}^N Q_{n\tau}^{(\sigma/2)0I}$ and summing over n and σ , the elements of the kinetic energy matrix are explicitly given by:

$$K_{\tau\nu,\tau'\nu'} = \frac{1}{2\mu\rho^2} \sum_{n\sigma} f_{\sigma/2,\nu}^N Q_{n\tau}^{\sigma/2,0,I} [16n(n+\sigma/2+1) + \sigma(\sigma+4)+15/4] Q_{n\tau'}^{\sigma/2,0,I} f_{\sigma/2,\nu'}^N. \quad (42)$$

The sum over n can be performed analytically by exploiting Eq. (27); the result is a tridiagonal matrix with respect to the discrete variable τ .

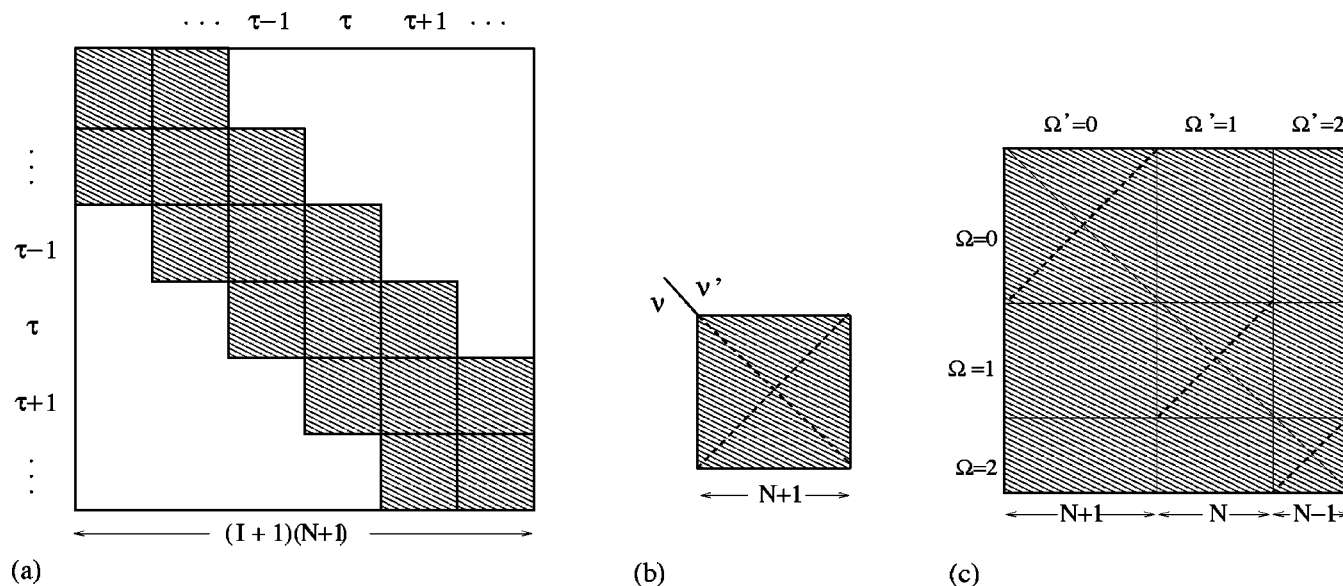


FIG. 2. Panel (a) illustrates the block-tridiagonal structure of the kinetic energy matrix. When $J=0$ each block [symmetric with respect to both the main and the secondary diagonals, see panel (b)] is of dimension $N+1$; the dashed lines indicate mirror symmetries. Panel (c) refers to the asymmetric case only and shows the structure of the a single block for $J=2$ and $\epsilon=1$, each sub-block enjoying the symmetries given in Eq. (62).

$$K_{\tau\nu,\tau'\nu'} = \frac{1}{2\mu\rho^2} \sum_{\sigma} f_{\sigma/2,\nu}^N [-C(\tau')\delta_{\tau,\tau'-1} + B(\tau')\delta_{\tau\tau'} - C(\tau'+1)\delta_{\tau,\tau'+1}] f_{\sigma/2,\nu'}^N, \quad (43)$$

where

$$B(\tau) = \sigma(\sigma+4) + 15/4 + 16[I(I/2+1) - 2\tau^2 + (I/2-\tau)\sigma/2] \quad (44)$$

are the elements along the main diagonal, and $C(\tau)$ and $C(\tau+1)$, already defined in Eq. (29),

$$C(\tau) = -16(I/2 - \tau + 1) \times [(I/2 + \tau)(I/2 + \tau + \sigma/2)]^{1/2} \quad (45)$$

specify the elements of the lower and upper tridiagonals, respectively. No computational effort is required at this step, being the sum over the quantum number n is performed analytically.

In (43) the sum over σ is made numerically evaluating trigonometric functions at the lattice points. The kinetic energy matrix, as shown in Fig. 2(a), is block tridiagonal. Diagonal blocks refer to different τ values; off diagonal blocks couple different grid points belonging to τ and $\tau \pm 1$. Inside each block, which are full, we have the couplings of different grid points labeled by the discrete variable ν , see Fig. 2(b).

The kinetic energy matrix is obviously symmetric. For reactions involving three different atoms the blocks are also symmetric with respect to the secondary diagonals, and the elements along all the diagonals are constant (circulant matrices). In the case of triatomic systems with two identical particles, from Eqs. (44) and (45), and exploiting the periodicity of trigonometric functions, we obtain that within each block

$$K_{\tau\nu,\tau'\nu'} = K_{\tau\nu',\tau'\nu} = K_{\tau(N-\nu),\tau'(N-\nu')} = K_{\tau(N-\nu'),\tau'(N-\nu)}. \quad (46)$$

Therefore, as illustrated in panel (b) of Fig. 2 the blocks are symmetric matrices with respect to both the main and secondary diagonals. This property allows a reduction of the number of elements to be calculated: only one out of four elements suffices to define the kinetic energy matrix. Moreover, when $\nu + \nu'$ is an even number

$$K_{\tau\nu,\tau'\nu'} = K_{\tau'\nu,\tau'\nu'} \quad (47)$$

and the kinetic energy matrix elements are the same for any τ .

By applying the orthogonal transformation in (41) to the potential energy matrix $V_{n\sigma n'\sigma'}$ defined in Eq. (10) we have:

$$V(\rho, 4\Theta, 2\Phi, \nu) = \sum_{nn'\sigma\sigma'} f_{\sigma/2,\nu}^N Q_{n\tau}^{\sigma/2,0,I} V_{n\sigma n'\sigma'}(\rho) \times Q_{n'\tau'}^{\sigma'/2,0,I} f_{\sigma'/2,\nu'}^N. \quad (48)$$

For large I , the sum over n (and n') is

$$\sum_n Q_{n\tau}^{\sigma/2,0,I} (\lambda/2 + 1)^{1/2} d_{\sigma/4,\sigma/4}^{\lambda/4} (4\Theta) \sim \left(\frac{I+1}{2}\right)^{1/2} \delta\left(4\Theta + \frac{2\tau}{I+1}\right) \quad (49)$$

and for large N , the sum over σ (and σ') is

$$\sum_{\sigma} \cos \sigma \Phi f_{\sigma/2, \nu}^N \sim \delta \left(2\Phi - \frac{\pi \nu}{N} \right). \quad (50)$$

For chemical reactions involving a homonuclear molecule only either sine or cosine functions are included as required to ensure the correct behavior with respect to the exchange of identical particles.

The potential energy matrix is diagonal and its elements are the values of the potential energy surface

$$\begin{aligned} V(\rho, 4\Theta_{\tau}, 2\Phi_{\nu}) \\ = \delta_{\tau\tau'} \delta_{\nu\nu'} \int V(\rho, 4\Theta, 2\Phi) \delta \left(\cos 4\Theta + \frac{2\tau'}{I+1} \right) \\ \times \delta \left(2\Phi - \frac{\pi \nu'}{N} \right) d \cos 4\Theta d 2\Phi \end{aligned} \quad (51)$$

at the lattice points selected by

$$\cos 4\Theta = \frac{-2\tau}{I+1} \quad (52)$$

and

$$\Phi = \frac{\pi \nu}{2N}. \quad (53)$$

In conclusion, in the symmetric hyperangular parametrization, we have to solve the following algebraic problem

$$\begin{aligned} \sum_{\tau' \nu'} [K_{\tau \nu \tau' \nu'} + V(\rho, 4\Theta_{\tau'}, 2\Phi_{\nu'}) \delta_{\tau\tau'} \delta_{\nu\nu'}] t_{i\tau' \nu'}(\rho) \\ = \varepsilon_i t_{i\tau \nu}(\rho) \end{aligned} \quad (54)$$

(where $K_{\tau \nu \tau' \nu'}$ is tridiagonal in τ) to compute the potential energy curves ε_i as function of ρ (see Ref. 7 for numerical implementations and results).

From the numerical point of view the hyperquantization algorithm efficiency is strictly related to the block tridiagonal structure of the kinetic energy matrix, see Fig. 2(a), which contains the coupling between points labeled by $\tau\nu$ and $\tau'\nu'$ on the surface of the hypersphere. This sparseness represents the main computational advantage of our procedure. The dimension of the matrix is $(I+1)(N+1)$, where $I+1$ and $N+1$ are the grid points of the angles Θ and Φ labeled by τ and ν , respectively, but the number of elements different from zero is only $3(I+1)(N+1)^2$. In our sample calculations of $F+H_2$,⁷ convergence typically requires I to be on the order of 10^3 and only 0.3% of the elements are different from zero. The percent of sparseness is on the average on the order of 99.7% and can be further increased, taking into account the stereospecificity of our discrete bases. Contributions to the reduction of the numbers of elements to be stored and manipulated come from the relative magnitude of the potential and kinetic energy matrix elements.

The computation of the matrix elements in (43) has revealed that for large values of the hyperradius each ν is coupled only with those ν' which are closer to it. In other words, each block of the kinetic energy matrix is strongly diagonally dominated. We take advantage of this by setting equal to zero the couplings for which $\nu - \nu'$ is larger than a

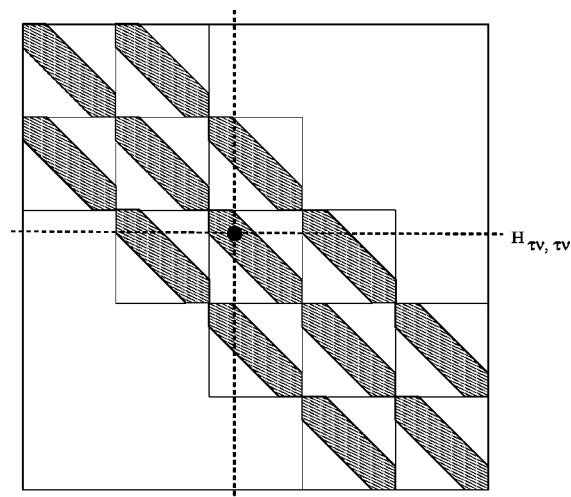


FIG. 3. Illustration of the sparseness of the Hamiltonian matrix: White and filled areas represent zero and nonzero elements, respectively. When an element $H_{\tau\nu, \tau\nu}$ on the main diagonal, corresponds to a potential energy greater than V_{\max} , the corresponding row and column are cut off and the dimension of the matrix is lowered. Being each block strongly diagonally dominated, the elements $H_{\tau\nu, \tau' \nu'}$ far from the main diagonal can be negligibly small, and we can cancel all those elements for which $\nu - \nu'$ is larger than a parameter D_{corner} , obtained by convergence tests. White areas inside each block illustrate qualitatively the extent of this reduction.

fixed value D_{corner} to be determined by numerical convergence experiments. Physically, this corresponds to setting to zero all couplings between points far away on the hypersphere and is a direct consequence of the stereospecificity of our bases. Typically, in our calculations⁷ the number of diagonals to be kept within each block are about 20% of the total and this corresponds to a reduction of about 60% of the elements to be stored. The efficiency of this reduction is qualitatively illustrated in Fig. 3.

The dimension of the Hamiltonian matrix can be further reduced by cutting off the row and the column corresponding to the element $H_{\tau\nu, \tau\nu}$ for which the potential energy $V(\rho, 4\Theta_{\tau}, 2\Phi_{\nu})$ is larger than a fixed value V_{\max} , determined from numerical convergence of the eigenvalues, (see Fig. 3). With this strategy, those regions on the surface of the hypersphere which are not relevant in the dynamics can be eliminated. The points $\tau\nu$ on the hypersphere where the potential energy surface is large in comparison with the kinetic energy can be eliminated, being the eigenvectors there are negligibly small. This is a natural reduction of the basis set. The extent of this reduction varies greatly with the hyperradius: for the $F+H_2 \rightarrow HF+H$ reaction, it ranges from 85% to 15% as ρ increases.⁷ The maximum efficiency is obtained in the reactant and product valleys, which are strongly localized on restricted areas on the surface of the hypersphere.

C. The asymmetric hyperangular parametrization

The hyperquantization algorithm in the asymmetric hyperangular parametrization is derived along the same line. In this case, the labels τ and ν for the eigenvectors now define the grid points of the internal angles χ and ϑ , respectively. The orthogonal transformation on the eigenvectors $t_{in' \ell' j'}$ in Eq. (18) is:

$$t_{in',\ell',j'}(\rho) = \sum_{\Omega',\tau',\nu'} Q_{j'-\Omega',\nu'}^{\Omega',\Omega',N} G_{j',\ell',\Omega'}^{J\epsilon} Q_{n',\tau'}^{\ell'+1/2,j'+1/2,I} \times t_{i\Omega',\tau',\nu'}(\rho), \quad (55)$$

where the grand angular momentum quantum number, λ , has been replaced by $2n+j+\ell$. Here the Hahn coefficients $Q_{n',\tau'}^{\ell'+(1/2),j'+(1/2),I}$ and $Q_{j'-\Omega',\nu'}^{\Omega',\Omega',N}$ are those defined in Eqs. (33) and (34), respectively, and $G_{j',\ell',\Omega'}^{J\epsilon}$ accounts for the transformation from space fixed frame to body fixed frame [see Eq. (21)].

When the transformation (55) is inserted into the eigenvalue problem in (18), multiplying the left-hand side by $Q_{j-\Omega,\nu}^{\Omega,\Omega,N} G_{j,\ell,\Omega}^{J\epsilon} Q_{n\tau}^{\ell+(1/2),j+(1/2),I}$ and summing over n, j and ℓ we obtain a new algebraic system:

$$\sum_{\Omega',\tau',\nu'} [K_{\Omega\tau\nu\Omega'\tau'\nu'} + V(\rho\chi\tau\vartheta_\nu)\delta_{\Omega\Omega'}\delta_{\tau\tau'}\delta_{\nu\nu'}] t_{i\Omega',\tau',\nu'}(\rho) = \varepsilon_i(\rho) t_{i\Omega\tau\nu}(\rho), \quad (56)$$

where, as in the symmetric case, the kinetic energy matrix turns out to be block tridiagonal, [see Fig. 2(a)]. The potential energy matrix is again diagonal and the kinetic energy matrix elements are explicitly:

$$K_{\Omega\tau\nu\Omega'\tau'\nu'} = \frac{1}{2\mu\rho^2} \sum_{nj\ell} Q_{j-\Omega,\nu}^{\Omega,\Omega,N} G_{j,\ell,\Omega}^{J\epsilon} Q_{n\tau}^{\ell+1/2,j+1/2,I} \times [4n(n+\ell+j+2) + (\ell+j)(\ell+j+4) + 15/4] Q_{n\tau'}^{\ell+1/2,j+1/2,I} \times G_{j,\ell,\Omega'}^{J\epsilon} Q_{j-\Omega',\nu'}^{\Omega',\Omega',N}. \quad (57)$$

For a given value of the total angular momentum J and parity ϵ , the sum over $n=0,\dots,I$ can be performed analytically by making use of the fact that the Hahn coefficients $Q_{n\tau}^{j+(1/2),\ell+(1/2),I}$ satisfy the difference equation (27) and the dual orthogonality relation (31). For j and ℓ fixed, only points with $\tau'=\tau$ and $\tau'=\tau\pm 1$ are coupled and the only elements different from zero are:

$$C(\tau) = -[(I+2\tau+2) \times (I-2\tau)(I-2\tau+2j+1)(I+2\tau+2\ell+3)]^{1/2}, \quad (58)$$

$$B(\tau) = 2(I-2\tau)(I+2\tau) + 2I(j+\ell+3) + (j+I)(j+\ell+4) + 15/4,$$

where $B(\tau)$ defines the elements in the main diagonal, $C(\tau+1)$ and $C(\tau)$ are the elements in the upper and lower tridiagonals, respectively. The sums over j and ℓ have to be calculated numerically, in particular the vector coupling coefficients $Q_{j-\Omega,\nu}^{\Omega,\Omega,N}$ and $G_{j,\ell,\Omega}^{J\epsilon}$ need be evaluated. The rotational quantum number j takes the values Ω,\dots,N and the orbital quantum number ℓ takes values which are compatible with the values of j and J previously fixed, see Eq. (21).

As for the previous case, let us comment on the symmetry properties of the kinetic energy matrix. The special case

of total angular momentum equal to zero deserves a separate discussion. When $J=0$, being also $j=\ell$, from Eq. (58) we note that:

$$C(\tau) = C(-\tau+1), \quad B(\tau) = B(-\tau), \quad (59)$$

these equations demonstrate that the kinetic energy matrix is symmetric with respect to both the main and secondary diagonals:

$$K_{\tau\nu,\tau'\nu'} = K_{\tau'\nu,\tau\nu'} = K_{-\tau\nu,-\tau'\nu'}. \quad (60)$$

From the symmetry of the $3j$ symbols when the signs of all three projections are reversed we have $Q_{j,\nu}^{00N} = (-)^{N-j} Q_{j,-\nu}^{00N}$ and therefore each block of the kinetic energy matrix is also symmetric with respect to both the main and the secondary diagonals:

$$K_{\tau\nu,\tau'\nu'} = K_{\tau\nu',\tau'\nu} = K_{\pi(-\nu),\pi'(-\nu')}. \quad (61)$$

In this case only one element out of 16 has to be evaluated and stored. For reactions where two atoms are equal, as for $A+B_2$, the exchange of identical nuclei has to be taken into account. The potential energy is now symmetric with respect to $\vartheta=\pi/2$ and, therefore, also with respect to a sign change for the discrete variable ν , which thus can be limited to non-negative values. The dimension of the matrix is halved and the number of elements to be stored is reduced to one quarter of the total. When B is heavier than A, as an alternative to the Jacobi coordinates, it may be useful to have the asymmetric parametrization of the Radau–Smith^{14,29} coordinates centered on the B atom. In this coordinate system the potential energy is symmetric with respect to $\chi=\pi/4$ or equivalently with respect to exchange of τ with $-\tau$. Only non-negative values of τ are involved with a reduction to one half both for the matrix dimension and for the number of elements.

When the total angular momentum is different from zero, Eq. (59) is not valid and the kinetic energy matrix loses its centrosymmetry. Inside a block [a diagonally dominated matrix of dimension $(J+1)(N+1)-J(J+1)/2$] we can identify sub-blocks labeled by $\Omega\Omega'$ as shown in Fig. 2(c) for the particular case $J=2$ and $\epsilon=+1$. In each sub-block, from the properties of the $3j$ symbol when we reverse the signs of all three projections we have

$$K_{\Omega\tau\nu,\Omega'\tau'\nu'} = (-1)^{\Omega+\Omega'} K_{\Omega\tau(-\nu),\Omega'\tau'(-\nu')}. \quad (62)$$

If $\Omega+\Omega'$ is an even number the sub-blocks are centrosymmetric and if it is an odd number they are skew-symmetric. The symmetry with respect to the main diagonal holds when $\Omega=\Omega'$. Moreover, by the fact that $B(\tau)$ depends separately on τ and on j and ℓ and that the Hahn coefficients $Q_{j-\Omega,\nu}^{\Omega,\Omega,N}$ enjoy the dual orthogonality with respect to j , the off-diagonal elements of the blocks along the main diagonal, $K_{\tau\nu,\tau\nu'}$, are independent of τ and replicate at different values of the discrete variable:

$$K_{\tau\nu,\tau\nu'} = K_{\tau'\nu,\tau'\nu'} \quad (63)$$

so the dependence on τ is exhibited only through the elements on the main diagonal.

It will next be shown that the potential energy will be represented by a diagonal matrix, whose elements are the

values of the potential energy surface $V(\rho\chi_\tau\vartheta_\nu)$ at the grid points labeled by the discrete variables τ and ν . We write:

$$V(\rho\chi_\tau\vartheta_\nu) = \sum_{nn'jj'\ell\ell'} Q_{j-\Omega,\nu}^{\Omega\Omega N} G_{j'\ell'\Omega}^{J\epsilon} Q_{n\tau}^{\ell'+1/2,j'+1/2,I} \\ \times V_{nj\ell n'j'\ell'} Q_{n'\tau'}^{\ell'+1/2,j'+1/2,I} G_{j'\ell'\Omega}^{J\epsilon} Q_{j'-\Omega',\nu'}^{\Omega'\Omega'N}, \quad (64)$$

where for $V_{nj\ell n'j'\ell'}$ we use the expressions given in Eq. (23). The summation over the labels n (and n') gives

$$\sum_n Q_{n\tau}^{\ell'+1/2,j'+1/2,I} H_{nj\ell}(\chi) \sim \left(\frac{I+1}{2}\right)^{1/2} \delta\left(\cos\chi + \frac{2\tau}{I+1}\right) \quad (65)$$

and the summation over j and j' gives

$$\sum_j Q_{j-\Omega,\nu}^{\Omega\Omega N} Y_{j\Omega}(\vartheta,0) \sim \left(\frac{N+1}{2}\right)^{1/2} \delta\left(\cos\vartheta + \frac{2\nu}{N+1}\right). \quad (66)$$

The summations over the orbital quantum numbers ℓ and ℓ' involve the coefficients of the transformation from space fixed frame to body fixed frame:

$$\sum_{\ell} G_{j\ell\Omega}^{J\epsilon} G_{j'\ell'\Omega}^{J\epsilon} = \delta_{\Omega\Omega'} \quad (67)$$

(an analogous relation is valid for ℓ'). The potential energy matrix elements

$$V_{\tau\nu} = \delta_{\tau\tau'} \delta_{\nu\nu'} \int V(\rho\chi\vartheta) \delta\left(\cos\chi + \frac{2\tau'}{I+1}\right) \\ \times \delta\left(\cos\vartheta + \frac{2\nu'}{N+1}\right) d\cos 2\chi d\cos\vartheta \quad (68)$$

coincide with the values of the potential energy surface at the grid points selected by:

$$\cos 2\chi_\tau = \frac{-2\tau}{I+1} \quad (69)$$

where $-I/2 \leq \tau \leq I/2$ and

$$\cos\vartheta_\nu = \frac{-2\nu}{N+1} \quad (70)$$

where $(-N+\Omega)/2 \leq \nu \leq (N-\Omega)/2$.

IV. PROPAGATION ALONG THE HYPERRADIAL COORDINATE

Here we describe the main use of the adiabatic eigenvalues ϵ_i and eigenvectors $t_{i\tau\nu}$ of the previous sections for calculating triatomic bound states and reactive cross sections. For bound states, especially of weakly bound complexes, a set of ordinary coupled second order differential equations in the hyperradius have to be solved with proper boundary conditions. Similarly, for reactions (see Part II⁷) the scattering matrix for a selected total angular momentum and parity is obtained by integrating a set of coupled-channel equations, and the solution to this problem is well understood and some efficient propagator techniques are available.⁴ The most consolidated approach is the diabatic by sector method:³⁰ the

range of ρ is divided up into small sectors and at the midpoint the calculation of ϵ_i and $t_{i\tau\nu}$ is carried out by applying the hyperquantization algorithm presented in Sec. III.

All the information that is needed to calculate reaction probabilities is contained in the overlap and interaction matrices. The construction of the latter matrix does not present any problem; it is computed by treating the adiabatic eigenstates as a diabatic basis, and we refer to the literature for the explicit formulas.³ The overlap matrix between eigenvectors of adjacent sectors is

$$\mathbf{O}_{1,2} = \tilde{\mathbf{t}}_1 \mathbf{t}_2, \quad (71)$$

where \mathbf{t}_1 and \mathbf{t}_2 are the eigenvector matrices computed at the center of the adjacent sectors denoted as 1 and 2, respectively. The square matrix $\mathbf{O}_{1,2}$ has dimension dictated by the number of the adiabatic eigenstates to be taken into account to describe accurately the dynamical behavior at the collision energies considered. For example, this number is 150 for the F+H₂ example system of Ref. 7. The matrices \mathbf{t}_1 and \mathbf{t}_2 are rectangular with $(I+1) \times (N+1)$ rows, labeled by the discrete variables τ and ν , and i_{\max} columns, where i is an integer number ordering the eigenvalues. In Sec. III we have illustrated how the cut-off parameter, V_{\max} , allows us to get rid of some rows and columns of the Hamiltonian matrix—the corresponding $t_{i\tau\nu}$ are set equal to zero and have not been stored. The overlap matrix serves to ensure the continuity of the hyperradial functions and their ρ derivatives. When the width of the sectors goes to zero it can be shown to be related to the nonadiabatic coupling matrix $\mathbf{P}(\rho)$.³¹

The hyperquantization technique offers the possibility of changing coordinates, reference frame or dimension of the basis along the hyperradial coordinate; this allows us to save computing time and to gain accuracy. When different grids are used in two adjacent sectors, the eigenvector matrices \mathbf{t}_1 and \mathbf{t}_2 have the same number of columns but not the same number of rows. In order to compute their overlap we need a rectangular matrix \mathcal{R} which projects the eigenvectors calculated in sector 2 into those of sector 1:

$$\mathbf{O} = \tilde{\mathbf{t}}_1 \mathcal{R} \mathbf{t}_2. \quad (72)$$

The projection matrix \mathcal{R} has $(I+1) \times (N+1)$ columns and $(I'+1) \times (N'+1)$ rows. For example, when we vary the dimension of the lattice of equally spaced points in $\cos 4\Theta$ and Φ (see the symmetric case of Sec. III B) the projection matrix is given by the product of the discrete functions defined in Eqs. (36) and (38), and its elements are explicitly

$$\mathcal{R}_{\tau\nu,\tau'\nu'} = \sum_n^{\min\{II'\}} \sum_{\sigma/2}^{\min\{NN'\}} f_{\sigma/2,\nu}^N f_{\sigma/2,\nu'}^{N'} Q_{n\tau}^{\sigma/2,0,I} Q_{n\tau'}^{\sigma/2,0,I'}. \quad (73)$$

If $I=I'$ and $N=N'$ the projection matrix \mathcal{R} coincides with the unit matrix, as it emerges from the consideration that the involved Hahn coefficients enjoy a dual orthogonality property [see Eqs. (31) and (40)]. In the same way we can obtain the projection matrix in the asymmetric case of Sec. III C. The success of these calculations is in part limited by the necessity of dealing with the high dimension of the bases used in numerical applications.

Let us consider now how it is possible to handle the case where a change of the coordinate system has to be performed. In this case, to construct the projection matrix, besides the full discrete basis, Rainal–Revaí coefficients³² are also needed (for numerical calculations of these coefficients see Ref. 33). For simplicity we refer to the particular case of total angular momentum equal to zero because when we switch over from the asymmetric to the symmetric hyperspherical coordinates, the Rainal–Revaí coefficients turn out to be simply Clebsch Gordan coefficients.^{8,34} The projection matrix elements are

$$\begin{aligned} \mathcal{P}_{\tau\nu,\tau'\nu'} = & \sum_{\sigma/2}^{\min\{NN'\}} \sum_n^{\min\{II'\}} f_{\sigma/2,\nu}^N Q_{n\tau}^{\sigma/2,0,I} \\ & \times \sum_j^{\min\{NN'\}} (-1)^{-\sigma/4} \left\langle \left(n + \frac{\sigma}{4} \right) \frac{\sigma}{4} \left(n + \frac{\sigma}{4} \right) \right. \\ & \left. - \frac{\sigma}{4} \middle| j0 \right\rangle Q_{j\nu}^{00N'} Q_{n\tau}^{j+1/2,j+1/2,I'}. \end{aligned} \quad (74)$$

When different arrangements of the three particles are considered, as for example the reactant and product channels, the Rainal–Revaí coefficients are more complicated

$$\begin{aligned} F_{jj'\sigma}^\lambda = & \exp(i\sigma\gamma) \left\langle \left(n + \frac{\sigma}{4} \right) \frac{\sigma}{4} \left(n + \frac{\sigma}{4} \right) - \frac{\sigma}{4} \middle| j0 \right\rangle \\ & \times \left\langle \left(n + \frac{\sigma}{4} \right) \frac{\sigma}{4} \left(n + \frac{\sigma}{4} \right) - \frac{\sigma}{4} \middle| j'0 \right\rangle. \end{aligned} \quad (75)$$

Here γ denotes the skewing angle of the reaction, i.e., the kinematic rotation from the set of the Jacobi vectors used in sector 1 to the one used in sector 2. The elements of the projection matrix are

$$\begin{aligned} \mathcal{P}_{\tau\nu,\tau'\nu'} = & \sum_{jj'}^{\min\{NN'\}} \sum_n^{\min\{II'\}} \sum_{\sigma/2}^{\min\{NN'\}} Q_{j\nu}^{00N'} Q_{n\tau}^{j+1/2,j+1/2,I'} \\ & \times F_{jj'\sigma}^\lambda Q_{j'\nu'}^{00N'} Q_{n\tau}^{j'+1/2,j'+1/2,I'}. \end{aligned} \quad (76)$$

The strategy of using different coordinates and grids is very useful in the scattering calculations and will be further discussed in the following paper.⁷

V. DISCUSSION AND CONCLUSION

In this paper we have presented a general quantum mechanical method for solving eigenvalue problems. In the theory of three-atom reactive scattering its applications are exemplified by calculating adiabatic eigenstates at fixed values of the hyperradius.⁷ The algorithm is based on the hyperspherical coordinates approach and exploits generalized vector coupling coefficients (Hahn polynomials) as the discrete analogs of hyperspherical harmonics. Applying the recurrence equation, the symmetries, the orthogonality and the dual orthogonality properties of these polynomials have allowed us to develop an algebraic formalism that is shown to provide a very useful tool to investigate the quantum dynamics of three-particle systems. In particular, we have given the theoretical background to evaluate the interaction and the

overlap matrices which are needed for the computation of the scattering matrix. The numerical implementation of the present technique is easily set up and is divided into two main parts: the construction of the Hamiltonian matrix and its diagonalization. The most time is consumed in the second step, because no integrals have to be calculated and the computation of the kinetic energy operator elements is analytical. From a computational point of view, the most attractive features are the sparseness and the high symmetry of the Hamiltonian matrix. These properties are exploited in the diagonalization by using the Lanczos algorithm with spectral transformation,³⁵ which is very well adapted to deal with sparse matrices.

The results obtained by applying the hyperquantization algorithm based on the symmetric hyperspherical coordinates on a benchmark system, i.e., the $F+H_2$ ($J=0$) reaction including the spin-orbit interaction, are accurate and competitive with other techniques, as shown in Ref. 7. The generalization of this methodology for any value of the total angular momentum is currently being implemented. The presence of body-frame singularities³⁶ makes this problem a complicated one. A reference Hamiltonian operator proposed in Ref. 2 is known to work well for collinearly dominated reactions. We have adapted our technique to compute the adiabatic eigenvalues at fixed values of the projection of the total angular momentum on the least inertia axis, and results and explicit formulas will be given elsewhere. For reactions with no collinear transition state, a Hamiltonian operator partition will be proposed where the singularities due to the oblate symmetric top configurations are removed.

Interest in the asymmetric hyperspherical parametrization from the viewpoint of the hyperquantization technique arises from the fact that the harmonic analysis eliminates all frame singularities, so from a theoretical point of view it is an optimal coordinate system. However, the hyperquantization algorithm as such is not expected to perform well when only one set of Jacobi coordinates is used. Thus for the time being this strategy has to be refined for practical cross-section calculations and improvements are expected by using an overcomplete basis which combines the sets appropriate for the relevant channels. In fact, the overlaps among the harmonic bases for various channels, a key ingredient to deal with overcompleteness, are known analytically (for three-body problems, they are Raynal–Revaí coefficients³²).

An extremely important feature of this methodology is that it can be easily generalized to more complex reactions than a three-atom system. In a recent paper³⁷ we have given the kinetic energy operator for the four-body problem in a system of symmetric or democratic hyperspherical coordinates which generalize those first introduced by Smith for the case of three particles. We have also provided the explicit expression of the interatomic distances necessary for the mapping of a four-atom potential energy surface in hyperspherical coordinates. Kinematic rotations for four-atom systems are also under study.³⁸ The extension of the hyperquantization technique to four-atom systems is therefore an objective of future work.

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