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Harmonic analysis and discrete polynomials. From semiclassical angular momentum theory to the hyperquantization algorithm

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Abstract. Orthogonal polynomials of a discrete variable have been widely investigated as fundamental tools of numerical analysis. This work aims to propose the extension of their use to quantum mechanical problems. By exploiting both their connection with coupling and recoupling coefficients of angular momentum theory and their asymptotic relationships (semiclassical limit) with spherical and hyperspherical harmonics, a discretization procedure, the hyperquantization algorithm, has been developed and applied to the study of anisotropic interactions and of reactive scattering. One of the most appealing features of this method turns out to be a drastic reduction of memory requirements and computing time for extensive dynamical calculations. Examples of the application of this technique to stereodirected dynamics via an exact representation for the **S** matrix as well as to the characterization of molecular beam polarization are also illustrated.

Key words: Hyperspherical harmonics – Discrete polynomials – Angular momentum

1 Introduction: vector coupling in quantum mechanics and generalized hypergeometric series

In quantum mechanics, couplings of angular momenta are described as orthogonal basis transformations which, according to the early developments essentially due to Wigner, correspond to the Clebsch–Gordan coefficients of group theory. Wigner's $3j$ coefficients describe the coupling between states $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ so to give $|j, m\rangle$. As quantum numbers vary in their allowed ranges (the j's according to triangularity conditions and $m_1 + m_2 = m$), they form orthonormal vectors. Arranged in matrices, they can be considered as matrix elements, where quantum numbers are indices for their allocations [1–7].

Even more crucial for angular momentum theory are the recoupling coefficients of Racah, which can be written as Wigner's $6j$ symbols. Among their properties, there are "pentagonal" and "hexagonal" sum rules and three-term recursive relationships that allow their efficient computation [8–10].

These coefficients can be written as single sums of the hypergeometric type [4–6]. Specifically, of the ${}_3F_2(1)$ and ${}_4F_3(1)$ type for $3j$ and $6j$ symbols, respectively. Note that the classical orthogonal polynomials of harmonic analysis (Jacobi, Gegenbauer, Legendre, etc.) are essentially Gaussian hypergeometric series, ${}_2F_1(x)$. This led to the discovery of many interesting properties, including symmetries which were not obvious from the physical standpoint [11,12], suggesting that their role could be wider than that in the context in which Wigner, Racah and other founders of quantum angular momentum theory introduced them.

The physical and mathematical viewpoints have led in recent years to important developments. Here, we will elaborate on the relevance of these advances from the point of view of applications to computational quantum mechanics. See the scheme in Fig. 1 for an illustration of the relationships which will be exploited in the following.

The next section outlines connections of coupling and recoupling coefficients with the orthogonal polynomials of a discrete variable, of use in numerical analysis. In Sect. 3 the semiclassical (high-j) limits of the coefficients are presented, exhibiting their asymptotic correspondence with spherical harmonics and rotation matrices spanning continuous angular ranges. Section 4 takes the opposite route: discrete orthogonal polynomials are used as discrete analogues of spherical (and hyperspherical) harmonics and explicit examples are given demonstrating the computational advantages of discretization procedures. An outlook and perspective of further applications are presented in the final section.

2 $3nj$ symbols and the discrete polynomials of numerical analysis

At the end of the 1950s interest was renewed in the mathematical theory of discrete polynomials, particularly relevant being the work by Hahn (See ref. [13]). For

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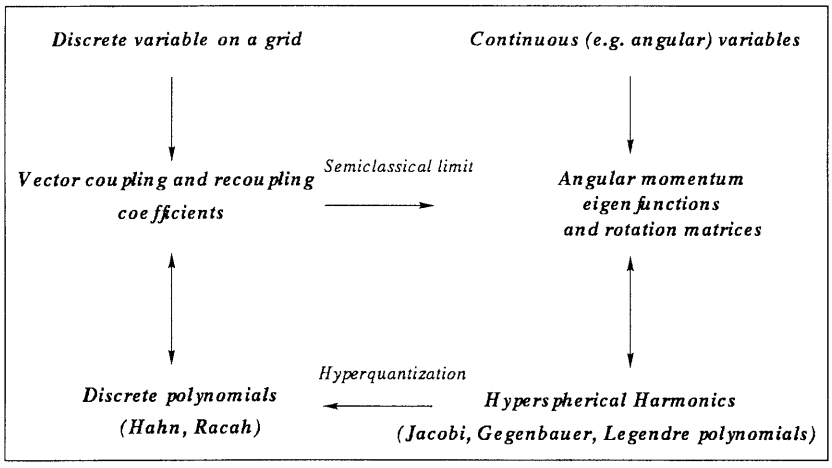

Fig. 1. Illustration of the correspondences among vector coupling and recoupling coefficients, discrete polynomials, angular momentum eigenfunctions, rotation matrices and hyperspherical harmonics within the framework of discrete–continuous (semiclassical limit) and reverse (hyperquantization) transformations

example, discrete polynomials (or better polynomials of a discrete variable) are briefly mentioned in a classic handbook of mathematical functions [14] and in a well-known treatise on numerical analysis [15].

Polynomials of a discrete variable appear to have been introduced by Chebyshev more than a century ago (a list is given in Ref. [14]). References [14, 15] illustrate their use for the best representation in the least-squares sense of functions tabulated on a finite discrete number of points.

These polynomials are orthogonal in a discrete range of the variable and can be written as hypergeometric sums. They are currently widely investigated [16] and, in recent years, a classification of them (Askey scheme [17]) has been proposed.

An interesting aspect is that the coefficients of angular momentum theory can be identified with particular cases of discrete polynomials. Specifically $3j$ coefficients, after proper normalization, can be identified with particular cases of Hahn polynomials [13]. As the simplest example, it can be verified that the identification (apart from phases and normalization) between the vector coupling coefficients and the discrete Chebyshev polynomials for integer values of their arguments is best obtained by directly comparing their explicit expressions.

At the top of the Askey scheme, as the most general of these polynomials, Askey and Wilson studied discrete polynomials, from which the others can be derived by limiting procedures [17]. These polynomials turn out to be generalizations of $6j$ coefficients (or Racah coefficients) so the name Racah's polynomials was given to them.

3 Spherical harmonics as the semiclassical limit of coupling coefficients

Semiclassical limits of $3j$ and $6j$ coefficients have been investigated for a long time [18–22]. Racah first derived an asymptotic formula relating $6j$ symbols and Legendre polynomials. Edmonds later generalized Racah's formula by substituting the Legendre polynomial with a rotation matrix. See also the work of Schulten and Gordon [8–10].

An important step forward was made some years later by Ponzano and Regge, who first studied, in a general context, the variation of Racah's coefficients as a function of their entries for large values of the arguments. They also discussed the geometry of the asymptotes of the $3j$ and $6j$ symbols, associating with each asymptotic $6j$ symbol a tetrahedron (Fig. 2a), whose edges had length $j+1/2$, where j is any entry in the $6j$ symbol and with each asymptotic $3j$ symbol a triangle (Fig. 2b), whose edges were labeled in the same manner.

The basic asymptotic formula relating $6j$ coefficients and rotation matrices is thus written as

$$\begin{Bmatrix} L & M & N \\ l & N+n & M+m \end{Bmatrix} \approx \frac{(-1)^{N+M+L+l+m}}{\sqrt{(2N+1)(2M+1)}} d^l_{nm}(\phi) \tag{1}$$

for $L, M, N \gg l, m, n$ and where

$$\cos\phi = \frac{(N+n+1/2)^2+(M+m+1/2)^2-(L+1/2)^2}{2(N+n+1/2)(M+m+1/2)} \; . \tag{2}$$

A further result relates the $3j$ symbol to a rotation matrix, for $N \gg l$

$$\begin{pmatrix} l & N+n & N \\ -\mu & \mu-\nu & \nu \end{pmatrix} \approx \frac{(-1)^{l-N-\nu}}{\sqrt{(2N+1)}} d^l_{n,\mu}(\theta) \; , \tag{3}$$

where

$$\cos\theta = \frac{2\nu}{N+1} \; . \tag{4}$$

Rotation matrices can be considered as particular cases of Jacobi polynomials, which enter in physics as the special functions in the theory of representation of continuous groups. Therefore, the correspondences previously enunciated among coupling and recoupling coefficients and rotation matrices also hold for spherical (and hyperspherical) harmonics, which are important particular cases.

Note also the limiting relationship between the $6j$ and $3j$ symbols:

$$\begin{Bmatrix} l & m & n \\ L & M & N \end{Bmatrix} \approx \frac{(-)^{-2(l+L)}}{(L+M+1)^{\frac{1}{2}}} \times \begin{pmatrix} l & m & n \\ N-M & L-N & M-L \end{pmatrix} \; . \tag{5}$$

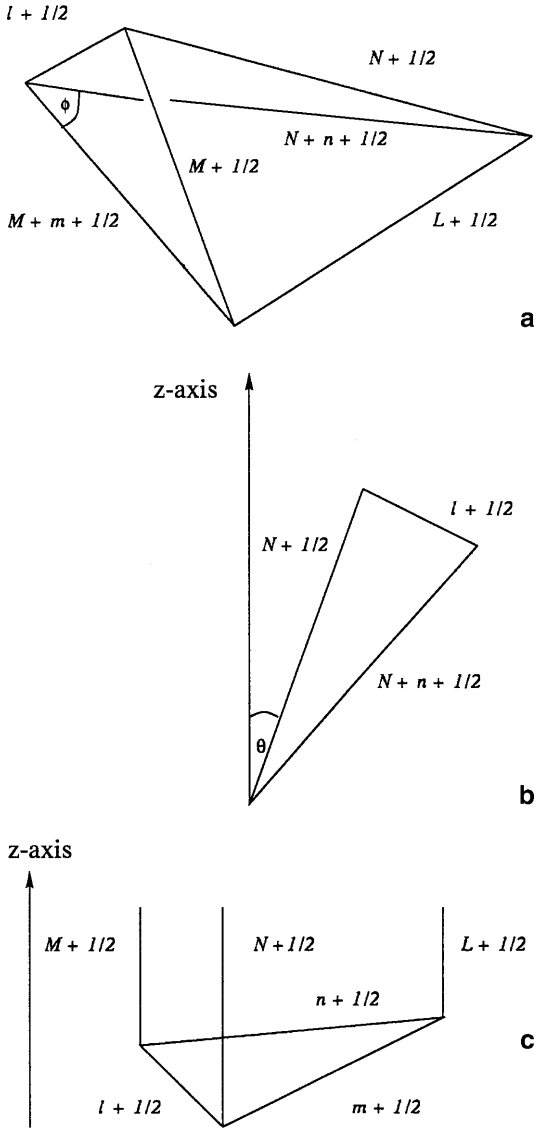

Fig. 2. Geometrical representations of the asymptotic behavior for coupling and recoupling coefficients: a tetrahedron for $6j$ (*panel a*), a triangle for $3j$ (*panel b*) and a distorted tetrahedron for the asymptotic correspondence among $6j$ and $3j$ symbols (*panel c*)

The geometrical interpretation of the above result discussed by Ponzano and Regge is shown in Fig. 2c. As L, M and N in the above $6j$ symbol grow larger, three of the vertices of the associated tetrahedron remain fixed, while the fourth one moves away from the others. This causes the edges labeled by L, M and N to become parallel to each other. These edges define a z-axis, with $N-M$, $L-N$ and $M-L$ being the projections of the edges labeled by l, m and n onto this axis. The triangle associated with the above $3j$ symbol is the unscaled triangle in the associated tetrahedron formed by the three fixed vertices.

Due to this asymptotic correspondence between $3j$ and $6j$ coefficients, Ponzano and Regge state that the $6j$ symbols are the basic ingredients of the theory. Compare also the key role of Racah's polynomials in the Askey scheme. Furthermore, it is important to realize that quantum numbers, appearing as angular momenta (or their projections), are identified with "angles" in the semiclassical limit (i.e. for high angular momenta): this property (remember that angular momentum and angular divergence of vectors are conjugate quantities) is the basis of a long investigation into the supposedly discrete structure of space-time. See Ref. [23] and references therein.

4 Hyperquantization: discrete analogues of spherical harmonics

The hyperquantization technique belongs to the class of direct approaches to the solution of Schrödinger's equation by finite difference. Nevertheless, it differs from other finite difference schemes, such as the discrete variable representation [24], in exploiting discrete analogues of orthonormal bases, i.e. hyperspherical harmonics, usually defined on continuous variables. Harmonics belong to the class of Jacobi polynomials and their discrete analogues, in this application, are Hahn polynomials, ${}_3F_2$ hypergeometric functions of unit arguments. These polynomials, orthogonal on lattice points, can be identified, in particular cases, with the Clebsch–Gordan coefficients in the quantum theory of angular momentum [13].

In a physical picture of this technique, discretization can be interpreted as a quantization of an artificial angular momentum vector, $\mathbf{A}$, of length $A+1/2$. Hyperquantization establishes a correspondence between this vector, with $A=N/2$, and the discretization of space into $N+1$ slices, convergence to exact results being achieved in the limit of large N [25, 26].

An important advantage is that this technique can be extended to any number of mathematical dimensions and it has found an application in different contexts, such as the study of anisotropic interactions, reactive scattering, stereodirected dynamics and analysis of molecular beam polarization.

4.1 Anisotropic potential

The quantum mechanical treatment of anisotropic interactions is based on the coupling among different channels, which can be expressed in terms of matrix elements involving sums over vector coupling and recoupling coefficients. Jacob and Wick [27] introduced the helicity formalism, leading to some simplifications resulting from the development of alternative reference frames corresponding to alternative coupling schemes. It is then possible to formulate the coupling in terms of quantum numbers which-correspond to approximate constants of motion.

Hund first introduced alternative coupling schemes for diatomic molecules carrying spin, electronic and rotational angular momenta. The correspondence between Hund's cases and the possible angular momentum coupling schemes at a given total angular momentum has been widely investigated [28].

For general anisotropic interactions it has been demonstrated that it is possible to introduce discretization procedures in some expressions of Racah's algebra, leading to the introduction of alternative coupling schemes, labeled by artificial quantum numbers, for the solution of the multichannel Schrödinger differential equation. See Refs. [25, 26, 29], for the mathematical formulation of the hyperquantization technique together with its application to anisotropic potential.

4.2 Reactive scattering

Within the hyperspherical approach, the dynamical characterization of a three-body problem is first accomplished by a quantization on the surface of a hypersphere (a sphere in a six-dimensional space) at fixed values of the hyperradius (a measure of total inertia), then coupled-channel equations are in general integrated by applying a propagator technique. For an elementary introduction, See Ref. [30]. The computation of the adiabatic eigenvalues containing information on the structure, rotations and internal modes (except that along the hyperradius) is typically very demanding from the computational point of view.

The hyperquantization algorithm has recently been employed in reactive scattering calculations, introducing a reformulation of the matrix representation of the total Hamiltonian, which turns out to be very sparse and with many symmetry properties, thus allowing a considerable reduction in the memory requirements for the storage and in the computing time involved in the building up and diagonalization of very large basis sets. This technique exploits the peculiar properties of the discrete analogues of hyperspherical harmonics, i.e. Hahn polynomials orthogonal on a discrete grid of points which span the interaction region, leading to a tridiagonal matrix representation of the kinetic energy operator and a diagonal representation of the interaction potential [31]. A particularly advantageous aspect of the method is that no integrals are required and the construction of the kinetic energy matrix is very simple.

Convergent dynamical calculations for the benchmark reaction F + H_2 have recently been performed, including fine-structure effect on the reactivity [32, 33].

4.3 Stereodirected representation

Reaction stereodynamics focuses on vector properties, such as angular momentum vector correlation and steric effects, of the reactive process under investigation.

Thanks to the development of molecular beam techniques with polarized lasers as well as electric and magnetic fields, experimental observation of stereodynamical properties has become feasible [34] and also their theoretical investigation has recently been performed using a time-independent hyperspherical coordinate method. Within this approach, it is possible to calculate the full **S** matrix, from which exact three-dimensional values of stereodynamical properties can be derived. Reaction stereodynamics studies can be carried out using alternative representations of the **S** matrix. Body-fixed representations, each of them taking a different vector of the arrangement as the quantization axis, are particularly advantageous. The stereodirected representation is characterized by the introduction of the steric quantum number, v, the projection of an artificial vector, **A**, precessing around **R** (the Jacobi vector pointing from the diatom center of mass to the third atom of the arrangement). As the modulus of this vector increases, the grid of discrete values of the precession angle more finely scans the angle, θ, between the Jacobi vectors. Different representations can be easily interconverted by means of orthogonal transformations, expressed in terms of Wigner $3j$ symbols, which preserve the symmetry and unitarity of the **S** matrix in each representation [22].

The exact three-dimensional method based on the stereodirected representation has recently been employed to calculate stereodynamical properties of the Li + HF [35, 36] and Na + HF [37] reactions.

4.4 Discrete multipole moments for polarization

The relationship between polarizability, anisotropy and the discretization of spatial distribution of the rotational angular momentum vector, **J**, has been widely investigated [38].

The discrete analogues of classical multipole moments of the angular momentum distribution, a_l^J, can be represented in terms of vector coupling coefficients as follows:

$$a_l^J = \frac{1}{N_J}\frac{1}{(2J+1)^{\frac{1}{2}}} \times \sum_{M=-J}^{+J}(-)^{J-M-1}\begin{pmatrix} J & J & l \\ M & -M & 0 \end{pmatrix} n_J^M \ , \tag{6}$$

where N_J is the total number of molecules in the rotational level J, M goes from $-J$ to J and $n_J(\theta)$ is the number of molecules whose **J** vector forms an angle θ with respect to the direction of the molecular beam.

By exploiting the orthogonality properties of vector coupling coefficients, it is possible to express the relative population of sublevel n_J^M in terms of the discrete analogues of the classical multipole moments of the angular momentum distribution by simply inverting Eq. (6):

$$n_J^M = N_J(2J+1)^{\frac{1}{2}}\sum_{l=0}^{2J}(-)^{J-M-1}\begin{pmatrix} J & J & l \\ M & -M & 0 \end{pmatrix} a_l^J \ . \tag{7}$$

It is possible to use the asymptotic relationship between Legendre polynomials and particular vector coupling coefficients with large angular momenta – a particular case of formulas in Sect. 3, taking into account that $d_{00}^l(\theta) = P_l(\cos\theta)$.

$$P_l(\cos\theta) \approx (2J+1)^{\frac{1}{2}}(-)^{J-M-1}\begin{pmatrix} J & J & l \\ M & -M & 0 \end{pmatrix} \tag{8}$$

for $J \gg l$, with $\cos\theta = -2M/(2J+1)$ discretizing the θ range (from 0 to π) on a grid of $2J+1$ points.

Classical multipole moments can thus be obtained after integration over θ:

$$a_l^J = \frac{(l+\frac{1}{2})}{N_J} \int_0^\pi n_j(\theta) P_l(\cos\theta) \tag{9}$$

and the classical expression for the spatial distribution of the rotational angular momentum can be discretized as follows:

$$n_j(\theta) = N_J \sum_{l=0}^{\infty} a_l P_l(\cos\theta) \ . \tag{10}$$

The relationship of the parameters a_l^J with the usual of $A_q^l(J)$ of the spherical tensor formalism for the description of orientation and alignment is briefly considered in Ref. [38].

5 Conclusions and perspectives: fitting of potential-energy surfaces

Let us look back to the examples and theory outlined in the previous sections. The last example (Sect. 4.4) leads to the speculation that in order to specify a quantum mechanical state one can actually eliminate continuous variables, such as those spanning an angular range. Instead there appear to emerge "bins" where states of definite angular momenta find their place. Actually, it is not often realized that "angles" are conjugate quantities with respect to angular momenta (Ref. [39], pp. 369–415). These "bins" are a discretization associated with uncertainty. In the stereodirected representation (Sect. 4.3), cones whose aperture angles are dictated by the uncertainty principle act as discrete funnels for entrance and exit reaction channels. In our hyperquantization algorithm for reactive (Sect. 4.2) or, in general, anisotropic (Sect. 4.1) interactions, the dynamics on continuous manifolds is "discretized" by introducing, as computational indices, quantities formally analogous to quantum numbers. The mathematical tools, Hahn and Racah polynomials (generalizations of $3j$ and $6j$ vector coupling and recoupling coefficients), are indeed the discrete analogues of the classic orthonormal polynomials of harmonic analysis on symmetric manifolds (providing the special functions for the representation of groups, such as rotation matrices and angular momentum wavefunctions). Their use for expansion basis for fitting and interpolating potential-energy functions is being investigated. The q extensions, the literature on which is growing motivated by implications both in topology and group theory and in particle physics and astrophysics [40–44], are also of particular interest for possible extensions to some of the applications outlined in this work.

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