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Discrete analogs of spherical harmonics and their use in quantum mechanics: The hyperquantization algorithm

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Summary. An algorithm for the solution of the Schrödinger equation in a discrete basis is illustrated with reference to the problem of quantization on spheres of any dimension (hyperquantization). It exploits the explicit construction of discrete analogs of spherical harmonics and leads to sparse matrix representations of the kinetic energy operator and a diagonal representation of the interaction potential. Applications are discussed for inelastic and reactive scattering.

Key words: Spherical harmonics–Discrete polynomials–Inelastic and reactive scattering

1. Introduction

In the applications of quantum mechanics, the solutions of the Schrödinger equation are often sought by expanding the unknown eigenfunctions in some bases, so to obtain an algebraic problem. Convergence of the procedure (or in computational terms over-all structure and dimensions of the required matrices to be stored and manipulated) is the main practical limitation. Physical motivations in the choice of bases are typically crucial in tackling problems, where exact simplifications (as those due to symmetries or conservation rules) are to be exploited to their best.

The technique here described belongs to the class of direct approaches to the solution of the Schrödinger equation by finite differences. It is illustrated with reference to eigenvalue problems as are encountered in a number of contexts, particularly for propagation techniques in the time-independent approach to inelastic and reactive scattering. Its use in variational or time-dependent approaches has to be assessed. It differs from other finite difference schemes, such as the discrete variable representations (DVR) [1], from being founded on the exploit of discrete analogs of orthonormal bases usually defined on continuous variables. These bases are orthonormal polynomial sets, and our representation requires the discrete counterparts of orthogonal polynomials, i.e. polynomials orthogonal on lattice points. The important advantage is that the procedure can be extended to any number of mathematical dimensions. We specialize the following presentation to the fundamental case of spherical (or hyperspherical, see below) harmonics. Since the harmonics [2] are representations of rotation groups they enjoy the property of being easily adapted to be eigenfunctions of symmetry operators and of any other basic property coming from conservation of angular momentum. So in a sense we will tackle the quantum mechanics of anisotropic interactions, where anisotropy may be in spaces of dimensions higher than physical, so that also many-body problems will be treated.

From the *mathematical* viewpoint, harmonics belong to the class of Jacobi polynomials, which are functions of the hypergeometric, ${}_2F_1$, family. Their discrete analogs belong to higher hypergeometric families: in our applications, we will use Hahn polynomials, ${}_3F_2$ hypergeometric functions of unit arguments. The latter discrete polynomials can be identified, in particular cases, with the Clebsch–Gordan or vector coupling coefficients in the quantum theory of angular momentum. This fact provided the first motivations [3] of our work and leads to a *physical* picture of the technique, whereby the discretization is interpreted as a quantization of an artificial angular momentum: The following Sect. 2 elaborates on this aspect, which together with previous considerations on mathematical features leads to the natural definition of this procedure as the *hyperquantization* algorithm (Sect. 3).

Section 4 considers the representation of interaction potentials in the discrete basis and Sect. 5 deals with the treatment of angular momentum exchange between a particle and a rotor, a basic model of atom molecule complexes and of rotational energy transfer in atom molecule collisions [4]. The handling of matrix elements is outlined in Sect. 6 and the structure of the interaction matrix is presented in Sect. 7. The extension to many-body problems is briefly illustrated (Sect. 8) with reference to the hyperspherical approach to bound states and rearrangement processes, for which the discrete analogs of hyperspherical harmonics have to be introduced. The paper concludes with some remarks in Sect. 9.

2. Hyperquantization: The physical background

In the quantum mechanical treatment of anisotropic interactions, coupling among channels typically appears as matrix elements involving sums over vector coupling and recoupling coefficients, and the formalism may become very complicated even in the simplest physical situations: however, "the complexity is to a certain extent of our own making" [5]. The introduction by Jacob and Wick of the helicity formalism [6] is just an example of simplifications which can be obtained by developing alternative reference frames. In quantum mechanics, alternative frames correspond to alternative coupling schemes: when it is possible to formulate the coupling in terms of quantum numbers which correspond to approximate constants of the motion, powerful approximations can be developed.

The idea is actually as old as quantum mechanics: it can be traced back to 1927, when Hund introduced alternative coupling schemes for diatomic molecules carrying spin and electronic and rotation angular momenta. The correspondence between Hund's cases and the possible angular momentum coupling schemes, at a given total angular momentum and spin has been treated in detail recently [7]. The relationship between this approach and frame transformation theory [8] is also apparent. The purpose of the present paper is to indicate how for general anisotropic interactions it is often possible to undo some expressions of Racah's algebra introducing discretization procedures, which amount to develop for multichannel Schrödinger's differential equation alternative coupling schemes labelled by artificial quantum numbers.

This work has some formal relationships with a discretization procedure extensively developed [1] to treat a large class of problems, including rotational excitation in atom-molecule collisions, and photodissociation of triatomic molecules. In the following, we show that a set of discretization schemes can be developed within the framework of angular momentum algebra introducing an artificial vector, say $\boldsymbol{a}$, of length $[a(a+1)]^{1/2}$. We establish a correspondence $a = N/2$ between this vector and the discretization of space into $N+1$ slices (hyperquantization). The use of nonphysical quantum numbers $N/2$ and their projections ν provides an attractive computational procedure, convergence to exact results being achieved in the limit of large N. With respect to previous discretization procedures, based on inversions of quadrature formulas [1], the developments presented here, being founded on the theory of group representations, have the advantage of allowing the easy introduction into the formalism of sharp spin and angular momentum states and of any symmetry which is characteristic of a given problem (parity, permutations of identical particles, . . .). Moreover, it appears to be well suited for implementation in the hyperspherical approach to many-body problems, as outlined in Sect. 8. The construction of a discrete representation of Schrödinger equation is considered in the next section. The discrete analogs of the harmonics, the basic tool for our developments, will be given explicitly.

In order to elucidate the physical picture which is behind the mathematics, we will exploit the fact that vector coupling and recoupling coefficients are the discrete analogs of orthogonal polynomials: this has been known for several years [9], and is being actively investigated from a formal point of view [10]. Physically, some of these relationships were in part to be anticipated by the knowledge that for high angular momenta the coefficients tend to particular cases of Jacobi polynomials (Wigner rotations matrices, spherical harmonics, Legendre polynomials) [11]. By explicitly identifying a vector coupling coefficient as the discrete Gram [12]-Chebishev [13] polynomial used in numerical analysis, we suggest in this work that the proposed discretizations have a further appealing feature, namely that of providing an interpretation in terms of least square approximations.

3. Hyperquantization on the sphere S^n

The solution of the time-independent Schrödinger equation is often searched starting by an expansion basis for the unknown wavefunction in a set of eigenfunctions for a simpler solvable problem that bears some relationship with the problem at hand. One generally obtains coupled equations whose practical solution strongly depends on the choice of the basis. The following procedure may work for any choice of the basis for whose elements we know a discrete representation, in the sense to be explained below. However we will focus on the solution of the Schrödinger equation on the surface of a sphere of any dimension (this is actually a fundamental problem frequently encountered in the applications): for this problem, we know the eigenfunctions of the kinetic energy part of the Hamiltonian [2] (basically the spherical harmonics which solve the corresponding Laplace equation); also, they enjoy the remarkable property that their discrete analogs can be obtained explicitly in a convenient algebraic formulation.

The Schrödinger equation for the quantization of a particle of mass m moving on the surface of an n-dimensional sphere S^n can be written

$$\left[-\frac{\hbar^2}{2m}\Lambda^2(\Omega_n) - \varepsilon_i + V(\Omega_n)\right]\Psi_i(\Omega_n) = 0 \tag{1}$$

where Ω_n is a collection of n angles parametrizing the surface of the sphere, V is the potential energy, and ε_i is the eigenvalue of the state i. The Laplacian operator Λ^2 has as known eigenfunctions the spherical harmonics Y_k:

$$\Lambda^2 Y_k(\Omega_n) = -\lambda(\lambda + n - 1)Y_k(\Omega_n)$$

where $\lambda = 0, 1, \ldots, \infty$ and the suffix k denotes the λ and the other $n - 1$ labels of the harmonics. In the example given in the next section, the space is the physically three-dimensional one, so we have the Laplacian acting on S^2, and λ is the physical orbital angular momentum. In general, we will also be interested in higher spaces [23]: for example, for the three body problem the Laplacian acts on S^5, and λ is the grand orbital angular momentum [14]. Often, the potential function V acts on a manifold of lower dimensionality than Ω_n.

The spherical harmonics enjoy orthonormal properties: in particular they are orthonormal with respect to integration on the sphere:

$$\int_{\Omega_n} Y_k^* Y_{k'} \, d\Omega_n = \delta_{kk'} \tag{2}$$

the star denoting complex conjugation.

Therefore they can be used to expand the total wavefunction:

$$\Psi_i(\Omega_n) = \sum_k g_{ki} Y_k(\Omega_n) \tag{3}$$

To exploit symmetries for the problems at hand it may be convenient to take particular linear combinations of harmonics, the most important case being to combine them to be eigenfunctions of total angular momentum. Although frequently physical requirements may justify a truncation of Eq. (3) to include only a finite number of harmonics, in general Eq. (3) has infinite terms and its convergence properties may be extremely poor.

Equations (3) in (1) transforms a partial differential equation into an algebraic eigenvalue problem:

$$\left[\frac{\hbar^2}{2m}\lambda(\lambda + n - 1) - \varepsilon_i\right]g_{ik} + \sum_{k'} V_{kk'} g_{ik'} = 0 \tag{4}$$

The matrix elements:

$$V_{kk'} = \int_{\Omega_n} Y_k(\Omega_n) V(\Omega_n) Y_{k'}(\Omega_n) \, d\Omega_n \tag{5}$$

are sometimes evaluated by expanding in harmonics the potential itself:

$$V(\Omega_n) = \sum_i V_i Y_i(\Omega_n) \tag{6}$$

thus allowing to evaluate Eq. (5) as an integral over three spherical harmonics for the sphere S^n: such an integration can be performed analytically exploiting the Clebsch–Gordan series for the rotation group SO(n).

The physical problem, i.e. essentially the nature of the function $V(\Omega_n)$, may suggest alternative representations for formulating the algebraic equation of Eq. (4): any orthogonal transformation of the harmonics leaves obviously the eigenergies invariant. Examples of transformations related to the choice of alternative coordinate frames and coupling schemes will be explicitly considered in the following. In the formulation of the three body problem in hyperspherical coordinates, the orthogonal transformation between the so called symmetrical and unsymmetrical representations has also been given explicitly [15, 2]. It is remarkable that often such orthogonal transformations, since they physically provide the connection between alternative vector coupling schemes, are mathematically represented by rotation matrices, Clebsch–Gordan and Racah coefficients, etc., i.e. the basic tools of angular momentum algebra.

The key step of the present problem is the realization that angular momentum algebra can also provide a *discrete representation* for the harmonics $Y_k(\Omega_n)$. We assume (and prove in the next section) that there exists a set of functions $Y^M_{k\mu}$ where the set of numbers M counts in how many elements the surface of the sphere has been divided, and μ is a set of labels for such elements; this establishes a one-to-one connection between μ and a set of points on the sphere, Ω^μ_n. The relationship between the finite denumerable set of harmonics (taken at the discrete values μ) and the infinite denumerable set of harmonics (which are continuous functions of angles Ω_n) is:

$$Y^M_{k\mu} = Y_k(\Omega^\mu_n), \quad \text{for } M \to \infty \tag{7}$$

the discrete analogue of the orthonormal property Eq. (2) being:

$$\sum_\mu Y^{M*}_{k\mu} Y^M_{k'\mu} = \delta_{kk'} \tag{8}$$

Instead of the infinite dimensional eigenvalue problem Eq. (4) we now have to solve:

$$\left[\frac{\hbar^2}{2m}\lambda(\lambda+n-1)-\varepsilon_i\right] g^M_{ki} + \sum_{k'} V^M_{kk'} g^M_{k'i} = 0 \tag{9}$$

where the matrix elements are obtained by:

$$V^M_{kk'} = \sum_\mu Y^{M*}_{k\mu} V^M_\mu Y^M_{k'\mu} \tag{10}$$

using the values V^M_μ the potential $V(\Omega_n)$ which attains at the values given by the correspondence between μ and Ω^μ_n, $V^M_\mu = V(\Omega^\mu_n)$.

Equation (9) provides a *finite basis representation* for the problem and the larger M the more faithful the discrete set of eigenfunctions g^M_{ki} and the eigenvalues ε_i will approximate those from Eq. (4). To solve Eq. (9), it is however *decisive* to consider an alternative representation (*a discrete variable representation*, according to Light's nomenclature [1]) performing an orthogonal basis transformation exploiting orthonormal properties of discretized harmonics (see, e.g., Eq. (8)):

$$g^M_{ki} = \sum_\mu Y^M_{k\mu} \zeta^M_{\mu i} \tag{11}$$

to obtain:

$$-\frac{\hbar^2}{2m}\sum_{\mu'} \Lambda^M_{\mu\mu'}\zeta^M_{\mu' i} + (-\varepsilon_i + V^M_\mu)\zeta^M_{\mu i} = 0 \tag{12}$$

where the coupling has been transferred from potential to kinetic energy and the corresponding matrix elements are algebraic quantities that can be computed independently of the problem at hand:

$$\Lambda^M_{\mu\mu'} = \sum_k Y^{M*}_{k\mu}\lambda(\lambda + n - 1)Y^M_{k\mu'} \tag{13}$$

and the potential is now diagonal. We recall that the set of labels k includes λ.

The next sections provide the effective construction of the discrete harmonics and explicit examples of the application of this approach.

4. Potential expansions in discrete harmonics

Consider then a general interaction potential $V(R, \Omega_n)$ depending on a radius R and a set of angles Ω_n [16]. The standard procedure requires the attack to the problem by first integrating over the angular variables Ω_n, and that is (often but not always) achieved by harmonic expansion of the interaction (see Eq. (6)), followed by computation of matrix elements. The harmonics must also be linearly combined to be eigenfunctions of total angular momentum, and of any other symmetry operators of the problem. By handling these matrix elements by orthogonal basis transformations one may obtain alternative formulations corresponding to alternative coordinate frames and coupling schemes.

The present algorithm, being a finite difference scheme as any discrete variable representation, eventually avoids all this and leads to the simplification that no matrix elements of the potential need be calculated (see, however, Sect. 6). Nonetheless, it is illuminating to illustrate the mathematical aspects of the procedure by the simplest example, that of the interaction between a rigid rotor and a structureless particle: this is the familiar model for the transfer between translational and rotational energy in the collisions of electrons or atoms with diatomic molecules [17, 4]. In this case, the interaction $V(R, \theta)$ depends only on the length R of the vector $\boldsymbol{R}$ which joins the particle and the rotor center of mass, and the angle θ which $\boldsymbol{R}$ forms with the rotor axis: Figure 1 shows relevant features of this problem.

Often, the interaction is expanded in Legendre polynomials:

$$V(R, \theta) = \sum_l v_l(R)P_l(\cos\theta) \tag{14}$$

where $v_l(R)$ is obtained by integration:

$$v_l(R) = (l + 1/2)\int_0^\pi P_l(\cos\theta)V(R, \theta)\sin\theta\, d\theta \tag{15}$$

Suppose now that the integration in Eq. (15) is done by a quadrature procedure, which needs only that $V(R, \theta)$ is taken at some discrete values of the angles θ_ν, with the suffix ν to be specified. Further, consider that a relationship ties Legendre polynomials and particular vector coupling coefficients with large angular momenta [11, 18]: specifically, as the integer N tends to infinity, we have,

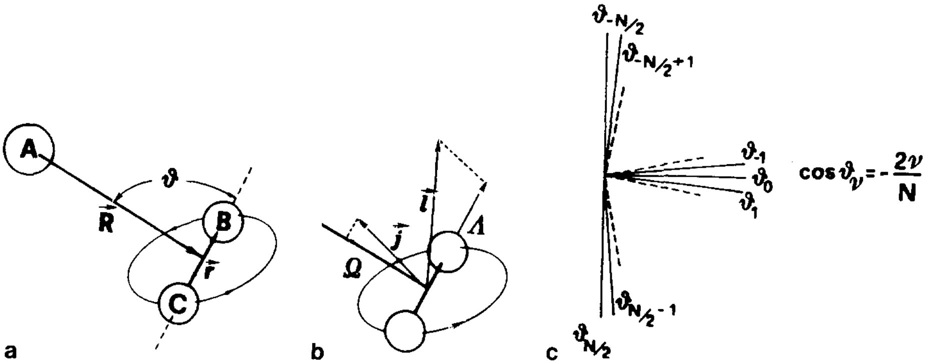

Fig. 1a–c. **a** and **b** illustrate the definitions of Jacobi vectors and angular momenta for the atom A interacting with the molecule BC. The rotational and orbital angular momenta $\boldsymbol{j}$ and $\boldsymbol{l}$ are associated to the $\boldsymbol{r}$ and $\boldsymbol{R}$ vectors, respectively; and their sum is indicated as J in the text. Projections (Ω, Λ) of $\boldsymbol{j}$ on R and of $\boldsymbol{l}$ on r are also shown. **c** illustrates the discretization in N slices (conveniently taken to be even) of the angular range $0 \leqslant \theta \leqslant \pi$, where θ is the angle between the Jacobi vectors. The label ν, which plays the role of a projection quantum number, varies in the range from $-N/2$ to $N/2$

as an approximation for l much smaller than N:

$$P_l(\cos\theta) \simeq [(N+1)/(2l+1)]^{1/2}(-)^{N/2-\nu-l}\left\langle \frac{N}{2}\frac{N}{2}\nu-\nu \middle| l0\right\rangle \tag{16}$$

where (Fig. 1):

$$\cos\theta_\nu = -2\nu/N \tag{17}$$

and ν assumes the $N+1$ values $-N/2$, $-N/2+1, \ldots, N/2-1, N/2$.

Therefore an approximation to Eq. (15) is:

$$v_l^N(R) \simeq [(2l+1)(N+1)/N^2]^{1/2}\sum_\nu(-)^{N/2-\nu-l}\left\langle \frac{N}{2}\frac{N}{2}\nu-\nu \middle| l0\right\rangle V^N(R,\theta_\nu) \tag{18}$$

where the index N denotes that $N+1$ quadrature points have been considered. But this can be inverted, by using the orthogonal properties of vector coupling coefficients, to give an approximation to Eq. (14):

$$V^N(R,\theta_\nu) = [N^2/(2l+1)(N+1)]^{1/2}\sum_l(-)^{N/2-\nu-l}\left\langle \frac{N}{2}\frac{N}{2}\nu-\nu \middle| l0\right\rangle v_l^N(R) \tag{19}$$

We have therefore found a discrete representation for the interaction, by introducing a mock quantum number $N/2$ and its projection ν, which we know tend to exactness as N is allowed to tend to infinity. Note that Eqs. (14) and (15) are fully consistent with Eqs. (18) and (19) through Eqs. (16) and (17) only when N is so large that 1 and 2 can be neglected.

An appealing feature of this discretization procedure is that it involves vector coupling coefficients, and therefore the discretization can be interpreted as the introduction of the artificial vector $\boldsymbol{a}$ of Sect. 2. But what is more, is that a striking relationship exists between the vector coupling coefficients in Eqs. (16), (18), and (19) and the Gram [12]–Chebyshev [13] polynomials, orthogonal in a discrete range, and used in numerical analysis for the best representation in the least square sense of functions tabulated for equally spaced grid points. This is apparently a particular case of more general relationships [10]. Equation (19) will be needed in Sect. 6.

5. The hyperquantization representation for atom-molecule collisions

Equation (16) is only the simplest instance of discretization of rotation matrix elements and spherical harmonics by introducing arbitrarily large quantum numbers. All these well-known formulas [18, 11] are usually (as in Ref. [7]) employed in the semiclassical limit. In the modern language, which identifies $3j$ and $6j$ symbols with ${}_3F_2$ and ${}_4F_3$ of unit argument, respectively, they correspond to limit relationships among these hypergeometric functions and the ordinary ${}_2F_1$, which include all the classical orthogonal polynomials. Finally, they can also be obtained as the finite difference solutions of Laplace equation. For the following example, we use a generalization of Eq. (16) to include a special spherical harmonic: for N tending to infinity, we have, for l much smaller than N and $m \geqslant 0$:

$$Y_{lm}(\theta_v, 0) \simeq [(N+1)/4\pi]^{1/2}(-)^{N/2-v-l}\left\langle \frac{N}{2}\frac{N}{2}+mv-v \,\middle|\, l0 \right\rangle \tag{20}$$

and v is still given by Eq. (17). This equation is useful for computing matrix elements, but more importantly, indicates explicitly how alternative coupling schemes can be devised. For the present problem (the particle-rotor A + BC case of Fig. 1), the Schrödinger equation in a body-fixed frame, at a given total angular momentum J and parity ε, can be written [4]:

$$\left[\left(\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+E\right)1 - W^{J\varepsilon}(R)\right]\vec{F}(R) = 0 \tag{21}$$

where the total interaction matrix is the sum of three terms:

$$W^{J\varepsilon}(R) = -Bj^2 - \frac{\hbar^2}{2\mu R^2}l^2 + V(R) \tag{22}$$

In these equations, μ is the reduced mass of the system A + BC, E the total energy, Bj^2 the diagonal matrix of the rotor energy levels. Equation (21) has to be solved for the radial functions $F_{j\Omega}$ under proper boundary conditions: it is an infinite set, which in practice has to be truncated to include only selected values of the rotor angular momentum j and its projection Ω along R (Fig. 1). Coupling (see next section and Fig. 2) is due to centrifugal matrix l^2, which is tridiagonal in this representation, being nonzero for $\Omega' = \Omega - 1, \Omega, \Omega + 1$, and to the matrix of the interaction $V(R)$ which is diagonal in Ω, but couples states with different j: its elements are given by:

$$\langle j\Omega \,|\, j'\Omega \rangle = 2\pi \int_0^{\pi} Y^*_{j\Omega}(\theta, 0)V(R, \theta)Y_{j'\Omega}(\theta, 0)\sin\theta \, d\theta \tag{23}$$

Use of Eq. (20) allows us to write the following discrete alternative to Eq. (23), valid for N much larger than j and j':

$$\begin{aligned}\langle j\Omega \,|\, V \,|\, j'\Omega \rangle \simeq \sum_v V^N(R, \theta_v)(-)^{N+2v-j-j'}\left\langle \frac{N}{2}\frac{N}{2}+\Omega v - v \,\middle|\, j0 \right\rangle \\ \times \left\langle \frac{N}{2}\frac{N}{2}+\Omega v - v \,\middle|\, j'0 \right\rangle\end{aligned} \tag{24}$$

when inserted in Eq. (21), the new radial functions $F^{JN}_{j\Omega}$ form a finite dimensional vector F^N, which tends to F as its dimension increases with N. In the language of Ref. [1], this is a *finite basis* representation. A *discrete variable* representation

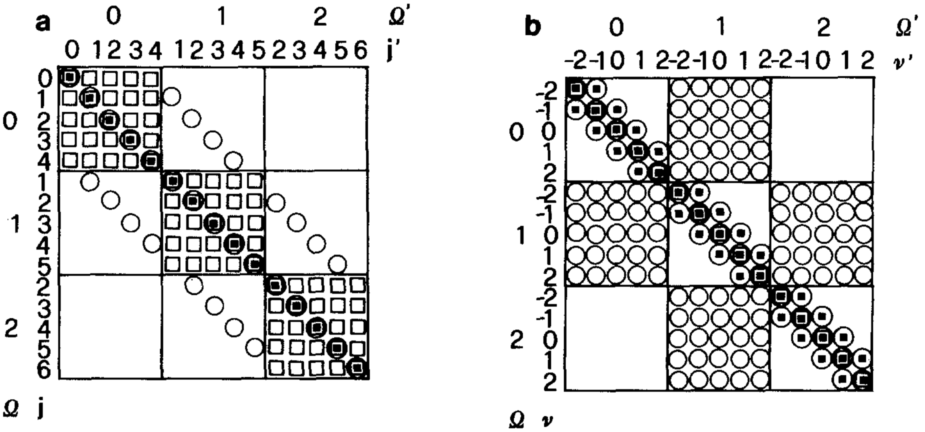

Fig. 2a, b. The left and right panels show the distribution of nonzero elements of the total interaction matrix in the $|j\Omega\rangle$ (case γ) and $|\nu\Omega\rangle$ (case α) representations respectively. The elements of the interaction potential matrix are indicated by *squares*. *Circles* and *black squares* correspond to the elements of the centrifugal (l^2) and rotational (j^2) matrices, respectively. The example illustrated in the figure is obtained for $N=4$ and for blocks $\Omega=0,1,2$

can be obtained by a similarity transformation with the orthogonal matrix whose elements are given in the r.h.s. of Eq. (20). This leads to insert in Eq. (21):

$$\begin{aligned} F^{JN}_{\nu\Omega} &= \sum_j (-)^{N/2-\nu+j} \left\langle \frac{N}{2}\frac{N}{2}+\Omega\nu-\nu \,\middle|\, j0 \right\rangle F^{JN}_{j\Omega} \\ &= \sum_j G^{N\Omega}_{\nu j} F^{JN}_{j\Omega}, \quad \Omega \leqslant j \leqslant N+\Omega \end{aligned} \tag{25}$$

for the radial functions:

$$\langle \nu\Omega \,|\, Bj^2 + \frac{\hbar^2}{2\mu R^2} l^2 \,|\, \nu'\Omega' \rangle \tag{26}$$

for the rotational and centrifugal matrices, and $V^N(R, \theta_\nu)$ for the potential matrix. In Eq. (26), the matrix of j^2 will be shown (Sect. 7 and Fig. 2) to be tridiagonal, connecting states with $\nu' = \nu - 1, \nu, \nu + 1$, while the centrifugal (l^2) term now couples also state with different ν. The interesting feature of this basis, where discretization is achieved by introducing artificial quantum numbers, is that the interaction potential appears diagonal assuming the values computed at the discrete set of angles θ_ν.

It is interesting to note that in this representation the Infinite Order Sudden approximation is obtained by neglecting off diagonal terms in [26], [4]. Actually, the whole procedure is very much reminiscent of the transition from Hund's cases (c) to (a) in the treatment of atoms carrying internal angular momenta and interacting to form a diatomic molecule [7]. In order to further exploit this analogy, we suggested [3, 4] indicating by Greek letters the corresponding cases in the rotation excitation problem of diatomic molecules, so that representations of Eqs. (21) and (23) can be denoted as case (γ), being a helicity representation in the sense of Jacob and Wick [6], and the discrete variable one as case (α): the corresponding space-fixed (ε) case is the standard Arthurs and Dalgarno formulation [17]. Representations corresponding to case (δ) can also be traced in the literature [8, 19]. They are all sources of useful decoupling approximations, and the same can be anticipated for the discrete basis representation introduced in this paper [4].

6. Recoupling of matrix elements

As an indication of alternative routes to essentially the same results, we note that it is possible to work directly on matrix elements [20], rather than discretizing the harmonics of the basis. When we know a discretized expansion for the interaction potential as exemplified in Sect. 4, then the recoupling schemes of angular momentum algebra may assist us in the manipulation of otherwise formidable algebraic sums. Thus, when in Eq. (24) one uses the potential expansion of Eq. (14), the integral can be performed analytically to give a sum of products of vector coupling coefficients [17]:

$$\langle j\Omega \,|\, V \,|\, j'\Omega\rangle = \sum_l v_l(R)[(2j+1)/(2j'+1)]^{1/2} \langle jl\Omega 0 \,|\, j'\Omega\rangle \langle jl00 \,|\, j'0\rangle \tag{27}$$

Consider now the following relationships [18] valid as $N/2$ goes to infinity faster than j, j', and l:

$$\langle jl00 \,|\, j'0\rangle \simeq [(2j+1)(2j'+1)]^{1/2}(-)^{j-l-N} \begin{Bmatrix} j & l & j' \\ N/2 & N/2 & N/2 \end{Bmatrix} \tag{28}$$

Inserted in Eq. (27), this gives, with the aid of the expansion:

$$\langle jl\Omega 0 \,|\, j'\Omega\rangle \begin{Bmatrix} j & l & j' \\ N/2 & N/2 & N/2 \end{Bmatrix} = \sum_{v\Omega} (-)^{\Omega+j+j'}[(2j+1)(2l+1)]^{-1/2}$$

$$\times \left\langle \frac{N}{2}\frac{N}{2} + \Omega v - v \,\middle|\, j0 \right\rangle \left\langle \frac{N}{2}\frac{N}{2} + \Omega v - v \,\middle|\, j'0 \right\rangle \left\langle \frac{N}{2}\frac{N}{2} v - v \,\middle|\, l0 \right\rangle \tag{29}$$

an expression for the matrix elements which can be checked to be equivalent to introducing Eq. (19) into Eq. (24).

The above examples show that the systematic introduction of artificial quantum numbers through the discrete analogs of spherical harmonics leads to matrix elements involving vector coupling and recoupling coefficients that can be manipulated to give new discrete variable representations. Their use provides alternative coupling schemes which may be of interest in many situations, in view of the fact that they may be easily transformed one from another through well defined orthogonal transformations. Finally, this procedure appears to be very promising with respect to possible extensions to cases of higher dimensionality, such as the three-body rearrangement problem in the hyperspherical formulation of chemical reactions [21]. These extensions require the explicit construction of the analogs of hyperspherical harmonics, and are considered in Sect. 8.

7. Structure of the interaction matrix

In the previous sections we have resumed the quantum mechanics of the scattering of an atom from a rigid rotor in a body-fixed frame at a given total angular momentum J and parity ε [4]. In particular, we have discussed the case γ, in which j and Ω are the quantum numbers that label the representation. This case has been discussed explicitly by Walker and Light [22] and Launay [23]. We recall (see Sect. 5 and Fig. 2) that in this diabatic representation the matrix associated with the rotational operator $\boldsymbol{j}^2$ is diagonal, the matrix of the centrifugal operator $\boldsymbol{l}^2$ is tridiagonal in Ω and the matrix of the interaction potential is block diagonal, in each block channels labeled by the same Ω and different j being coupled. In Fig. 2 we illustrate the structure of the total interaction matrix $\boldsymbol{W}^{J,\varepsilon}$, Eq. (22) in this case γ, or $|j\Omega\rangle$ basis. The same structure of course applies in its discretized counterpart, which we denote $\boldsymbol{W}_{\gamma}^{N,J,\varepsilon}$.

We are interested in alternative representations for which the interaction potential matrix is diagonal (case α and β). In the following we describe the procedure to evaluate the total interaction matrix $\boldsymbol{W}^{N,J,\varepsilon}$ in case α, which can be indicated as $|v\Omega\rangle$ (case β, the representation $|\Lambda v\rangle$, is obtained by consistently interchanging j and l and Ω and Λ [4]). The two alternative diabatic representations are connected by an orthogonal transformation $\boldsymbol{G}^{N\Omega}$:

$$\boldsymbol{W}_{\alpha}^{N,J,\varepsilon} = \tilde{\boldsymbol{G}}^{N\Omega}\boldsymbol{W}_{\gamma}^{J,\varepsilon}\boldsymbol{G}^{N\Omega} \tag{30}$$

whose elements $\boldsymbol{G}_{jv}^{N\Omega}$ are as in Eq. (25). Note that the matrix $\boldsymbol{G}^{N\Omega}$ is orthogonal with respect to all values of j and Ω allowed by the existence of vector coupling coefficients, and does not depend on the parity quantum number $\varepsilon = \pm 1$. Parity leads to block diagonalization [22, 23] of the whole problem in two sets, which differ in the allowed range of Ω, which spans the allowed positive integers, including 0 for $\varepsilon = \pm 1$ and starting from 1 for $\varepsilon = -1$.

For a given total angular momentum J we fix N, where $N + 1$ specifies the number of points of the potential which have been selected. In order to have the matrix $\boldsymbol{G}^{N\Omega}$ orthogonal with respect to j and v (the projection of $N/2$) all the values of $j - \Omega$ varying between 0 and N have to be taken, e.g. when $\Omega = 0$ then $0 \leqslant j \leqslant N$, when $\Omega = 1$ then $1 \leqslant j \leqslant N + 1$, and so on.

In the application to *homonuclear* molecules, as in Ref. [4], only even or odd j states are allowed. Correspondingly, there is a symmetry in the potential, $V(\cos\theta_v) = V(\cos\theta_{-v})$. The $\boldsymbol{G}^{N\Omega}$ matrix elements are conveniently written:

$$\boldsymbol{G}_{jv}^{N\Omega} = [2(1 + \delta_{v0})^{-1}]^{1/2}(-)^{N/2 - v + j}\left\langle \frac{N}{2}\frac{N}{2} + \Omega v - v \middle| j0 \right\rangle \tag{31}$$

where N here is assumed even, and v now covers the positive range, including 0 for the case when even j's are allowed, and starting from 1 when odd j's are allowed.

In general, the matrix $\boldsymbol{G}^{N\Omega}$ is block diagonal, there are as many blocks as the values of Ω which are allowed, and each block is $(N + 1)(N + 1)$ dimensional. The rows are labelled by j and the columns by v. The elements of this matrix are Clebsch–Gordan coefficients as stated in the previous section. The $\boldsymbol{G}^{N\Omega}$ matrix diagonalizes the matrix of the interaction potential, whose elements in the discrete representation are the values of the potential at θ_v. The matrix elements of the operator $\boldsymbol{j}^2$ in the basis $|j\Omega\rangle$ are:

$$\langle j\Omega | \boldsymbol{j}^2 | j\Omega\rangle = j(j + 1) \tag{32}$$

In the discrete $|v\Omega\rangle$ representation (case α) this diagonal matrix becomes tridiagonal and channels $|v\Omega\rangle$ and $|v'\Omega\rangle$ are now coupled, the only nonzero elements being:

$$\begin{aligned}\langle v\Omega | \boldsymbol{j}^2 | v'\Omega\rangle &= (N + \Omega)(\Omega + 1) + 2(N/2 - v)(N/2 + v) \quad \text{for } v' = v\\ &= \{(N/2 \pm v)(N/2 + 1 \mp v)[(N + 1)\Omega + \Omega^2]\\ &\quad + (N/2 \pm v)^2(N/2 + 1 \mp v)^2\}^{1/2} \quad \text{for } v' = v \pm 1\end{aligned} \tag{33}$$

The matrix elements of the operator $\boldsymbol{l}^2$ in the $|j\Omega\rangle$ basis are [23]:

$$\begin{aligned}\langle j\Omega|\boldsymbol{l}^2|j\Omega'\rangle &= J(J+1) - 2\Omega^2 + j(j+1) \quad \text{for } \Omega' = \Omega \\ &= -\{[J(J+1) - \Omega(\Omega \pm 1)] \\ &\quad \times [j(j+1) - \Omega(\Omega \pm 1)]\}^{1/2} \quad \text{for } \Omega' = \Omega \pm 1 \end{aligned} \tag{34}$$

In the basis $|v\Omega\rangle$ they are transformed according to the following formulas:

$$\begin{aligned}\langle v\Omega|\boldsymbol{l}^2|v'\Omega\rangle &= J(J+1) - 2\Omega^2 + (N+\Omega)(\Omega+1) \\ &\quad + 2(N/2 - v)(N/2 + v) \quad \text{for } v' = v \\ &= \{(N/2 \pm v)(N/2 + 1 \mp v)[(N+1)\Omega + \Omega^2] \\ &\quad + (N/2 \pm v)^2(N/2 + 1 \mp v)^2\}^{1/2} \quad \text{for } v' = v + 1 \end{aligned} \tag{35}$$

$$\langle v\Omega|\boldsymbol{l}^2|v'\Omega'\rangle = \sum_{j=\Omega}^{N-\Omega} \left\langle \frac{N}{2}\frac{N}{2} + \Omega v - v \,\middle|\, j0 \right\rangle \langle j\Omega|\boldsymbol{l}^2|j\Omega'\rangle \left\langle \frac{N}{2}\frac{N}{2} + \Omega' v' - v' \,\middle|\, j0 \right\rangle \tag{36}$$

where $\Omega' = \Omega + 1$. In Fig. 2 we illustrate the structure of the total interaction matrix in this discrete representation.

8. Extension and implementations of the algorithm to reactive collisions

The matrix representations for the $\boldsymbol{j}^2$ and $\boldsymbol{l}^2$ operators obtained in the previous section show that the kinetic energy operator in this approach reduces to a matrix whose structure is extremely *sparse* and whose elements are expressible either explicitly or as simple sums, *independent* of the system under consideration. Both features are important when numerical implementation of the algorithm is considered. Besides obvious simplifications in programming and storing, the structure suggests that advantages may be achieved in parallel performing of operations regarding different energies, angular momenta, interactions.

The diagonal structure of the interaction potential avoids a common computational bottleneck, i.e. the integration procedures needed to generate matrix elements in conventional approaches. Furthermore, in problems where the interaction is strongly localized in configuration space, the present algorithm shows the advantage (common to finite difference schemes) of natural *truncations* of the basis.

Extensions to reactive collisions is natural in the hyperspherical formalism, where the procedure leads to an orthonormal basis for the expansion of the three-body wavefunctions at fixed values of the hyperradius: its utility is sought for the calculation of adiabatic eigenvalues and nonadiabatic coupling. In our formalism we exploit the fact that a finite set of Hahn polynomials is the discrete analog of an infinite set of Jacobi polynomials [24]. Since hyperspherical harmonics are related to the latter [2], Hahn polynomials are used to build up the discrete analogs of the harmonics themselves. It turns out that the Hahn polynomials coincide up to normalization and weight with $3j$ symbols generalized [25] to any angular momentum, and consequently they enjoy the properties of the vector coupling coefficients (orthogonality, dual orthogonality, recurrence relation, difference equation).

A hyperquantization algorithm is developed [26], within the framework of this hyperangular momentum algebra, introducing an artificial vector which divides the space into boxes and whose projections select the lattice points. These orthogonal discrete basis sets are also of interest for finding useful decoupling schemes for the three-body dynamical problem. These schemes involve the full or partial conservation of quantum numbers corresponding to angular momenta, their projections and their generalizations on the hypersphere. Orthogonal transformations among representations appropriate between the various reaction channels and intermediate states of the reaction have been worked out and can be exploited both for simplifying complete calculations and for the qualitative description of the rearrangements process.

The possibility of alternative grids, for example exploiting a quadratic grid allowed by the dual Hahn polynomials and also the various choices of hyperspherical coordinates [2, 15, 21] are being explored.

9. Concluding remarks

In conclusion, the simple structure of the algorithm here considered lends itself to take advantage of any progress in storing and manipulating large matrices. Physically motivated approximations can be easily implemented in computationally advantageous form, since the procedure provides a transparent set of quantum numbers, some physical and some artificial: so for example a coupled state scheme in the atom-diatom problem, corresponding to Ω conservation, leads to a tridiagonal representation, seen in Fig. 2 by deleting the off-diagonal l^2 matrix elements, see also Ref. [4]. Finally it is noted that nonphysical quantum numbers, such as v in previous sections and Fig. 1, although can be merely viewed as labels of lattice points, convey information on the role of spatial configurations of quantum mechanical systems. They label molecular orientations. Some indications of the insight that these representations imply for atom-molecule van der Waals complexes emerged in a previous study [4]: further work is in progress to exploit these labels of molecular orientations for inelastic and reactive collisions.

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References

1. Lill JV, Parker GA, Light JC (1982) Chem Phys Lett 89:483; Heather RW, Light JC (1983) J Chem Phys 79:147. See Muckerman JT (1990) Chem Phys Lett 173:200 for recent developments
2. Aquilanti V, Cavalli S, Grossi G (1986) J Chem Phys 85:1362
3. Aquilanti V, Grossi G (1985) Lett Nuovo Cimento 42:157
4. Aquilanti V, Beneventi L, Grossi G, Vecchiocattivi F (1988) J Chem Phys 89:751
5. Goldberger ML, Watson KM (1964) Collision theory. Wiley, New York, p 882
6. Jacob M, Wick GC (1959) Ann Phys 7:404
7. Aquilanti V, Grossi G (1980) J Chem Phys 73:1165; Aquilanti V, Grossi G, Laganà A (1981) Nuovo Cimento 63b:7
8. Chang ES, Fano U (1972) Phys Rev A6:173
9. Vilenkin NY (1968) Special functions and the theory of group representations. Am Math Soc, Providence, R.I.

10. Smorodinskii YA, Suslov SK (1982) Sov J Nucl Phys 35:108; (1982) 36:623 and references therein; Smirnov YF, Suslov SK, Shirokov AM (1984) J Phys A17:2157; Atakishiyev NM, Suslov SK (1985) J Phys A18:1583; Pluhar Z, Smirnov YF, Tolstoy VN (1986) J Phys A19:21
11. Rose ME (1957) Elementary theory of angular momentum. Wiley, New York; Edmonds AR (1960) Angular momentum in quantum mechanics. Princeton, New Jersey; Brink DM, Satchler GR (1968) Angular momentum. Clarendon, Oxford; Varshalovic DA, Moskalev AN, Khersonskii VK (1988) Quantum theory of angular momentum. World Scientific, Singapore; Zare RN (1988) Angular momentum. Wiley, New York
12. Hildebrand FB (1956) Introduction to numerical analysis. McGraw-Hill, New York, p 287
13. Abramowitz M, Stegun IA (eds) (1965) Handbook of mathematical functions. Dover, New York, p 790
14. Smith FT (1960) Phys Rev 120:1058
15. Aquilanti V, Grossi G, Laganà A (1982) J Chem Phys 76:1587
16. Fano U (1981) Phys Rev A24:2402
17. Arthurs AM, Dalgarno A (1960) Proc Roy Soc A256:540
18. Alder K, Bohr A, Huus T, Mottelson B, Winther A (1956) Rev Mod Phys 28:432; Brussaard PJ, Tolhoek HA (1957) Physica 23:955; Schulten K, Gordon RG (1975) J Math Phys 16:1971
19. Khare V (1978) J Chem Phys 68:4361
20. Dickinson AS, Certain PR (1968) J Chem Phys 49:4209
21. Aquilanti V, Grossi G, Laganà A (1982) Chem Phys Lett 93:174; Aquilanti V, Cavalli S, Laganá A (1982) Chem Phys Lett 93:179; Aquilanti V, Cavalli S (1987) Chem Phys Lett 141:309; Aquilanti V, Cavalli S, Grossi G, Anderson RW (1990) J Chem Soc Faraday Trans 86:1681
22. Walker RB, Light JC (1975) Chem Phys 7:84
23. Launay JM (1976) J Phys B9:1823
24. Erdelyi A (1953) Higher trascendental functions, vol 2. McGraw-Hill, New York; Karlin S, McGregor JL (1961) Scripta Math 26:33
25. Kil'dyushov MS (1972) Sov J Nucl Phys 15:113
26. Aquilanti V, Cavalli S, Grossi G, Anderson RW (in preparation)