J. Phys. B: At. Mol. Opt. Phys. **32** (1999) R1–R37. Printed in the UK PII: S0953-4075(99)94632-1

TOPICAL REVIEW

Geometry and symmetries of multi-particle systems

U Fano†, D Green‡, J L Bohn§ and T A Heim‖

† Physics Department and James Franck Institute, University of Chicago, Chicago, IL 60637, USA
‡ Department of Physics, PO Box 208120, Yale University, New Haven, CT 06520, USA
§ JILA, University of Colorado, Boulder, CO 80309, USA
‖ Department of Physics and Astronomy, University of Basel, CH-4056 Basel, Switzerland

Received 21 October 1998

Abstract. The quantum dynamical evolution of atomic and molecular aggregates, from their compact to their fragmented states, is parametrized by a single collective radial parameter. Treating all the remaining particle coordinates in d dimensions democratically, as a set of angles orthogonal to this collective radius or by equivalent variables, bypasses all independent-particle approximations. The invariance of the total kinetic energy under arbitrary d-dimensional transformations which preserve the radial parameter gives rise to novel quantum numbers and ladder operators interconnecting its eigenstates at each value of the radial parameter.

We develop the systematics and technology of this approach, introducing the relevant mathematics tutorially, by analogy to the familiar theory of angular momentum in three dimensions. The angular basis functions so obtained are treated in a manifestly coordinate-free manner, thus serving as a flexible generalized basis for carrying out detailed studies of wavefunction evolution in multi-particle systems.

1. Introduction

The challenge for atomic and molecular theory to deal with progressively larger aggregates of electrons and nuclei suggests treating them in terms of global parameters, in contrast to the usual independent-particle approach [1–4]. Globally one may represent each configuration of N particles by a single vector $\boldsymbol{R}$ identified by $3(N-1)$ internal coordinates with the origin at its centre of mass. $\boldsymbol{R}$'s modulus R thus represents the aggregate's overall size, while its direction $\hat{\boldsymbol{R}}$ specifies its geometry, i.e. the layout of the constituents' relative locations and orientations. Quantum dynamics then controls wavefunctions of $\boldsymbol{R}$ that emphasize $\hat{\boldsymbol{R}}$'s evolution from a compact to a fragmented structure as R grows.

In the centre-of-mass frame, the reduced two-body Coulomb problem separates in spherical coordinates. Extending the system by adding more particles, the *kinetic* energy retains its three-dimensional spherical symmetry as a subset of its symmetry in higher dimensions. This remark suggests concentrating the search for appropriate coordinates on the kinetic energy. Hyperspherical coordinates prove suitable for our task, by combining the symmetries of particles' kinetic energies into a unified internal kinetic energy of the whole aggregate. This procedure ensures an accurate description in the compact limit where the aggregate's kinetic energy predominates.

In a first step, hyperspherical coordinates separate $\boldsymbol{R}$'s modulus R from its direction $\hat{\boldsymbol{R}}$, the latter being represented by parameters analogous to the polar coordinates of physical space. The polar-coordinate symmetries, embodied in the familiar formalism of angular

momentum theory, thus extend automatically to $\boldsymbol{R}$'s $(3N-3)$-dimensional treatment. Our proposed perspective of hyperspherical coordinates as extending the three-dimensional spherical symmetry to higher dimensions affords advantages far beyond the technical aspect of providing a convenient coordinate system. Separating the single hyper-radius R from a large number of hyper-angles, and focusing on the symmetries under transformations of these hyper-angles, allows one to handle most of the many degrees of freedom in a multi-particle system analytically. For example, explicit calculation of angular integrals may be avoided in much the same way as in ordinary three-dimensional angular momentum theory by replacing such overlaps with coupling coefficients derived directly from the symmetry under (d-dimensional) rotations. A second example employs the *coordinate-independent* representation of d-dimensional transformations [5–8] to construct complete sets of hyperspherical harmonics, higher-dimensional analogues of spherical harmonics, *without* solving partial differential equations in any specific coordinate system. This application proceeds much as in three dimensions, where all harmonics may be built recursively from a single function once the appropriate 'laddering' operators are identified. The resulting flexibility in choosing centre-of-mass coordinate frames is crucial in the case of a multi-particle system with its evolving structure, because no single reference frame proves appropriate throughout the *entire* evolution.

The hyper-radius R serves as the 'evolution parameter' of wavefunctions $\Psi(R;\hat{\boldsymbol{R}})$, whose $\hat{\boldsymbol{R}}$-dependent features evolve with increasing R toward their alternative fragmentation terminals. In more detail, the hyper-radius R of an N-body aggregate of masses $m_1, m_2, \ldots, m_N$, located at coordinates $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ from the centre of mass, is given by

$$R = \left(\sum_{i=1}^{N} \frac{M_i r_i^2}{\mathcal{M}} \right)^{1/2} \qquad \mathcal{M} = \sum_{i=1}^{N} M_i. \tag{1.1}$$

In the special case of charged, point-like constituents (electrons and nuclei) relevant to atomic and molecular applications, the Schrödinger equation governing the aggregate's evolution takes the hydrogen-like form, in atomic units (au) [1],

$$\left[-\frac{1}{2\mathcal{M}} \left(\frac{\mathrm{d}^2}{\mathrm{d}R^2} + \frac{\Delta_{\hat{\boldsymbol{R}}}}{R^2} \right) + \frac{Z(\hat{\boldsymbol{R}})}{R} \right] R^{(3N-4)/2} \Psi(R;\hat{\boldsymbol{R}}) = E\, R^{(3N-4)/2} \Psi(R;\hat{\boldsymbol{R}}). \tag{1.2}$$

The factors $R^{(3N-4)/2}$, proportional to the square root of a hypersphere's area with radius R, correspond to the familiar factor r of wavefunctions in physical space. Note how $(3N-4)/2$ reduces to unity for the H atom, where $N=2$. Separation of these factors affords non-zero values of Ψ at $R=0$ and removes first derivatives from (1.2).

The general theory of hyperspherical coordinates (originally conceived for three-body scattering problems) dates to the 1950s [9–12]. Since then, hyperspherical methods have been fruitfully applied to a wide variety of many-body phenomena ranging from quantum chemistry to particle physics, as illustrated, for example, by several contributions in [13].

Delves [14, 15] pioneered the method's application to shell-model calculations of nuclei. To this day, the hyperspherical approach remains a standard tool in nuclear physics, notably in the study of halo nuclei [16], three-nucleon systems [17], as well as large nuclei [18] and even subnuclear (quark) structure [19]. (For reviews on hyperspherical methods in the context of nuclear physics, see e.g. [20–22].)

In the seemingly very different context of reactive scattering in quantum chemistry, the participating atoms' coordinates have typically been cast in hyperspherical form, their motions being governed by effective potentials [23–25]. Besides molecular reactions [26–32], the hyperspherical approach also applies to molecular structure [33] and quantum phase effects in chemical reactions [34, 35].

These applications required more general and mathematical investigations on the structure and properties of hyperspherical functions [36–39], with a special focus on additional quantum-physical features such as antisymmetrization in fermion systems [40–42] and internal structures of an N-particle system in three-dimensional space [43].

Applications of hyperspherical methods to doubly excited states of two-electron systems in atomic physics [1, 2] resulted in a complete classification scheme for these states [44–47], based on systematic investigations of the wavefunctions' structure [48–51]. Connections with molecular structure [52, 53] arising from these classifications have more recently afforded extending the hyperspherical approach to systems with several heavy particles besides electrons (i.e. to molecules) [54]. In three-body Coulomb problems, hyperspherical methods have become computationally competitive through the 'hyperspherical close-coupling method' [55], and more recently in the form of 'diabatic-by-sector' numerical methods [56]. Another extension employing over-complete basis sets afforded determining accurately resonances of very high-lying doubly excited states close to the threshold for double ionization [57, 58]. Thus, the hyperspherical approach covers essentially the entire energy range from the ground state, through the 'Wannier region' around threshold for full disintegration, to energies high above this regime (see, e.g., [59]). Besides the two-electron atom and generic three-body Coulomb systems, studies have focused on doubly excited many-electron atoms [60, 61], with several forays into atoms with three [62–66] or even more *excited* electrons [67–69]. Moreover, the treatment of highly excited atoms in external fields [70, 71] has extended the list of successful applications of the hyperspherical method in yet another direction. Currently, physically adapted Sturmian basis sets promise further advances in broader contexts [72]. Reviews on various aspects of the hyperspherical approach in atomic physics may be found, for example, in [73–75]. See also [76] for a discussion of the reliability of the hyperspherical adiabatic method.

Our equation (1.2) implies going a step further, extending hyperspherical coordinates to all constituents, electrons and nuclei, governed by their Coulomb interactions. Equation (1.2) thus represents an exact Schrödinger equation, and all calculations proceeding from (1.2) will be completely *ab initio* [3, 4, 77–79].

We intend in this review to encompass all types of applications of hyperspherical coordinates. Thus the definition (1.1) need only extend over the dynamically relevant variables for a given problem, ignoring, for instance, the coordinates of electrons belonging to closed shells. In this context note already the interplay between 'motions' on widely different (time) scales: at each fixed hyper-radius R, a 'geometrical' structure emerges resulting from the faster motion in the hyper-angular coordinates; the emerging structure then evolves on a different scale as R increases. This theme—central to the hyperspherical method—serves as a guideline throughout the present paper. As a qualitative illustration, consider the following hyperspherical description of a water molecule H_2O, a system consisting of ten electrons, two protons and an oxygen nucleus. In a preliminary step towards *ab initio* construction of this molecule, a hyperspherical procedure would fill first the closed inner shells of the constituent atomic cores, in this case only the K shell of O^{6+}. Recognizing the vast difference between electronic and nuclear motion, the electronic motion is 'parametrized' by the cores' arrangement. For each core arrangement, the electronic motion is analysed to find the most favourable electron distribution. This analysis proceeds in a hyperspherical representation of the valence electrons as a single entity consisting at the outset of a group of six electrons joined by two single electrons, as suggested by the core charges. Analogous procedures for the construction and transformation of such 'Jacobi trees' will be outlined in section 2. The particular arrangement of the cores should manifest itself in the hyper-radius R_e associated with the set of valence electrons alone, once the latter

are attached to the cores. The angular coordinates specifying the geometrical arrangement of the valence electrons depend parametrically on their own hyper-radius R_e, which is in turn parametrized by the 'size' and 'shape' of the nuclei (or cores). The latter is itself described by a set of hyperspherical coordinates, $\{R_N, \alpha_N, \theta_N\}$, to be introduced in section 2, thereby completing the hierarchy of geometrical structures governed by the interplay of hyper-radial and angular motions, and of electronic and atomic motions. The dynamical evolution of the 'shape' characterizing the cores' arrangement should minimize the energy of the whole molecule for the correct molecular geometry, while the hyper-angles characterizing the distribution of valence electrons should indicate that four of them are essentially attached to the O^{6+} core, with the remaining two pairs forming the bonds holding the molecule together. Without attempting to carry out the computational details of this description, the present paper introduces techniques required for its implementation. Namely, we intend to focus on the universal (i.e. coordinate-independent) aspects of hyperspherical coordinates and harmonics, to be implemented upon identifying the suitable Jacobi coordinates of a specific system.

Returning to equation (1.2), we note that features of Ψ are discrete, owing to the finite extent of hyperspherical surfaces, being accordingly represented by appropriate quantum numbers and nodal structures rather than by coordinates, much as they are in three dimensions; their interpretation will, however, require not only adequate mastery of high-dimensional geometry, a subject of this paper, but also of the dynamical interplay between light electrons and heavy nuclei. Equation (1.2) should serve to calculate energy eigenfunctions for *any* atom, molecule or analogous aggregate. Its solution for 'collision complexes' formed by colliding molecules will provide the relevant scattering matrix directly, as indicated in section 5, bypassing the calculation and study of energy surfaces.

The structure of (1.2) parallels that of the atomic H equation, being actually its extension to multi-particle systems. Its first term represents the kinetic energy of the hyper-radial motions, its second term that of the hyper-angular motions, and its last term the potential energy, which—being the sum of Coulomb interactions among all of the aggregate's particle pairs—scales as R^{-1}. The evolution of Ψ's angular part as a function of R, foreign to hydrogen, stems from the non-zero value of the commutator $[\Delta_{\hat{\boldsymbol{R}}}, Z(\hat{\boldsymbol{R}})]$.

Equation (1.2) preserves instead hydrogen's invariance under coordinate rotations by securing invariance of the kinetic energy operator $\Delta_{\hat{\boldsymbol{R}}}/2\mathcal{M}$ under rotations of $\hat{\boldsymbol{R}}$ about the centre of mass, by mass weighting the coordinates as described in the following. Sets of mutually independent eigenfunctions of $\Delta_{\hat{\boldsymbol{R}}}$'s, analogues of spherical harmonics called 'hyperspherical harmonics', serve to expand (1.2) into a system of coupled ordinary differential equations in the variable R, analogous to those of atomic physics. The 'effective atomic number' operator $Z(\hat{\boldsymbol{R}})$ turns then into a matrix with rows and columns labelled by hyperspherical quantum numbers.

Simple examples of such harmonics in d dimensions have been formulated [80, 81], the corresponding eigenvalues of $\Delta_{\hat{\boldsymbol{R}}}$ having long been known. These examples, to be discussed in section 3, provide solutions for the second-order eigenvalue problem of $\Delta_{\hat{\boldsymbol{R}}}$ in specific coordinate systems for d dimensions. Developing an appropriate systematics of multi-variable hyperspherical harmonics suited to each system (and thus coordinate-independent) constitutes, however, a major objective, to be approached in section 4 on the basis of symmetries alone.

The importance of such a description cannot be overemphasized. The distribution of $\boldsymbol{R}$'s multi-dimensional direction $\hat{\boldsymbol{R}}$ should represent specific features of each system flexibly, near and far from its centre of mass as well as at intermediate ranges. At short ranges, where the system is compact, this distribution should minimize the centrifugal effect represented by the eigenvalue of $\Delta_{\hat{\boldsymbol{R}}}$ in (1.2). At large ranges, where the system fragments, $\hat{\boldsymbol{R}}$'s distribution should

represent alternative, mutually orthogonal, fragmentation channels. Both of these contrasting representations can be achieved in terms of flexible 'Jacobi (or centre-of-mass) coordinate' sets, interrelated by algebraic transformations, the subject of section 2.2.

The present paper develops implications of the quantum discovery that pairs of variables conjugate in Hamiltonian dynamics are actually related by Fourier transformations, whereby dynamics reduces to kinematics, more generally to *geometry* (whence stems this paper's title). Expanding equation (1.2) in hyperspherical harmonics reflects but one aspect of these implications; Jacobi coordinates provide a second aspect.

The angular Laplacian's eigenvalue in d dimensions reads $\lambda(\lambda + d - 2)$, with integer λ. Thus, the system of coupled equations resulting from expansion of (1.2) into hyperspherical harmonics parametrized (in part) by the hyper-angular momentum λ is formally infinite, owing to the infinite range of λ, and seems accordingly impractical. Key circumstances, however, reduce its size generally to a modest level.

(a) For low-lying channels, the centrifugal term of (1.2), whose numerator rises as λ^2, quenches the amplitude of Ψ's components with large values of λ to negligible levels at small hyper-radius R.
(b) Correspondingly, its Coulomb term (prevailing at large R) has eigenvalues similarly spread over many orders of magnitude, its lowest one approximating the lowest dissociation threshold for molecules or ionization threshold for single atoms and its highest one approaching the threshold for full disintegration of the system.
(c) The range of λ values of practical relevance thus depends critically on the energy range relevant to each step of evolution. So do accordingly the dimensions of the corresponding set of hyperspherical harmonics and of the relevant $Z(\hat{\boldsymbol{R}})$ matrix.

Early calculations [77–79] have accordingly shown the range of λ values relevant at each value of R to be modest, thus affording ready numerical integration of (1.2). Each infinitesimal '$\mathrm{d}R$' step of this integration generates an infinitesimal rotation of the $\Psi(R; \hat{\boldsymbol{R}})$ wavefunction by $[Z(\hat{\boldsymbol{R}})/R]\mathrm{d}R$ in the $\hat{\boldsymbol{R}}$-space. The broad range of applications envisaged in the present paper rests on the power of its underlying recursive procedures and on the characteristic aptitude of computer technologies to apply such procedures step by step.

The vector $\boldsymbol{R}$, representing the structure of a multi-particle aggregate and constructed by *recursive* procedures, has been resolved above into its magnitude R and direction $\hat{\boldsymbol{R}}$, corresponding to the aggregate's size and shape, respectively. The aggregate's shape, in turn, needs *articulating* into appropriate parameters—multipole moments, for instance—representing structural features of each system, a task presenting a challenge to be approached in section 5 in terms of equation (1.2)'s eigenchannel solutions $\Phi_{\rho(R)}(\boldsymbol{R})$. An elementary example of such developments is afforded by noting that an aggregate's fragmentation elongates its shape, thus minimizing its moment of inertia about a symmetry axis. Analogous features should be identified systematically and utilized in specific applications.

The following sections should introduce the reader to analytical tools serving to treat atoms and molecules of increasing size: (a) coordinate systems whose dimensionality extends recursively and flexibly, adaptable to particle sets with different masses arising in molecular structure and collisions (section 2); (b) prototype examples of hyperspherical harmonics suitable for multi-electron atomic systems with a single heavy centre (section 3); (c) systematics of harmonics labelled by eigenvalues of commuting operator sets $\{H_i\}$, adapted to the evolving structures of atoms and molecules at increasing R (section 4). Section 5 will outline an analytical procedure to integrate (1.2), displaying the evolution of relevant wavefunctions and thereby casting the results of previous algebraic developments [7, 8] into a more explicit geometrical framework.

The wide range of symmetry applications, resulting from invariance under coordinate rotations and thus relevant for our application to quantum mechanics, is currently covered appropriately by [82]. Terminology drawn from [7, 8] will appear in '. . . ', but familiarity with these references is not assumed.

2. Linear coordinate transformations in higher dimensions

Physical-space expansions into spherical harmonics hinge on their geometrical and kinematical behaviour under coordinate rotations, labelled as the 'angular-momentum theory'. Their extension to larger coordinate sets affords flexibility for displaying geometrical and kinematical features of multi-particle systems, at the price of extending and elaborating each system's treatment.

Whereas, in a three-dimensional prototype, rotations about the x-axis, i.e. in the yz-plane, are not independent of rotations about the z-axis because of involving the z-axis itself, in a multi-dimensional setting rotations about different axes are independent *insofar* as they operate in *separate* planes. Each elementary coordinate rotation is then properly identified, in multi-dimensional settings, as occurring within (or parallel to) the plane through a given *pair of coordinate axes*, rather than as preserving a single invariant axis. Independent rotations thus occur in *non-crossing planes*, rather than within a single one, for example, in the xy- and zt-planes in four dimensions. In d dimensions the number of independent rotations is readily seen to equal the largest integer not exceeding $d/2$, i.e. $d/2$ for even values of d and $(d-1)/2$ for odd d. This number, called the *rank* of each transformation group [7, 8], is usually indicated as $\ell = [d/2]$.

Independent Hermitian infinitesimal-rotation operators, corresponding to

$$l_z = -\mathrm{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -\mathrm{i}\frac{\partial}{\partial \varphi} \tag{2.1}$$

in three dimensions, are indicated generically by H_i, here and in the following. Their analytic (differential or algebraic) expression, often analogous to (2.1), depends on a group's structure and on coordinate choices to be described later. The elementary example of the helium atom, consisting of three particles and described in terms of six coordinates $\{x_1, y_1, z_1, x_2, y_2, z_2\}$ with the origin at its centre of mass, involves three independent rotations represented, for example, by

$$-\mathrm{i}\left(x_1\frac{\partial}{\partial y_1} - y_1\frac{\partial}{\partial x_1}\right) \qquad -\mathrm{i}\left(x_2\frac{\partial}{\partial y_2} - y_2\frac{\partial}{\partial x_2}\right) \qquad -\mathrm{i}\left(z_1\frac{\partial}{\partial z_2} - z_2\frac{\partial}{\partial z_1}\right). \tag{2.2}$$

The first two of these expressions are plainly analogues of the single-particle l_z; the interpretation of the last one—intermixing two particles' coordinates—remains obscure at this point. Note also that finite rotations are familiarly represented by exponential functions of infinitesimal operators, as in the example of rotation by an angle φ about a z-axis, represented by

$$\mathrm{e}^{\mathrm{i}\varphi l_z}. \tag{2.3}$$

Maximal sets of commuting operators $\{H_i\}$, such as the three operators in (2.2), perform in multi-dimensional settings the function performed by l_z for three-dimensional rotations; their eigenvalues are also integers of either sign, often called *'weights'*. After separating the centre-of-mass motion of an N-particle aggregate, its $3N-3$ internal coordinates are partitioned typically in three-dimensional subsets of *single-particle* coordinates. Subsets of independent infinitesimal rotation operators are then conjugate to angles $\varphi_i = \tan^{-1}(y_i/x_i)$ ranging from 0 to 2π, and thus effectively boundless. These three-dimensional coordinate

subsets may also include angles $\theta_i = \tan^{-1}((x_i^2 + y_i^2)^{1/2}/z_i)$, θ_i's range being restricted by centrifugal potentials near each of its poles. Angular coordinates representing $\tan^{-1}(r_i/r_j)$ of single-particle distances from a centre of mass are similarly confined by boundary conditions. For the purpose of illustration, replace the Cartesian coordinates of helium with six (frequently used) hyperspherical coordinates, namely,

$$\begin{aligned} R &= (x_1^2 + y_1^2 + z_1^2 + x_2^2 + y_2^2 + z_2^2)^{1/2} \\ \alpha &= \tan^{-1}\left(\frac{x_2^2 + y_2^2 + z_2^2}{x_1^2 + y_1^2 + z_1^2}\right)^{1/2} \\ \theta_i &= \tan^{-1}\left(\frac{(x_i^2 + y_i^2)^{1/2}}{z_i}\right) \qquad i = 1, 2 \\ \varphi_i &= \tan^{-1}\left(\frac{y_i}{x_i}\right). \end{aligned} \tag{2.4}$$

These definitions map the indistinguishability of electrons onto a *novel symmetry* under the reflection $\alpha \to \pi/2 - \alpha$. The operators (2.2) now take the form, analogous to the last expression in (2.1),

$$-\mathrm{i}\frac{\partial}{\partial\varphi_1} \qquad -\mathrm{i}\frac{\partial}{\partial\varphi_2} \qquad -\mathrm{i}\frac{\partial}{\partial\tan^{-1}(\cos\theta_2 \sin\alpha/\cos\theta_1\cos\alpha)}. \tag{2.5}$$

Note that sets of commuting operators $\{H_i\}$ are subject to coordinate transformations among equivalent sets. They are, in fact, suited to represent invariants of relevant particle subsystems. Each of these sets in d dimensions is complemented by a much larger set of (generally) non-commuting operators, analogues of $l_x \pm \mathrm{i}l_y$ in three dimensions that raise or lower the m quantum number of spherical harmonics $Y_{lm}(\theta, \varphi)$, respectively. Thereby one reaches the total of $d(d-1)/2$ (increasing quadratically with d) unrestricted linear infinitesimal transformations in d dimensions. Most of these operators characteristically involve coordinates of different particles, thus correlating their motions, e.g. combinations of equation (2.1)'s analogues

$$J_{ij}^{xy} = -\mathrm{i}\left(x_i\frac{\partial}{\partial y_j} - y_j\frac{\partial}{\partial x_i}\right) \qquad J_{ij}^{xx} = -\mathrm{i}\left(x_i\frac{\partial}{\partial x_j} - x_j\frac{\partial}{\partial x_i}\right) \qquad i \neq j \tag{2.6}$$

would raise and/or lower eigenvalues of operator pairs $\{H_i, H_j\}$. (The upper indices of the J symbol denote the physical-space components, while its lower labels signify particles' indices, together specifying the relevant variable pair in the d-dimensional space.)

This and analogous considerations enlarge the scope of our study considerably, yielding a total of $d(d-1)/2 = (3N-3)(3N-4)/2$ infinitesimal operators for N particles in $d = 3(N-1)$ dimensions. The resulting wealth of operators will be introduced here and developed later. As each H_i involves two coordinates, odd values of d imply that one coordinate, often labelled by 0, fails to be included in any of the ℓ H_i's, even though contributing to the set (2.6).

To establish contact with the relevant mathematical theory of Lie groups and Lie algebras [7, 8, 82], we observe that the set of linear infinitesimal rotation operators in d dimensions considered in this section forms the 'special orthogonal group' of transformations, designated as $SO(d)$; the term 'special' referring to exclusion of dilations. Quantum mechanics extends this group to include the analogous complex transformations forming the unitary group $SU(d)$ of transformations that preserve the complex Hermitian form $\sum_k x_k x_k^*$ instead of its real quadratic analogue. The full unitary group $U(d)$ results from adding multiplication with a complex phase $\exp(\mathrm{i}\alpha)$ to its 'special' version $SU(d)$. The real part of the Hermitian form is preserved by orthogonal transformations, its imaginary part by 'symplectic' transformations

that preserve bilinear forms *odd* under permutations of their elements, such as the spin invariant $u_{1/2}u^*_{-1/2} - u^*_{1/2}u_{-1/2}$.

2.1. Symmetry under rotation reversal; ladder operators

Reversal of a rotation's direction is represented, e.g. in (2.1), by switching the sign of the coordinate y or of the imaginary unit, thereby reversing the sign of the operators l_z and of their eigenvalues m. Symmetry under this reversal has been highlighted in [7, 8] by replacing pairs of coordinate labels (x_i, y_i) with pairs (x_i, x_{-i}), thus replacing y_i in (2.6). The index i thus runs over $(1, 2 \ldots, \ell)$, being complemented by an x_0 for spaces of odd dimension d. Spherical coordinates then include ℓ azimuths φ_i, with odd parity under rotation reversal, and ℓ polar angles θ_i, changed by this reversal into $\pi - \theta_i$.

Here we preserve the familiar notation with coordinate pairs (x_i, y_i), pointing out that the rotation reversal is often complemented with the reflection through the coordinate plane xz, which automatically reverses the sign of y_i. The resulting combination reverses the handedness ('chirality') of each particle's space coordinates (x, y, z).

Note first that, whereas the physical space operators (l_x, l_y) change by unity the eigenvalues m of l_z, each of the N-particle operators (2.6) shifts the eigenvalues $\{m_i, m_j\}$ of an operator *pair* $\{H_i, H_j\}$. Whereas combinations $(l_x \pm \mathrm{i}l_y)$ act as 'ladder' operators raising or lowering the eigenvalues m of l_z by unity, combinations of *four* among these N-particle analogues (2.6) raise or lower eigenvalue *pairs* simultaneously. The resulting rather elaborate classification of operators became a central feature of the algebraic treatment [7, 8]; we shall follow a more direct approach.

Recall how the ladder operators of physical space, $l_x \pm \mathrm{i}l_y$, emerge as non-Hermitian combinations of the Hermitian pair (l_x, l_y). Similarly, non-Hermitian 'raising' and 'lowering' conjugate operators, designated here generically as $(a^\dagger, a)$, respectively, may be viewed as combinations of two pairs of Hermitian operators, $a^\dagger + a$ and $\mathrm{i}(a^\dagger - a)$, symmetric and antisymmetric, respectively. Recall also that the physical-space Hermitian operators (l_x, l_y) are antisymmetric and symmetric, respectively, under reflection through the xz-plane, according to standard 'Condon–Shortley' conventions. A heuristic approach to constructing ladder operators might thus start by identifying combinations of operators (2.6) that are symmetric and antisymmetric, without resorting to Lie-algebra procedures.

Now consider the example of infinitesimal operators pertaining to the four-coordinate set $\{x_i, y_i, x_j, y_j\}$. Besides the commuting pair $\{H_i, H_j\}$, denoted here as $\{(x_i, y_i), (x_j, y_j)\}$, the set of operators includes the ones from (2.6), labelled (x_i, y_j) and (x_i, x_j), respectively, as well as the additional two (x_j, y_i), (y_i, y_j), totalling six operators, four of which intermix i and j coordinates. This last subset gives rise to two pairs of symmetric and antisymmetric Hermitian operators, and thence to two pairs of desired non-Hermitian operators, one of them 'raising–raising', designated as $(++)$, together with its conjugate $(--)$, and 'raising–lowering' operators $(+-)$ and $(-+)$. Commutators among these operators generate other operators of the set, much as commutators among the $\boldsymbol{l}$ components do, as detailed in appendix A. This particular example, with ladder operators appearing simply as combinations of two components acting on m_i and m_j in a way familiar from $SO(3)$, is not generic for $SO(d)$. Instead its structure is due to the well known feature of orthogonal groups that $SO(4)$ factors into a pair of $SO(3)$ subgroups. A related example familiar in physics is afforded by the factoring of the (proper) Lorentz group $SO(3, 1)$ into $SU(2) \times SU(2)$, with 'spinors' of opposite chirality [82] (chapter 11). Reference [7] derives these results algebraically.

Returning once again to the physical-space operators $l_x \pm \mathrm{i}l_y$, recall how they transform elements of a spherical harmonics set $\{Y_{lm}\}$ into one another. They serve further to identify

a set's range, for example, by causing its 'highest-weight' element $Y_{ll}(\theta, \varphi)$ to vanish when acted upon by $l_x + \mathrm{i}l_y$. The ladder operators outlined above will perform an analogous role for the much larger and multi-faceted sets of hyperspherical harmonics. To this end one may combine the operators (2.6) first into pairs symmetric and antisymmetric in their (i, j) indices,

$$J_{ij}^{xy\pm} = \frac{1}{\sqrt{2}}\left(J_{ij}^{xy} \pm J_{ji}^{xy}\right) = \frac{1}{\sqrt{2}}\left(J_{ij}^{xy} \mp J_{ij}^{yx}\right) \tag{2.7a}$$

since $J_{ji}^{yx} = -J_{ij}^{xy}$. These Hermitian operators are then paired into non-Hermitian operators,

$$J_{ij\pm}^{xy} = J_{ij}^{xy+} \pm \mathrm{i}J_{ij}^{xy-}. \tag{2.7b}$$

The heuristically introduced operators of type (2.7*b*) fail to act correctly as ladder operators. Nevertheless, examples of ladder operators with a similar structure arising as superpositions of *four* operators (2.6) will appear in (4.11*a*)–(4.11*c*), playing a key role in section 4. (Combinations (2.6) that instead include the unpaired variable x_0 of odd-dimensional systems do not lend themselves to the symmetrization (2.7*a*), being thus more nearly analogous to the three-dimensional (l_x, l_y).)

The numbers of infinitesimal operators (2.6) and of the resulting ladder operators increase quadratically with the numbers of particles and of the corresponding coordinates. It will turn out in following sections, however, that a number ℓ of *linearly independent* 'raising–lowering' operator *pairs*, equal to the number of commuting operators H_i, suffices to generate complete orthogonal sets of hyperspherical harmonics. Each of those sets corresponds to a choice of relevant coordinates and of the $\{H_i\}$ set.

The coordinates and their infinitesimal rotations, developed thus far in this section, would intermix in their dynamical applications with the inertial effects of the mass differences among various particles. These complications can, however, be removed by appropriate mass weighting of the coordinates as anticipated in section 1 and implemented next.

2.2. Jacobi coordinates

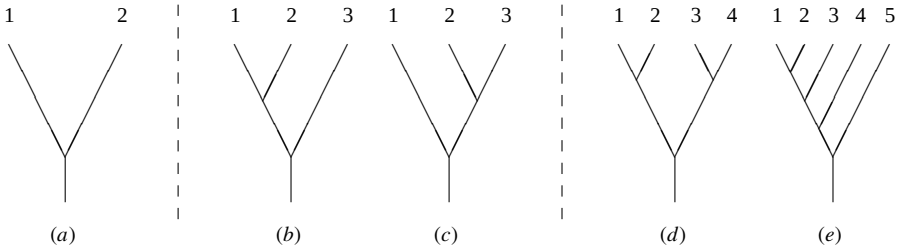
Mass weighting of coordinates has served in section 1 to define the hyper-radius R conveniently, contrasting it with the angular coordinates represented by $\hat{\boldsymbol{R}}$. Analogous devices serve to weight appropriately the components of $\hat{\boldsymbol{R}}$ pertaining to particles with different masses M_i, making them homogeneous, and thus removing the Laplacian $\Delta_{\hat{\boldsymbol{R}}}$'s explicit dependence on single-particle masses. To this end, generic sets of 'Jacobi coordinates' have been introduced long ago [12], replacing the single-particle $\boldsymbol{r}_i$ by vectors $\boldsymbol{\xi}_i$ with the mass weighted dimension mass$^{1/2}$ length.

Alternative sets of Jacobi coordinates occur, reflecting alternative groupings of particles, properly weighted by the mass of each group through linear transformations with *dimensionless* coefficients. These sets are in turn interconnected by dimensionless linear transformations, each of whose steps amounts to *rotation in one plane*. Handling of Jacobi coordinates thus becomes laborious even though each step be elementary.

Jacobi coordinates prove essential by identifying each fragmentation channel through a particular *Jacobi tree* separating at its base into two branches corresponding to the relevant fragments. One thus displays the evolution of each particle-aggregate toward a specific fragmentation channel by the structure of relevant tree-shaped Jacobi coordinates. The label 'Jacobi tree' reflects the evolution of a multi-particle system fragmenting (i.e. 'branching out') from a trunk into separate systems. (Developing a multi-particle wavefunction toward one among its alternative fragmentations presents instead an upside down view of that tree.)

We show below a few simple prototype Jacobi trees, whose upper endings correspond to single-particle labels. Permutation of two particles is represented by rotating (a) about its

trunk. Changing (*b*) into (*c*), often referred to as *transplanting* of branch 2, corresponds to the prototype transformation of hyperspherical harmonics. Generic transformations resolve into sequences of permutations and transplantations. Tree (*e*) is often called 'canonical'. Multi-particle systems are represented by correspondingly articulated trees.



The Jacobi trees just introduced serve to characterize multi-particle systems by their *hierarchy of composition*, i.e. by indicating the order in which particles are joined to form subcomplexes of the entire aggregate. The labels thus refer to particle indices. A similar concept re-appears in a further context: analogous trees illustrate *coordinate systems* and their transformations, their branches labelling appropriate angles in $\hat{\boldsymbol{R}}$'s decomposition [20, 68, 69]. Rotation of tree (*a*) by an angle $0 \leqslant \varphi \leqslant 2\pi$ represents a simple rotation about an axis. Variation of a coordinate $0 \leqslant \theta \leqslant \pi$ maps onto the angle between two branches.

Alternative sets of Jacobi coordinates $\hat{\boldsymbol{R}}$ thus correspond to different tree structures. This circumstance adds further elaboration to our procedure, yet serves to display the evolution of whole aggregates. These aspects have not been apparent in the initial applications of the present approach, dealing with very few particles, even though necessarily underlying the treatment of any multi-particle system. Each transformation of hyperspherical harmonics resolves accordingly into a transformation from one to another set of Jacobi coordinates and a transformation of the corresponding harmonics.

Note the 'hierarchical' aspect of Jacobi-tree construction, which adds particles *sequentially*, contrasting with the 'democratic' view of the multi-particle coordinates leading to the *quadratic* increase of the number of (2.6) operators as a function of the particle number N.

Once again: each step dealing with Jacobi coordinates is elementary, but the number and combinations of different steps are large, a characteristic generally encountered in computer operations requiring adequate strategy and planning. Such operations may properly articulate into successive phases. We anticipate, for example, in dealing with molecules, to build first each atom's inner shells independently, by Cavagnero's procedure [67–69], combining later the resulting atomic ions with the residual atomic electrons.

Similarly, the following sections present first alternative combinations of three particles, lying in a plane with their centre of mass, into alternative *pairs* of mutually independent collective coordinates $\boldsymbol{\xi}$, followed by transformations among these pairs. Combinations of larger particle sets into further $\boldsymbol{\xi}$'s will be dealt with next, utilizing analogous procedures recursively. Even more extensive procedures will hinge on experience in treating large multi-particle aggregates.

2.2.1. A three-particle prototype. The positions $\boldsymbol{r}_i$, $i = 1, 2, 3$, of a three-particle set identify a plane where their centre of mass also lies. These positions are represented by these co-planar vectors, but their *internal* kinematics involves only two independent Jacobi coordinate vectors, $\boldsymbol{\xi}$, with $3(N-1) = 6$ degrees of freedom.

The standard procedure for constructing Jacobi coordinate vectors considers first the positions of two among these particles, 1 and 2 here, with masses M_1 and M_2 and positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, respectively. These input data combine into a first Jacobi vector weighted by the square root of the pair's 'reduced mass' $M_{12} = M_1 M_2/(M_1 + M_2)$, namely,

$$\boldsymbol{\xi}_{12} = \sqrt{M_{12}}(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{2.8}$$

whose centre of mass lies in the plane at

$$\boldsymbol{r}_{12} = \frac{M_1 \boldsymbol{r}_1 + M_2 \boldsymbol{r}_2}{M_1 + M_2}. \tag{2.9}$$

The next step combines the first pair, with mass $M_1 + M_2$ and centre-of-mass position $\boldsymbol{r}_{12}$, with the third particle lying at $\boldsymbol{r}_3$. This step is performed in accordance with (2.8) yielding the second Jacobi vector,

$$\boldsymbol{\xi}_{12,3} = \sqrt{M_{12,3}}(\boldsymbol{r}_{12} - \boldsymbol{r}_3) \tag{2.10}$$

with the reduced mass

$$M_{12,3} = \frac{(M_1 + M_2)M_3}{M_1 + M_2 + M_3}. \tag{2.11}$$

(The comma-separated subscripts indicate the particle subcomplexes to be joined.)

An additional feature relates the Jacobi vector (2.10) to its alternatives corresponding, for example, to the permutation of indices 1 and 3, i.e. $(1, 2, 3) \rightarrow (3, 2, 1)$, yielding the two-dimensional vector rotation

$$\{\boldsymbol{\xi}_{32},\ \boldsymbol{\xi}_{32,1}\} = \{\boldsymbol{\xi}_{12}\cos\beta - \boldsymbol{\xi}_{12,3}\sin\beta,\ \boldsymbol{\xi}_{12}\sin\beta + \boldsymbol{\xi}_{12,3}\cos\beta\} \tag{2.12}$$

by the angle

$$\beta = \tan^{-1}\sqrt{\frac{M_2(M_1 + M_2 + M_3)}{M_1 M_3}}. \tag{2.13}$$

Analogous *kinematic rotations* correspond to cyclic permutations of indices.

2.2.2. Extension to multi-particle aggregates. The formulation of equation (2.10), with elements from (2.8), has clearly recursive character. It implies that any pair of Jacobi vectors, $\{\boldsymbol{\xi}_p, \boldsymbol{\xi}_q\}$, representing two subaggregates of particles centred at $\boldsymbol{r}_p$ and $\boldsymbol{r}_q$ with masses M_p and M_q, respectively, combines effectively into a single vector

$$\boldsymbol{\xi}_{pq} = \sqrt{\frac{M_p M_q}{M_p + M_q}}(\boldsymbol{r}_p - \boldsymbol{r}_q). \tag{2.14}$$

Similarly, restructuring of any 'Jacobi tree' diagram, which represents a specific sequence of particle combinations forming an aggregate, resolves into sequences of vector-pair $\{\boldsymbol{\xi}_p, \boldsymbol{\xi}_q\}$ rotations within a plane, analogous to that represented by (2.12). Such restructurings have been discussed amply in [20] under the name of 'timber transformations', the word 'timber' being suggested by association with 'Jacobi tree'. The simple underlying principle, stated in that reference, lies in the feasibility to resolve any rotation in multi-dimensional spaces into a sequence of plane rotations, a feature familiar for the three-dimensional rotations of physical space. Appendix B exemplifies this procedure.

Transformations between different Jacobi trees prove highly relevant to our subject of atomic and molecular few-particle systems for the following reason. The Coulomb coefficient $Z(\hat{\boldsymbol{R}})$ results familiarly from contributions proportional to the reciprocal distances between the $N(N-1)/2$ particle pairs. Flexible sets of Jacobi coordinates afford treating each

of these distances as a single coordinate, to be combined with others, thus avoiding the familiar need to expand each term of $Z(\hat{\boldsymbol{R}})$ into a multipole series. Thereby determining Coulomb interaction matrix elements reduces to calculating integrals over $1/r$ rather than over $1/|\boldsymbol{r}_i - \boldsymbol{r}_j|$.

3. Sample hyperspherical harmonics

The familiar spherical harmonics, $Y_{lm}(\theta, \varphi)$, serve as tensorial base sets for $(2l+1)$-dimensional transformations induced by rotations of the physical-space coordinates. In multi-dimensional contexts analogous base sets of hyperspherical harmonics serve the same purpose. The name 'harmonics' identifies them as eigenfunctions of the angular Laplacian operator $\Delta_{\hat{\boldsymbol{R}}}$ in the $(d-1)$-dimensional space of $\hat{\boldsymbol{R}}$ with eigenvalues $-\lambda(\lambda + d - 2)$.

To understand the term $d-2$ in this eigenvalue formula, note first that it reduces to unity for $d = 3$ yielding the familiar eigenvalue $l(l+1)$ of the squared orbital angular momentum. The unit in this expression corresponds to the *single* angular coordinate θ that accompanies the angle φ in polar coordinates. Its contribution to the eigenvalue, namely l, corresponds to the 'zero-point energy', 'hl', of a unit-mass particle oscillating along the θ coordinate in the centrifugal field generated by its rotation along φ with quantum number l. The occurrence of $d-1$ dimensions for the vector $\hat{\boldsymbol{R}}$ raises the number of its coordinates, besides φ, from unity to $d-2$, thus accounting for the eigenvalue term $d-2$.

As the pair of angles (θ, φ) identifies a direction of physical space, an equal number of indices (l, m) identifies a harmonic belonging to a $(2l+1)$-dimensional set, with the magnetic quantum number m labelled as a 'weight' and l in the role of 'highest weight'. Extending this parametrization to d-dimensional spaces requires us to describe sets of hyperspherical harmonics $Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$, where λ replaces the 'highest weight' l, the vector $\boldsymbol{\mu}$ represents a set of $d-2$ complementary labels and $\hat{\boldsymbol{R}}$ a corresponding set of $d-1$ angles.

This extension provides the main tool for the quantum mechanics of multi-particle systems, as indicated in section 1 anticipating the relevance of the hyperspherical harmonics and of their treatment in [77, 80]. Recall that the position vector $\boldsymbol{R}$ of an N-particle set (in its centre-of-mass frame) has $d = 3(N-1)$ dimensions. The wavefunctions $\Psi(\boldsymbol{R})$ of such a system, envisaged in section 1, are conveniently expanded in hyperspherical harmonics in analogy to expansions in spherical harmonics [77]. Their Schrödinger equation reduces similarly to a system of coupled ordinary differential equations in the 'hyper-radius' R.

The symbol for hyperspherical harmonics, $Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$, replaces the index l of spherical harmonics by the index λ corresponding to the eigenvalue $-\lambda(\lambda + d - 2)$ of the $(d-1)$-dimensional angular Laplacian $\Delta_{\hat{\boldsymbol{R}}}$. This index also denotes the degree of the homogeneous 'harmonic' polynomial products $R^{\lambda}Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$. The second index $\boldsymbol{\mu}$ replaces the index m of spherical harmonics with a corresponding set of $d-2$ parameters (the dimension of $\hat{\boldsymbol{R}}$ less 1) that identify a specific harmonic of degree λ.

Expanding wavefunctions of a multi-dimensional $\boldsymbol{R}$ utilizes 'complete orthogonal sets' of hyperspherical harmonics. Completeness is achieved by extending the range of λ adequately. Only a finite set of harmonics, however, proves relevant at any finite value of R, higher values being effectively excluded by a generalized centrifugal potential at small R, as noted in section 1. (This potential, involving the λ parameter, includes contributions from derivatives of variables corresponding to the α coordinate in (2.4) and representing the quantum mechanical resistance of particles to compression by boundary conditions.) As R increases more and more hyperspherical harmonics start contributing to the relevant wavefunctions, requiring adequate frame transformations to reflect the appropriate fragmentation channels, as outlined

in section 5. Orthogonality requires identifying, for each λ value, an adequate set of vectors $\boldsymbol{\mu}$ corresponding to the simple set of integer values $|m| \leqslant l$ of the spherical harmonics and to the relevant set of $\hat{\boldsymbol{R}}$ components. Here, higher dimensionality implies more elaborate sets of $\boldsymbol{\mu}$ vectors.

Generating these sets in d dimensions, labelled by $(d-2)$-dimensional vectors $\boldsymbol{\mu}$, relies in essence on separating the Laplacian's variables. In the three-dimensional prototype $Y_{lm}(\theta, \varphi)$, the m label arises as an eigenvalue of the l_z operator representing the number of nodes of the corresponding eigenfunction $\sin^{|m|}\theta\, \mathrm{e}^{\mathrm{i}m\varphi}$, whereas the remaining $l - |m|$ nodes pertain to the θ variable. For hyperspherical harmonics, sets of section 2's ℓ commuting operators H_i may provide corresponding quantum numbers m_i and eigenfunctions. The residual $\lambda - \sum_i |m_i|$ nodes would then pertain to the $d - \ell - 1$ residual variables, analogues of θ.

Whereas alternative orthogonal sets of spherical harmonics pertain to alternative orientations of the $\hat{\boldsymbol{z}}$ coordinate axis in three-dimensional space, analogous sets of hyperspherical harmonics pertain to alternative selections of ℓ commuting operators $\{H_i\}$, not necessarily based on a coordinate set as they were in section 2. Whereas spherical harmonics $Y_{lm}(\theta, \varphi)$ depend on the 'longitude' φ with $|m|$ 'meridian' nodes and on the 'co-latitude' θ with $l - |m|$ 'parallel' nodes, subdividing their plots into separate 'lobes', hyperspherical harmonics depend—for particular coordinates—on 'longitudes' φ_i, each with $|m_i|$ nodes, and on the nodal distribution in the remaining coordinates. Additional components of $\boldsymbol{\mu}$ pertain to alternative partitions of λ that delimit the range of the parameters $|m_i|$ as well as of additional coordinates. Note how the number of $\boldsymbol{\mu}$ components increases *linearly* with the number N of particles, contrasting again with the operators (2.6), whose number increases *quadratically* with N.

Consider now how the features of hyperspherical harmonics bear on equation (1.2)'s expansion: the value of $\Delta_{\hat{\boldsymbol{R}}}$ in its centrifugal term depends *only* on the parameter λ of each harmonic, whereas the coefficient $Z(\hat{\boldsymbol{R}})$ of its Coulomb term resolves for an N-particle set into $N(N-1)/2$ terms $\sim R/|\boldsymbol{r}_i - \boldsymbol{r}_j|$, cast as matrices in the $\{\lambda\boldsymbol{\mu}\}$ basis. The flexibility afforded by selecting the ℓ operators H_i and the remaining $d - \ell - 1$ coordinates should serve here to avoid, or at least minimize, resorting to multipole expansion of each term.

We anticipate that coordinate rotations in d dimensions transform generally any harmonic $Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$ into a superposition of the harmonics of its whole orthogonal set with coefficients $D^{\lambda}_{\boldsymbol{\mu}',\boldsymbol{\mu}}$ analogous to those that serve to transform spherical harmonics and form a 'representation' of the rotation group. This feature rests on the multi-dimensional rotations' aptitude to resolve into sequences of two-dimensional rotations, thereby affording us to express any $D^{\lambda}_{\boldsymbol{\mu}',\boldsymbol{\mu}}$ coefficient in terms of more familiar three-dimensional Wigner's Euler-angle functions $d^{(l)}_{m'm}$. The occurrence of alternative sets $\{Y_{\lambda\boldsymbol{\mu}}\}$ with the same λ value reflects the multiplicity of the infinitesimal operator basis. Systematic classifications of alternative sets $\{Y_{\lambda\boldsymbol{\mu}}\}$, appropriate to the number and structure of their coordinates, shall rest on the subgroup chains of the relevant group, as outlined below. With this background we describe now two sample harmonics' sets.

3.1. A generic structure

Laplacian equations for hyperspherical harmonics in d dimensions,

$$[\Delta_{\hat{\boldsymbol{R}}} + \lambda(\lambda + d - 2)]Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}}) = 0 \tag{3.1}$$

lend themselves to solution by separation of variables, since $\Delta_{\hat{\boldsymbol{R}}}$ amounts to a sum of terms $f(\hat{\boldsymbol{R}})(\partial/\partial x_i)\, g_i(\hat{\boldsymbol{R}})(\partial/\partial x_i)$ with metric coefficients $f(\hat{\boldsymbol{R}})$ and $g_i(\hat{\boldsymbol{R}})$. Their prototype example is afforded by the Schrödinger equation for the He atom, with $N = 3$ (one nucleus and

two electrons), $d = 3(N-1) = 6$, and with three polar coordinates (2.4), yielding [9]

$$\Delta_{\hat{\boldsymbol{R}}} = \frac{1}{\sin^2\alpha\cos^2\alpha}\frac{\partial}{\partial\alpha}\sin^2\alpha\cos^2\alpha\frac{\partial}{\partial\alpha} + \frac{1}{\cos^2\alpha}\left[\frac{1}{\sin\theta_1}\frac{\partial}{\partial\theta_1}\sin\theta_1\frac{\partial}{\partial\theta_1} + \frac{1}{\sin^2\theta_1}\frac{\partial^2}{\partial\varphi_1^2}\right]$$
$$+\frac{1}{\sin^2\alpha}\left[\frac{1}{\sin\theta_2}\frac{\partial}{\partial\theta_2}\sin\theta_2\frac{\partial}{\partial\theta_2} + \frac{1}{\sin^2\theta_2}\frac{\partial^2}{\partial\varphi_2^2}\right]$$
$$= \frac{1}{\sin 2\alpha}\left(\frac{\partial^2}{\partial\alpha^2} + 4 - \frac{\boldsymbol{l}_1^2}{\cos^2\alpha} - \frac{\boldsymbol{l}_2^2}{\sin^2\alpha}\right)\sin 2\alpha \qquad (3.2)$$

whose form on the last line arises from renormalizing the harmonics $Y_{\lambda\mu}$ by the volume element $\sin 2\alpha$.

A familiar approach [1–4] to solving (3.1) with the angular Laplacian (3.2) assumes first $Y_{\lambda\mu}$ to depend on (φ_1, φ_2) through a factor $\exp(\mathrm{i}m_1\varphi_1 + \mathrm{i}m_2\varphi_2)$, whereby each $(\partial/\partial\varphi_i)^2$ element of (3.2) amounts to $-m_i^2$. Thereafter each of the square brackets in (3.2) reduces to $-l_i(l_i+1)$, provided $Y_{\lambda\mu}$ depends on each θ_i through the associated Legendre function $\sin^{m_i}\theta_i\ P_{l_i}^{m_i}(\cos\theta_i)$, with the relevant 'highest weight' l_i thus limiting the range of $|m_i|$. The residual operator on the right of (3.2) then has eigenvalues $-\lambda(\lambda+4)$, with λ partitioned as $l_1 + l_2 + 2n$, and with the 'Jacobi polynomial' eigenvector $P_n^{(l_2+1/2, l_1+1/2)}(\cos 2\alpha)$, according to (22.6.4) of [83]. (The factor 2 multiplying n and α in these expressions stems from the exponents and coefficients in the functions of α in (3.2)). The eigenvector of (3.1) reads thus

$$Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}}) = \cos^{l_1}\alpha\ \sin^{l_2}\alpha\ P_n^{(l_2+1/2, l_1+1/2)}(\cos 2\alpha)\ Y_{l_1m_1}(\theta_1, \varphi_1)\ Y_{l_2m_2}(\theta_2, \varphi_2) \qquad (3.3)$$

with the expected five-component $\boldsymbol{\mu} \equiv \{n, l_1, m_1, l_2, m_2\}$, and with the spherical harmonic factors $Y_{l_im_i}(\theta_i, \varphi_i)$.

The set of harmonics (3.3), with a given value of λ, consists of a number of elements w, the dimensionality of the relevant space. This number depends on the number of alternative partitions of λ into (l_1, l_2, n) consistent with the relation $\lambda = l_1 + l_2 + 2n$, and on the alternative $2l_i + 1$ values of each m_i. The prototype example of $\lambda = 2$ leads to the partitions: $(2, 0, 0)$, $(0, 2, 0)$, $(0, 0, 1)$, $(1, 1, 0)$ and, in turn, to $5+5+1+9 = 20$ harmonics. Different partitions of λ yield hyperspherical harmonics with alternative nodal patterns, reflecting alternative sharing of rotational kinetic energy in different modes. The algebraic determination of w is discussed in [7, 8, 82] and outlined in section 4. The general expression [8] for w reduces in the present case ($d = 6$) to $(\lambda+3)(\lambda+2)^2(\lambda+1)/12$.

Notice how the eigenvalue parameters $(l_1, l_2, 2n)$ play the role of 'weights' in (3.3), each of them amounting to the 'highest weight' for a subgroup of the rotation group $SO(d = 6)$, thus contributing to the 'highest weight' $\lambda = l_1 + l_2 + 2n$ of the $SO(6)$ harmonics (3.3). The symmetry under the sign reflection ($m \to -m$) (cf section 2.1) manifests itself in these harmonics not only through the symmetry of each factor $Y_{l_im_i}$, but also through the parity of the polynomial P_n, which is even or odd for even or odd values of the 'pseudo-weight' n, combined with interchange of its upper indices. Note also how n substitutes for the weight m_3, an eigenvalue of the third operator (2.5), which fails to commute with the operators $\boldsymbol{l}_i^2$ even though commuting with $(\partial/\partial\varphi_1)$ and $(\partial/\partial\varphi_2)$.

The harmonics (3.3) provide, of course, a basis for expanding correlated electron wavefunctions in helium, in the form $\Psi(R; \hat{\boldsymbol{R}})$ of section 1, with the direction $\hat{\boldsymbol{R}} \equiv \{\alpha, \theta_1, \varphi_1, \theta_2, \varphi_2\}$ [77, 78]. The expansion coefficients $\Psi_{n,l_1,m_1,l_2,m_2}(R)$ then represent desired features of the relevant eigenfunction $\Psi(R; \hat{\boldsymbol{R}})$. This representation does, however, emphasize single-electron aspects of the state through its parameters (l_i, m_i) rather than through the global features anticipated in section 1.

Note, on the other hand, that the procedure presented above to construct the harmonics (3.3) applies *recursively* to $(N > 3)$-particle systems, as should the previous comments, with

the following qualifications: extending (3.3) to $N > 3$ particles involves $N-1$ spherical harmonics $Y_{l_i m_i}(\theta_i, \varphi_i)$, initially independent of one another, and $N-2$ Jacobi polynomials in $\cos 2\alpha_j$ with the full set of $3N-4$ variables. The index pairs of these polynomials, replacing the single particle $(l_i + \frac{1}{2})$ of (3.3), reflect, however, the *total* angular momenta, $\boldsymbol{L}$ or $\boldsymbol{J}$, of paired particle subsets as determined by relevant *hierarchical* additions of single-particle momenta [68]. Note also how the structure of the harmonics (3.3), and of their higher-dimensional analogues, exploits the commutability of the base operators $\{H_i\}$ and of their corresponding subgroup structure, with a notable exception: the angle α as defined in (2.4) does not coincide with the arctan of the third operator H_i of (2.5).

3.2. An alternative structure

The particular subgroup structure of (3.3) stresses the single-particle features of each system, contrary to section 1's emphasis. We turn now accordingly to Avery's [80] alternative construction of harmonics that emphasizes different elements, dealing with $d = 3N-6$ unspecified coordinates besides a spherical harmonic $Y_{lm}(\theta, \varphi)$, without reference to single-particle positions. This approach thus utilizes a single eigenvector $\mathrm{e}^{\mathrm{i}m\varphi}$ of a *single* operator H_i, contrasting with the full set occurring in (3.3) and its extensions to $N > 3$.

As a preliminary to complementing a single spherical harmonic Y_{lm} with additional variables, Avery [80] views the Legendre polynomial $P_l(\cos\theta)$, invariant under rotations about the z-axis, as the particular Gegenbauer polynomial $C_l^{\alpha}(\cos\theta)$ with $\alpha = \frac{1}{2}$ (as defined in [83], table 22.6) extending it from 3 to $d = 3(N-1)$ dimensions by setting its parameter α at $d/2-1$, and replacing l with λ ($d = 6$ in our example). It also replaces $\cos\theta$ with the scalar product of unit vectors $\hat{\boldsymbol{R}} \cdot \hat{\boldsymbol{R}}'$, where $\hat{\boldsymbol{R}}'$ corresponds to the reference axis $\hat{\boldsymbol{z}}$. The hyperspherical harmonic

$$C_{\lambda}^{d/2-1}(\hat{\boldsymbol{R}} \cdot \hat{\boldsymbol{R}}') \tag{3.4}$$

is thus invariant under d-dimensional rotations of $\hat{\boldsymbol{R}}$ about a fixed axis $\hat{\boldsymbol{R}}'$ (i.e. rotations labelled by a single parameter φ), as well as under rigid rotations of the pair $\hat{\boldsymbol{R}} \cdot \hat{\boldsymbol{R}}'$. Note that Gegenbauer (as Legendre) polynomials consist of only even or only odd powers for even or odd values of λ or l, respectively.

As the spherical harmonics Y_{lm} are generated from $P_l(\cos\theta)$ by operators $l_x \pm \mathrm{i}l_y$, harmonics $Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$ are generated from (3.4) by infinitesimal operator analogues of $l_x \pm \mathrm{i}l_y$, each of them combining a derivative, which lowers by unity the degree of their operand, with a compensating factor linear in a coordinate, thus replacing a nodal line of the operand with a different coordinate's nodal line. (Typically, the operator $l_x + \mathrm{i}l_y$, as applied to Y_{lm} with non-negative m, is equivalent to $\mathrm{e}^{\mathrm{i}\varphi} \sin\theta(\partial/\partial\cos\theta)$: its partial derivative reduces Y_{lm}'s polynomial dependence on $\cos\theta$ by one degree, thus removing one parallel-line node, its first factor adds instead a meridian-line node implied by the vanishing of its real or imaginary parts. To trace out this effect more explicitly, recast the operator in the form

$$l_x + \mathrm{i}l_y = -\mathrm{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) = -(x + \mathrm{i}y)\frac{\partial}{\partial z} + z\left(\frac{\partial}{\partial x} + \mathrm{i}\frac{\partial}{\partial y}\right).$$

The first term on the right-hand side of this expression, when applied to the function $Y_{lm}(\theta, \varphi)$ with a non-negative m value, raises its m index by one unit through the combined action of its two factors: the first factor, $x + \mathrm{i}y = r\sin\theta\,\mathrm{e}^{\mathrm{i}\varphi}$ combines with the same factor within Y_{lm}, thus raising by one unit the number of its meridian-line nodes as well as the exponent of its $\sin^m\theta$ factor. Its second factor $(\partial/\partial z)$, equivalent here to $r^{-1}(\partial/\partial\cos\theta)$, reduces by one unit the degree of Y_{lm}'s polynomial dependence on $\cos\theta$, thus suppressing one of its parallel-line

nodes. The second term on the right of the operator's expression cancels instead the function $Y_{lm}(\theta, \varphi)$ by setting it to zero.)

A direct analogue of the successive action of $l_x + \mathrm{i}l_y$ operators on $P_l(\cos\theta)$ would apply to the Gegenbauer polynomial (3.4) a sequence of corresponding operators acting on components of $\hat{\boldsymbol{R}}$. A novel aspect emerges, however, at this point, since $\hat{\boldsymbol{R}}$ has several components orthogonal to $\hat{\boldsymbol{R}}'$ acted upon by alternative operators in alternative sequences. Such alternative sequences will occur in section 4, whereas [80] avoids them by treating all $\hat{\boldsymbol{R}}$ components uniformly, besides their physical-space subset $\hat{\boldsymbol{R}} \equiv \{\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta\}$.

To this end, [80] follows the frequent practice of complementing an initial two-dimensional component ($\cos\varphi$ or $\sin\varphi$) by multiplying it with the factor $\sin\theta$ and adding a further $\hat{\boldsymbol{R}}$ component $\cos\theta$, whereby $\hat{\boldsymbol{R}}$ retains its unit magnitude. Iterating this extension $d-3$ times yields the canonical set of $\hat{\boldsymbol{R}}$ components

$$\begin{aligned}
&\cos\theta_1\\
&\sin\theta_1\cos\theta_2\\
&\vdots\\
&\sin\theta_1\sin\theta_2\cdots\cos\theta_{d-2}\\
&\sin\theta_1\sin\theta_2\cdots\sin\theta_{d-2}\sin\varphi\\
&\sin\theta_1\sin\theta_2\cdots\sin\theta_{d-2}\cos\varphi.
\end{aligned} \tag{3.5}$$

For the purposes of orientation consider that, if all $\hat{\boldsymbol{R}}$ components had comparable magnitudes, each value of $\cos\theta_i$ would be of order $1/d$, and hence each θ_i would be close to $\pi/2$. After elimination of $R\cos\theta_1$, the factor $R\sin\theta_1$ of all successive components would represent their total magnitude. The successive factors $\sin\theta_i$ then contribute to reduce the effective residual components of $\hat{\boldsymbol{R}}$ progressively.

The set of integer components of the vector label $\boldsymbol{\mu}$, non-negative and of decreasing magnitude, is similarly indicated by

$$\boldsymbol{\mu} \equiv \{\mu_1, \mu_2, \ldots, \mu_j, \ldots \mu_{d-1}\} \tag{3.6}$$

with $\mu_{d-1} \equiv |m|$, m being the multiplier in the harmonic's phase $m\varphi$. The difference between successive components (3.6), $\mu_j - \mu_{j+1} \geqslant 0$, represents the number of nodes in the jth harmonic's dependence on $\cos\theta_j$, including the $|\mu_{d-1}|$ nodes implied by the phase factor $\mathrm{e}^{\mathrm{i}m\varphi}$. The set of harmonics compatible with these specifications, for the same prototype values $\lambda = 2$ and $d = 6$ as for the harmonics (3.3), has likewise 20 elements.

The resulting hyperspherical harmonic, equation (3.69) of [80], consists thus mainly of products of $d-2$ Gegenbauer polynomials,

$$Y_{\lambda\boldsymbol{\mu}} = N_{\lambda\boldsymbol{\mu}} \prod_{j=1}^{d-2} (\sin\theta_j)^{\mu_{j+1}} C_{\mu_j-\mu_{j+1}}^{\alpha_j+\mu_{j+1}}(\cos\theta_j)\, \mathrm{e}^{\mathrm{i}m\varphi}. \tag{3.7}$$

The combined degree of this harmonic, equalling its total number of nodes, amounts to $\sum_{j=1}^{d-2}(\mu_j - \mu_{j+1}) = \lambda$, including the $\mu_{d-1} \equiv |m|$ nodes attributable to the $\mathrm{e}^{\mathrm{i}m\varphi}$ factor. The α index of each Gegenbauer polynomial consists of two terms, α_j and μ_{j+1}, the first of which, $\alpha_j = (d-j-1)/2$, corresponds to the actual dimensionality of all the (3.7) factors with indices larger than j. The second term, μ_{j+1}, represents the additional effective dimensionality attributable to the factors $(\sin\theta_j)^{\mu_{j+1}}$ (whose combination with $C_{\mu_j-\mu_{j+1}}^{\alpha_j+\mu_{j+1}}$ amounts to an analogue of the associate Legendre function $P_l^m(\cos\theta)$). The remaining factor of (3.7), $N_{\lambda\boldsymbol{\mu}}$, represents the normalization factor contributing to the orthonormalization of each set of harmonics (3.7) with equal λ and alternative $\boldsymbol{\mu}$ indices.

Each factor $(\sin\theta_j)^{\mu_{j+1}}$, which decays rapidly as θ_j approaches a pole (at 0 or π), corresponds to the factor $(\sin\theta)^{|m|}$ of associate Legendre functions, which reflects the centrifugal potential generated by its factor $e^{im\varphi}$. Indeed, the exponent μ_{j+1} equals the total number of nodes in (3.7) factors with indices larger than j, which contribute a centrifugal potential to the equation governing $C^{\alpha_j+\mu_{j+1}}_{\mu_j-\mu_{j+1}}$; each difference $\mu_j - \mu_{j+1}$ corresponds to a separation parameter $l_i(l_i+1)$ in the construction of the harmonics (3.3).

In conclusion, the present construction of hyperspherical harmonics has followed two approaches: (a) solving the (angular) Laplace equation by separation of variables, leading to the harmonics (3.3) and extensible to higher dimensions; (b) constructing the harmonics (3.7) by a sequence of Gegenbauer polynomial factors (also separating variables), complemented by factors $(\sin\theta_j)^{\mu_{j+1}}$, analogues of the $(\sin\theta)^m$ of spherical harmonics and similarly generated by applying infinitesimal operators $\sin\theta(\partial/\partial\cos\theta)$ to the invariant Gegenbauer harmonic (3.4).

These approaches differ in their coordinates as well as in their dynamical implications: no physical specification of the $\hat{\boldsymbol{R}}$ components θ_j has occurred in approach (b). Approach (a) has relied on the single-particle coordinates and on their interrelations introduced in (3.2), namely $\{0 \leqslant \alpha \leqslant \pi/2,\ 0 \leqslant \theta_i \leqslant \pi,\ 0 \leqslant \varphi_i \leqslant 2\pi\}$. (The limited range of α coordinates reflects their definition through ratios of non-negative variables.) Approach (b) has utilized, in (3.5), ratios of $\hat{\boldsymbol{R}}$ components restricted to real values of either sign, in addition to a *single* complex phase, without explicit reference to single-particle coordinates (considered elsewhere in [80]). The occurrence of two (or more) complex-coordinate phases in approach (a) utilizes the commuting operator set $\{H_i\}$, a dynamical element foreign to approach (b). Intermediate approaches, utilizing that set partially, appear readily accessible.

4. Classification and construction of hyperspherical harmonics

Section 3 introduced hyperspherical harmonics for two different sets of coordinates, relying on single-particle features to a different extent. Both sets of hyperspherical harmonics are characterized as 'harmonic polynomials', i.e. as eigenfunctions of the angular Laplacian, obtained directly by separation of variables. Their construction thus ties each of these harmonics to a particular choice of coordinates.

In contrast, sections 1 and 2 repeatedly stressed the need for flexibility in the choice of coordinates to describe the evolution of an atomic or molecular complex from its compact to its fragmented states. Having familiarized the reader with properties of hyperspherical harmonics in the preceding section, we now introduce harmonics which are essentially frame independent, thus bypassing extensive frame transformations necessary for harmonics tied to a particular set of coordinates. We describe here a procedure to generate complete sets of harmonics *independent* of the choice of coordinates. Consequently, the same set of harmonics serves throughout the entire evolution process, frame transformations reducing to the task of expressing the harmonics in whichever coordinate system appears appropriate at any given stage of the evolution, without a change to the basic structure of the functions themselves.

The key feature enabling a definition of harmonics without separation of variables in the Laplacian's eigenfunction equation rests on identifying the Laplacian's symmetry under rotations in d dimensions. Section 2 described these transformations in terms of *first-order* infinitesimal rotation operators. We will now construct functions based on $\{H_i\}$-operators and on the corresponding ladder operators only. Because these functions will possess the underlying symmetry of the Laplacian, they are 'harmonics' *a fortiori*.

The present task amounts to extending the *classification* of spherical harmonics by their label pair (l, m) to multi-dimensional systems, in accordance with procedures to construct such harmonics. To this end recall that:

(a) The l label of Y_{lm} identifies both an eigenvalue of the *second-order* angular Laplacian $\boldsymbol{l}^2$ and the range $0 \leqslant |m| \leqslant l$ of its second label.
(b) The label m itself is an eigenvalue of the *first-order* operator l_z.
(c) Alternative equivalent sets of harmonics correspond to alternative orientations of the z-axis.
(d) Complete sets of spherical harmonics $Y_{lm}(\theta, \varphi)$ emerge by operating on the invariant harmonic $P_l(\cos\theta)$ with the conjugate pair of ladder operators $l_x \pm \mathrm{i}l_y$, or alternatively operating with the lowering $l_x - \mathrm{i}l_y$ alone on the 'highest-weight' harmonic $Y_{ll}(\theta, \varphi)$.

Corresponding remarks on hyperspherical harmonics outline here this section's development:

(a) We have seen how the multi-dimensional label λ performs l's role in identifying eigenvalues of the relevant multi-dimensional angular Laplacian. Alternative partitions of λ's value will similarly delimit the ranges of m's analogues.
(b) Analogues of m are the integer (or half-integer) eigenvalues m_i of the ℓ first-order commuting operators $\{H_i\}$ introduced in section 2. These sets are viewed as components of a vector $\boldsymbol{m}$ in the space subtended by the operators $\{H_i\}$. They were noted, however, in section 3.1 not to be fully compatible with the corresponding parameter set $\{l_i\}$ that delimits each $\{|m_i|\}$'s range, equation (3.3)'s label n replacing the eigenvalue m_3 of a different equation. Harmonic eigenvectors of the $\{H_i\}$'s will, nevertheless, be identified by convenient sets of $\boldsymbol{m}$ components, i.e. by lattice points in the ℓ-dimensional $\{H_i\}$ space.
(c) Alternative equivalent sets of hyperspherical harmonics correspond to alternative orientations of a vector $\boldsymbol{\lambda}$ in the relevant $\{H_i\}$ space and to alternative analyses of a system's dynamics. Transformations of coordinates and/or of the $\{H_i\}$ set yield equivalent sets of hyperspherical harmonics.
(d) Hermitian-conjugate ladder operators, analogues of the physical space's $l_x \pm \mathrm{i}l_y$, will emerge as superpositions $E_{\boldsymbol{\alpha}}$ of Hermitian *pairs*—as anticipated in section 2—with vector labels $\boldsymbol{\alpha}$, each label with unit-magnitude components in the $\{H_i\}$ space, being thus represented by diagonal vectors in that space. Linearly independent ℓ-dimensional *subsets* of these operators, denoted by $\{E_{\boldsymbol{\eta}_s}\} \equiv \{E^{\dagger}_{-\boldsymbol{\eta}_s}\}$, $s = 1, \ldots, \ell$, suffice for the present task [7, 8], as well as for encompassing all the far more numerous ladder operators by their own appropriate superpositions.

A sample set of harmonics emerging in this framework will be displayed at the end of section 4.3.

Quantum numbers m_i, eigenvalues of H_i operator subsets, serve to classify '(quasi)-invariants' of multi-particle systems. Such is the J_z component of the invariant angular momentum $\boldsymbol{J}$ of isolated systems. Two m_i components pertain to a molecule rotating about a symmetry axis of lower inertia in its 'body frame'. Three m_i's characterize atomic Rydberg states, one of them pertaining to their inner core, one to the Rydberg electron and one to their vector sum. A plethora of such m_i's might pertain to a turbulent fluid.

In the absence of quasi-invariants, other than the total $\boldsymbol{J}$'s, the single label m of (3.7) may suffice, but a number ($\leqslant \ell$) of additional m_i's, judiciously chosen with reference to the system's structure, helps in classifying harmonics $Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$, and the corresponding multi-particle wavefunctions.

Geometrical elements of classification also emerge from the nodal patterns of harmonics, as noted in section 3. The Laplacian's separability into coordinates x_i, stressed at the outset

of section 3.1, affords real solutions of the several resulting one-dimensional equations in x_i (with appropriate boundary or periodic conditions) to be characterized by n_i nodes, yielding altogether $\sum_i n_i$ nodes, a total basically equal to the eigenvalue λ. Real hyperspherical harmonics with equal λ differ then by their λ's partitions into the relevant n_i.

For the specific purpose of constructing sets of hyperspherical harmonics, sets of $E_{\pm\eta_s}$ operators, analogues of the physical-space 'ladder operators' $l_x \pm \mathrm{i}l_y$, complement sets of H_i conveniently, much as the $l_x \pm \mathrm{i}l_y$ complement l_z. To this end, the total angular momentum's $J_z \equiv H_1$ may be complemented by appropriate H_i and thence by corresponding ladder operators $\{E_{\eta_s}\} \equiv \{E^{\dagger}_{-\eta_s}\}$. In principle, quantum numbers m_s (of either sign) of the desired harmonics then represent the number of $E_{\pm\eta_s}$ having acted on the invariant harmonic $C_n^{\alpha}(\hat{\boldsymbol{R}} \cdot \hat{\boldsymbol{R}}')$, equation (3.4). In practice, the derivation of hyperspherical harmonics for a given λ proceeds more appropriately by acting on the analogue of the spherical $Y_{ll}(\theta, \varphi)$ with sequences of lowering operators $E_{-\eta_s}$, since the 'highest-weight' hyperspherical harmonic is uniquely defined.

The m_s values raised or lowered by $E_{\pm\eta_s}$ operators in this procedure are delimited by the relevant 'highest-weight' eigenvalue λ of $J_z \equiv H_1$, viewed as a vector $\boldsymbol{\lambda}$ directed along a particular axis and expanded as

$$\boldsymbol{\lambda} = \sum_s \lambda_s \boldsymbol{\eta}_s. \tag{4.1}$$

The partition coefficients λ_s are integers (or half-integers) insofar as both $\boldsymbol{\lambda}$ and the $\boldsymbol{\eta}_s$ are vectors of the $\{H_i\}$ space with coefficients of integer (or half-integer) magnitude. The λ_s values serve thus as 'highest weights', analogues of (3.3)'s l_i, for the m_s quantum numbers. The m_s themselves are viewed as components of a 'magnetic vector'

$$\boldsymbol{m} = \sum_s m_s \boldsymbol{\eta}_s \equiv \sum_i m_i \hat{\boldsymbol{h}}_i \tag{4.2}$$

the vectors $\boldsymbol{\eta}_s$ and $\hat{\boldsymbol{h}}_i$ (the latter pointing in the direction perpendicular to the plane of rotation identified by H_i in section 2) being themselves interrelated by integer (or half-integer) coefficients.

An analogue of the spherical harmonics equation defining the range of m,

$$(l_x \pm \mathrm{i}l_y)\, Y_{l,\pm l}(\theta, \varphi) \equiv (l_x \pm \mathrm{i}l_y)^{l+1} P_l(\cos\theta) = 0 \tag{4.3}$$

is formulated for a hyperspherical harmonic $Y_{\lambda_s \eta_s}(\hat{\boldsymbol{R}})$, whose degree is highest (i.e. can be raised no further by the ladder operator E_{η_s}), in the form

$$E_{\eta_s} Y_{\lambda_s \eta_s}(\hat{\boldsymbol{R}}) = 0. \tag{4.4}$$

When E_{η_s} is cast as a first-order differential operator, equation (4.4) determines that particular 'highest-weight' harmonic.

Operating on each of these 'highest-weight' harmonics with successions of 'lowering' $E_{-\eta_s}$ operators generates complete sets of hyperspherical harmonics, as detailed in the following sections.

4.1. Operations on the m_i parameters

The m_i quantum numbers, eigenvalues of the operators H_i, belong in the $\hat{\boldsymbol{h}}_i$ 'space', being raised or lowered in value by $E_{\boldsymbol{\alpha}}$ or $E_{\pm\eta_s}$ operators *external* to that space, just as the m eigenvalues of l_z are shifted by $l_x \pm \mathrm{i}l_y$ operators with axes orthogonal to $\hat{\boldsymbol{z}}$. As the ladder operators $l_x \pm \mathrm{i}l_y$ of physical space are viewed as 'eigenvectors' of l_z through the commutator

equations $[l_z, l_x \pm \mathrm{i}l_y] = \pm(l_x \pm \mathrm{i}l_y)$, sets of ladder operators $E_{\boldsymbol{\alpha}}$ are defined as solutions of the commutator-equations' set,

$$[H_i, E_{\boldsymbol{\alpha}}] = \alpha_i E_{\boldsymbol{\alpha}} \qquad \alpha_i = \pm 1 \text{ or } 0 \qquad \text{for} \quad i = 1, 2, \ldots, \ell \tag{4.5}$$

implying that $H_i E_{\boldsymbol{\alpha}} u_i = (m_i + \alpha_i) E_{\boldsymbol{\alpha}} u_i$ for the eigenvector u_i of H_i with eigenvalue m_i.

Basic elements for solving (4.5) emerge from the introduction and properties of infinitesimal rotation operators (2.2) and (2.6) in section 2.

(a) Commutators $\left[H_i, J^{xy}_{jk}\right]$ *vanish* unless one of the variables (x_j, y_k) is common to both operators. If one is, the commutator equals a related $J^{x'y'}_{j'k'}$ times a *unit-magnitude* coefficient, much as the three-dimensional commutator of l_z with l_x or l_y does.

(b) Accordingly each $E_{\boldsymbol{\alpha}}$ reduces to a linear combination of a *few* J^{xy}_{jk} with $|\alpha_i| = 1$ or 0; $\alpha_i = \pm 1$ thus corresponds to raising or lowering m_i. The commutator of a pair of Hermitian-conjugate ladder operators $[E_{\boldsymbol{\alpha}}, E_{-\boldsymbol{\alpha}}]$ is itself Hermitian, specifically a multiple of the unit operator.

(c) The directions of $\boldsymbol{\alpha}$ (or $\boldsymbol{\eta}_s$) vectors in the $\hat{\boldsymbol{h}}_i$ space run in that space at equal distances between pairs of $\hat{\boldsymbol{h}}_i$'s.

(d) For d even, the resulting operators $E_{\boldsymbol{\alpha}}$ (or $E_{\boldsymbol{\eta}_s}$) shift the values of *two* m_i parameters by unity simultaneously, thus *preserving the parity* of the $\sum_i m_i$. The same holds for most of the ladder operators for odd-dimensional systems, too, with the following exception: odd-dimensional systems include a single operator $E_{\boldsymbol{\eta}_s}$ (one among a subset of ℓ operators $E_{\boldsymbol{\alpha}}$) acting on a single m_i, whose contribution violates the parity conservation.

Appendix A outlines a procedure to identify raising and lowering operators.

These elements, developed originally in [5, 6], afford a basis for constructing complete sets of hyperspherical harmonics by *transforming* a *single* prototype harmonic with *complete sets* of $E_{\boldsymbol{\alpha}}$ (or $E_{\boldsymbol{\eta}_s}$) operators. Preferred prototypes have a *single non-zero* value of m_i parameters, typically $\{m_1 = \lambda, m_{j\neq 1} = 0\}$. An initial $E_{\boldsymbol{\alpha}}$ operator will lower m_1's value by one unit, raising that of one $|m_{j\neq 1}|$ from 0 to 1. Alternative successions of analogous operators thus generate complete sets of λ-degree harmonics, all of whose vectors $\{\boldsymbol{m}\}$ prove compatible with the initial $\boldsymbol{m} \equiv \{\lambda, 0, 0, \ldots, 0\}$, i.e. with $\sum_i |m_i| \leqslant \lambda$ and (in the even-dimensional case) $(-1)^{\sum_i m_i} = (-1)^{\lambda}$. An initial prototype harmonic convenient for this purpose reads, in the notation of (3.3),

$$\cos^{\lambda}\alpha \sin^{\lambda}\theta_1 \, \mathrm{e}^{\mathrm{i}\lambda\varphi_1} \equiv \left(\frac{x_1 + \mathrm{i}y_1}{R}\right)^{\lambda} \tag{4.6}$$

with 'highest-weight' exponents λ corresponding to $l_1 = m_1 = \lambda$, $l_2 = m_2 = 0, n = 0$ in (3.3).

The allowed range of each among the several $\boldsymbol{m}$ components m_i is limited by the condition $|m_i| \leqslant \lambda_i$, each λ_i being an element of the partition

$$\lambda = \sum_i \lambda_i \qquad \lambda_i \geqslant 0 \qquad -\lambda_i \leqslant m_i \leqslant \lambda_i \tag{4.7}$$

which reflects, in turn, specific sequences of the relevant $E_{\boldsymbol{\alpha}}$ applications. Two (or more) of the $\boldsymbol{m}$ 'weight vectors' thus generated may coincide, being labelled 'multiple weights', reached by alternative operator sequences equivalent in this respect. The total number of alternative $\boldsymbol{m}$ vectors generated by the present procedure, denoted by w in section 3, includes combined contributions of multiple weights. These w values, representing the dimension of the accessible $\{\boldsymbol{m}\}$ set and of its corresponding set of hyperspherical harmonics, are discussed for d-dimensional rotations in [82] (section 10.2) and for various other groups in [7, 8].

The harmonics' symmetry under rotation reversals, discussed in section 2.1, implies for even-dimensional spaces (where the parity conservation mentioned in item (d) above holds strictly) the relationship of hyperspherical harmonics

$$Y_{\lambda,-\boldsymbol{m}}(\hat{\boldsymbol{R}}) = (-1)^{\lambda} Y^{*}_{\lambda \boldsymbol{m}}(\hat{\boldsymbol{R}}). \tag{4.8}$$

4.2. Operations on the m_s parameters

Equation (4.2) shows parallel expansions of a 'weight vector' $\boldsymbol{m}$ into the eigenvalues $\{m_i\}$ and $\{m_s\}$ of the commuting operators $\{H_i\}$ and of the ladder-operator labels $\{\boldsymbol{\eta}_s\}$. These alternative base sets span the same ℓ-dimensional space with different orientations and different metric scales set, respectively, by the H_i eigenvalues m_i with unit spacing and by the $\boldsymbol{\eta}_s$ vectors with (in general) *two* unit-magnitude components and resulting squared-magnitudes $\boldsymbol{\eta}_s \cdot \boldsymbol{\eta}_s = 2$. Section 4.1 has stressed how ladder operators shift *pairs* of m_i parameters simultaneously, contrasting with $E_{\pm\boldsymbol{\eta}_s}$'s shift of a *single* m_s parameter. The simpler action on the m_s thus simplifies the construction of hyperspherical harmonics' sets.

This simplification is partly compensated by a restriction imposed on $\{m_s\}$ sets by their equivalence to $\{m_i\}$, implied by (4.2) and represented by requiring

$$2\frac{\boldsymbol{m} \cdot \boldsymbol{\eta}_s}{\boldsymbol{\eta}_s \cdot \boldsymbol{\eta}_s} = r_s - q_s \tag{4.9}$$

whose non-negative integers r_s and q_s specify, respectively, how many times *in direct succession* the operators $E_{-\boldsymbol{\eta}_s}$ and $E_{\boldsymbol{\eta}_s}$ can be applied to $\boldsymbol{m}$. (For details on this equation, see section 10.1 of [7], or sections 13.5 and 15.2 of [8].)

Two critical elements underlie (4.9): (a) equation (4.2) establishes a linear relationship between the parameter sets $\{m_i\}$ and $\{m_s\}$; (b) the last relation in (4.7) restricts the range of each m_i sharply. Equation (4.9) restricts then the ladder operators' $E_{\pm\boldsymbol{\eta}_s}$ action on (4.6) or on any hyperspherical harmonic, shifting the relevant m_s value by one unit, through a sharp *selection rule*: the resulting value of m_s *must* satisfy (4.9).

Within this framework one constructs complete sets of hyperspherical harmonics in d dimensions by:

(a) selecting a coordinate system according to section 2;
(b) constructing an appropriate set of ℓ commuting operators $\{H_i\}$;
(c) constructing corresponding sets of ℓ ladder operators $\{E_{\boldsymbol{\eta}_s}\}$ and $\{E_{-\boldsymbol{\eta}_s} \equiv E^{\dagger}_{\boldsymbol{\eta}_s}\}$, in first-order differential form;
(d) determining a 'highest-weight' hyperspherical harmonic, characterized by a vector $\boldsymbol{\lambda}$ with components λ_i in the $\{H_i\}$ basis and λ_s in the equivalent $\{\boldsymbol{\eta}_s\}$ basis, by solving the relevant equation (4.4). (The prototype 'highest-weight' harmonic (4.6) pertains to $\boldsymbol{\lambda} = \{\lambda, 0, 0, \ldots\}$ in the $\{H_i\}$ basis.);
(e) applying to this 'highest-weight' harmonic (sequences of) the lowering operators $E_{-\boldsymbol{\eta}_s}$, with $1 \leqslant s \leqslant \ell$, for a total of $2\lambda_s$ times each, to yield the succession of harmonics $Y_{\lambda_s m_s}(\hat{\boldsymbol{R}})$, terminating at $m_s = -\lambda_s$, remaining, however, *within the constraints* of (4.9) which often prevents lowering one m_s value ahead of other $m_{s'}$'s.

4.3. Sample derivation of harmonics' sets

We apply here the procedure just outlined to the three-particle system of section 3.1, forming an $SO(6)$ geometry, utilizing the same notation and thus taking care of the prescription items (a) to (c), except for selecting a set of $\boldsymbol{\eta}_s$ vectors. This set, with components indicated by α_i in (4.5), is conventionally [8] chosen as

$$\boldsymbol{\eta}_1 \sim \{1, -1, 0\} \qquad \boldsymbol{\eta}_2 \sim \{0, 1, -1\} \qquad \boldsymbol{\eta}_3 \sim \{0, 1, 1\} \tag{4.10}$$

thus implicitly relating each m_s number to the m_i in (4.2). Note how the first of these vectors is not orthogonal to the following orthogonal pair, and the set of three is linearly independent.

We set the value of λ in (4.6) at 2 for simplicity, thus fixing the λ_s values in (4.1) at $\{2, 1, 1\}$. The relevant Cartesian ladder operators corresponding to the set of $\{H_i\}$'s equation (2.2) take the form

$$E_{\pm\eta_1} = -\mathrm{i}\left[(x_1 \pm \mathrm{i}y_1)\frac{\partial}{\partial(x_2 \pm \mathrm{i}y_2)} - (x_2 \mp \mathrm{i}y_2)\frac{\partial}{\partial(x_1 \mp \mathrm{i}y_1)}\right]$$
$$= \tfrac{1}{2}\left[J_{12}^{xx} + J_{12}^{yy} \mp \mathrm{i}\left(J_{12}^{xy} - J_{12}^{yx}\right)\right] \tag{4.11a}$$
$$E_{\pm\eta_2} = -\mathrm{i}\left[(z_1 \mp \mathrm{i}z_2)\frac{\partial}{\partial(x_2 \mp \mathrm{i}y_2)} - (x_2 \pm \mathrm{i}y_2)\frac{\partial}{\partial(z_1 \pm \mathrm{i}z_2)}\right]$$
$$= \tfrac{1}{2}\left[J_{12}^{zx} + J_{22}^{zy} \pm \mathrm{i}\left(J_{12}^{zy} - J_{22}^{zx}\right)\right] \tag{4.11b}$$
$$E_{\pm\eta_3} = -\mathrm{i}\left[(z_1 \pm \mathrm{i}z_2)\frac{\partial}{\partial(x_2 \mp \mathrm{i}y_2)} - (x_2 \pm \mathrm{i}y_2)\frac{\partial}{\partial(z_1 \mp \mathrm{i}z_2)}\right]$$
$$= \tfrac{1}{2}\left[J_{12}^{zx} - J_{22}^{zy} \pm \mathrm{i}\left(J_{12}^{zy} + J_{22}^{zx}\right)\right]. \tag{4.11c}$$

Introducing, for the sake of compactness, the elementary operator notations,

$$K_{\pm}^{(i)} = \cos\theta_i \frac{\partial}{\partial\theta_i} \pm \mathrm{i}\frac{1}{\sin\theta_i}\frac{\partial}{\partial\varphi_i} \tag{4.12a}$$
$$L_{\pm}^{(i)} = \mathrm{e}^{\pm\mathrm{i}\varphi_i}\left(\pm\frac{\partial}{\partial\theta_i} + \mathrm{i}\cot\theta_i\frac{\partial}{\partial\varphi_i}\right) \qquad i = 1, 2 \tag{4.12b}$$

we recast (4.11*a*)–(4.11*c*) in polar coordinates, corresponding to $\{H_i\}$'s of (2.5):

$$E_{\pm\eta_1} = -\frac{\mathrm{i}}{2}\mathrm{e}^{\pm\mathrm{i}(\varphi_1-\varphi_2)}\left(\sin\theta_1\sin\theta_2\frac{\partial}{\partial\alpha} - \tan\alpha\sin\theta_2 K_{\pm}^{(1)} + \cot\alpha\sin\theta_1 K_{\mp}^{(2)}\right) \tag{4.13a}$$
$$E_{\pm\eta_2} = -\frac{\mathrm{i}}{2}\left[\mathrm{e}^{\pm\mathrm{i}\varphi_2}\left(\cos\theta_1\sin\theta_2\frac{\partial}{\partial\alpha} + \tan\alpha\sin\theta_1\sin\theta_2\frac{\partial}{\partial\theta_1} + \cot\alpha\cos\theta_1 K_{\pm}^{(2)}\right) - \mathrm{i}L_{\pm}^{(2)}\right] \tag{4.13b}$$
$$E_{\pm\eta_3} = -\frac{\mathrm{i}}{2}\left[\mathrm{e}^{\pm\mathrm{i}\varphi_2}\left(\cos\theta_1\sin\theta_2\frac{\partial}{\partial\alpha} + \tan\alpha\sin\theta_1\sin\theta_2\frac{\partial}{\partial\theta_1} + \cot\alpha\cos\theta_1 K_{\pm}^{(2)}\right) + \mathrm{i}L_{\pm}^{(2)}\right]. \tag{4.13c}$$

The prototype harmonic (4.6) with $\lambda = 2$ reads as $\cos^2\alpha\sin^2\theta_1\,\mathrm{e}^{\mathrm{i}2\varphi_1}$, with λ_i and λ_s components $\{2, 0, 0\}$ and $\{2, 1, 1\}$, respectively. Operators $E_{-\eta_s}$ can be applied to this expression directly, with full attention to the condition (4.9). This condition excludes at the outset acting on this harmonic with either lowering operator $E_{-\eta_2}$ or $E_{-\eta_3}$, which change $m_{i=2}$ and $m_{i=3}$ from their initial 0 value without affecting $m_{i=1}$ that retains its highest value 2, thus violating the limitations on the m_i; only $E_{-\eta_1}$ operates on the harmonic (4.6) correctly. Sets of harmonics are grouped into 'layers' according to the number of lowering operators that have been applied to the 'highest-weight' harmonic in the process. Successive steps of lowering the m_s quantum numbers are similarly restricted, but afford alternative actions of lowering operators, as displayed in table 1. We actually show the first five layers of harmonics, with the $\sum_s m_s \geqslant 0$, the harmonics with negative values being obtained from these by complex conjugation according to (4.8).

Table 1 also illustrates the effect of non-vanishing commutators between ladder operators: different ordering of the same ladder operators may yield *different* harmonics with the *same* label $\boldsymbol{m}$, i.e. a *degenerate* eigenvalue, such as $\boldsymbol{m} = \{0, 0, 0\}$ in table 1. Furthermore, while the procedure demonstrated in table 1 will give the correct number of *linearly independent*

Table 1. Hyperspherical harmonics for a three-particle system ($d = 6$) and generalized angular momentum $\lambda = 2$. The functions are constructed by acting on the 'highest-weight' harmonic $(\cos\alpha \sin\theta_1 \exp[\mathrm{i}\varphi_1])^\lambda$ with different sequences of ladder operators, as indicated in the third column. The first two columns list the m quantum numbers in the $\boldsymbol{\eta}_s$ and H_i bases, respectively, while the last column identifies the harmonics as *superpositions* of functions (3.3) by listing their corresponding labels $\{n, l_1, m_1, l_2, m_2\}$. Indentation in the last two columns indicates a continuation line of a single entry.

m_s	m_i	Operator sequence	Resulting harmonic, not normalized	$\{n, l_1, m_1, l_2, m_2\}$
$\{2, 1, 1\}$	$\{2, 0, 0\}$		$\cos^2\alpha \sin^2\theta_1 \, \mathrm{e}^{\mathrm{i}2\varphi_1}$	$\{0, 2, 2, 0, 0\}$
$\{1, 1, 1\}$	$\{1, 1, 0\}$	$E_{-\boldsymbol{\eta}_1}$	$2\mathrm{i}\cos\alpha \sin\theta_1 \, \mathrm{e}^{\mathrm{i}\varphi_1} \sin\alpha \sin\theta_2 \, \mathrm{e}^{\mathrm{i}\varphi_2}$	$\{0, 1, 1, 1, 1\}$
$\{0, 1, 1\}$	$\{0, 2, 0\}$	$E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_1}$	$-2\sin^2\alpha \sin^2\theta_2 \, \mathrm{e}^{\mathrm{i}2\varphi_2}$	$\{0, 0, 0, 2, 2\}$
$\{1, 0, 1\}$	$\{1, 0, 1\}$	$E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1}$	$2\cos^2\alpha \sin\theta_1 \cos\theta_1 \, \mathrm{e}^{\mathrm{i}\varphi_1} + 2\mathrm{i}\cos\alpha \sin\theta_1 \, \mathrm{e}^{\mathrm{i}\varphi_1} \sin\alpha \cos\theta_2$	$\{0, 2, 1, 0, 0\}$, $\{0, 1, 1, 1, 0\}$
$\{1, 1, 0\}$	$\{1, 0, -1\}$	$E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_1}$	$2\cos^2\alpha \sin\theta_1 \cos\theta_1 \, \mathrm{e}^{\mathrm{i}\varphi_1} - 2\mathrm{i}\cos\alpha \sin\theta_1 \, \mathrm{e}^{\mathrm{i}\varphi_1} \sin\alpha \cos\theta_2$	$\{0, 2, 1, 0, 0\}$, $\{0, 1, 1, 1, 0\}$
$\{1, 0, 0\}$	$\{1, -1, 0\}$	$E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1}$	$2\mathrm{i}\cos\alpha \sin\theta_1 \, \mathrm{e}^{\mathrm{i}\varphi_1} \sin\alpha \sin\theta_2 \, \mathrm{e}^{-\mathrm{i}\varphi_2}$	$\{0, 1, 1, 1, -1\}$
$\{0, 1, 0\}$	$\{0, 1, -1\}$	$E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_1}$	$2\mathrm{i}\cos\alpha \cos\theta_1 \sin\alpha \sin\theta_2 \, \mathrm{e}^{\mathrm{i}\varphi_2} + 2\sin^2\alpha \sin\theta_2 \cos\theta_2 \, \mathrm{e}^{\mathrm{i}\varphi_2}$	$\{0, 1, 0, 1, 1\}$, $\{0, 0, 0, 2, 1\}$
$\{0, 0, 1\}$	$\{0, 1, 1\}$	$E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1}$	$2\mathrm{i}\cos\alpha \cos\theta_1 \sin\alpha \sin\theta_2 \, \mathrm{e}^{\mathrm{i}\varphi_2} - 2\sin^2\alpha \sin\theta_2 \cos\theta_2 \, \mathrm{e}^{\mathrm{i}\varphi_2}$	$\{0, 1, 0, 1, 1\}$, $\{0, 0, 0, 2, 1\}$
$\{0, -1, 1\}$	$\{0, 0, 2\}$	$E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1}$	$\frac{2}{3}[\cos^2\alpha(3\cos^2\theta_1 - 1) - \sin^2\alpha(3\cos^2\theta_2 - 1)]$	$\{0, 2, 0, 0, 0\}$, $\{0, 0, 0, 2, 0\}$,
			$+\frac{2}{3}\cos 2\alpha + 4\mathrm{i}\cos\alpha \cos\theta_1 \sin\alpha \cos\theta_2$	$\{1, 0, 0, 0, 0\}$, $\{0, 1, 0, 1, 0\}$
$\{0, 0, 0\}$	$\{0, 0, 0\}$	$E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1}$	$-\frac{2}{3}\mathrm{i}[\cos^2\alpha(3\cos^2\theta_1 - 1) - \sin^2\alpha(3\cos^2\theta_2 - 1)]$	$\{0, 2, 0, 0, 0\}$, $\{0, 0, 0, 2, 0\}$,
			$+\frac{4}{3}\mathrm{i}\cos 2\alpha$	$\{1, 0, 0, 0, 0\}$
$\{0, 0, 0\}$	$\{0, 0, 0\}$	$E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_2} E_{-\boldsymbol{\eta}_1}$	$\frac{2}{3}[\cos^2\alpha(3\cos^2\theta_1 - 1) + 2\sin^2\alpha(3\cos^2\theta_2 - 1)]$	$\{0, 2, 0, 0, 0\}$, $\{0, 0, 0, 2, 0\}$,
			$+\frac{2}{3}\cos 2\alpha$	$\{1, 0, 0, 0, 0\}$
$\{0, 1, -1\}$	$\{0, 0, -2\}$	$E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_1} E_{-\boldsymbol{\eta}_3} E_{-\boldsymbol{\eta}_1}$	$\frac{2}{3}[\cos^2\alpha(3\cos^2\theta_1 - 1) - \sin^2\alpha(3\cos^2\theta_2 - 1)]$	$\{0, 2, 0, 0, 0\}$, $\{0, 0, 0, 2, 0\}$,
			$+\frac{2}{3}\cos 2\alpha - 4\mathrm{i}\cos\alpha \cos\theta_1 \sin\alpha \cos\theta_2$	$\{1, 0, 0, 0, 0\}$, $\{0, 1, 0, 1, 0\}$

harmonics, these may not necessarily be *orthogonal* (with the usual definition of a Hermitian scalar product as an integral over the relevant space: $(f, g) = \int f^* g \, \mathrm{d}\boldsymbol{x}$). For a more detailed discussion of the issues of multiple eigenvalues and orthogonalization of harmonics in the general case, see e.g. [8, 84].

Finally, recasting $\{H_i\}$ from (2.2) as

$$\begin{aligned} H_i &= -\mathrm{i}\left[(x_i + \mathrm{i}y_i)\frac{\partial}{\partial(x_i + \mathrm{i}y_i)} - (x_i - \mathrm{i}y_i)\frac{\partial}{\partial(x_i - \mathrm{i}y_i)}\right] \qquad i = 1, 2 \\ H_3 &= -\mathrm{i}\left[(z_1 + \mathrm{i}z_2)\frac{\partial}{\partial(z_1 + \mathrm{i}z_2)} - (z_1 - \mathrm{i}z_2)\frac{\partial}{\partial(z_1 - \mathrm{i}z_2)}\right] \end{aligned} \tag{4.14}$$

and using (4.11*a*)–(4.11*c*), we note that manipulating harmonics by means of ladder operators is most easily performed in generic Cartesian coordinates, where the harmonics take the form of products with generic factors $[(x_i \pm \mathrm{i}y_i)/R]^{|m_i|}$ [84].

4.4. Harmonics for application to atoms and molecules

Different sets of hyperspherical harmonics serve to represent different aggregates, at different stages of their development. More specifically, each set reflects the structure of the relevant 'Jacobi tree' introduced in section 3.2, whose 'growth' mirrors the integration of the relevant equation (1.2), as a function of its hyper-radius R. We deal here with particular aspects of harmonics selection, beginning with the remark that, at low R values where centrifugal potentials prevail, governing the single particles, the set described in section 3.1 may prove adequate, complemented possibly by the set of section 3.2. The following sections deal with two particular aspects of our subject.

4.4.1. Symmetrized harmonics. Particle aggregates include generally subsets of identical particles: electrons, of course, but also atomic nuclei such as the numerous protons of hydrocarbons. As a preliminary to the eventual requirement of antisymmetrizing wavefunctions under permutation of fermion positions, or analogous operations on bosons, it often proves convenient to select at the outset harmonics' sets that are invariant under permutation of all identical-particle variables [41, 42]. This preliminary operation serves particularly to reduce the dimension of each harmonics' set.

Typically each electron pair may rotate about its centre of mass only with orbital momenta equal to an even (odd) multiple of $\hbar$ when in a singlet (triplet) spin state. The same holds familiarly for the nuclear states of para- (ortho-)molecular hydrogen. This restriction reduces the relevant sets' dimensions by exponential factors when applied to large sets of identical particles, complemented by enforcing the corresponding symmetry between different particle pairs, a more laborious procedure known as the selection of 'fractional parentage' ([85] and [82], chapter 8), but applied more conveniently at the outset of any calculation.

4.4.2. Expansion of whole-state representations. Expanding the whole solution $\Psi(\boldsymbol{R})$ of (1.2) into hyperspherical harmonics may also serve to illustrate the resulting representation of a multi-particle state. The set of hyperspherical harmonics must, however, be complemented for this purpose by a harmonic function of the hyper-radius R, a generalization of the familiar Bessel functions in two dimensions and of their related 'spherical Bessel' functions in three dimensions. The required harmonic functions of R belong once again to the Bessel function family.

The spherical Bessel function equation for three dimensions, equation (10.1.1) of [83], differs from the standard Bessel function equation for two dimensions (9.1.1), by: (a)

a coefficient $2 = d - 1$ inserted before its first-derivative term, and (b) its eigenvalue $n(n+1) = (n+\frac{1}{2})^2 - \frac{1}{4}$ replacing the standard eigenvalue ν^2. Similarly, the hyperspherical Bessel function for d dimensions differs by (a) a coefficient $d-1 \equiv 3N-4$ inserted before its first-derivative term, and (b) its eigenvalue $\lambda(\lambda+d-2)+(d-1)(d-3)/4 = (\lambda+(d-2)/2)^2 - \frac{1}{4}$ replacing ν^2. The resulting Bessel function will thus be of integer or fractional order $\lambda + (d-2)/2$, with a corresponding pre-factor arising from the $R^{(3N-4)/2}$ coefficient of our equation (1.2), as anticipated in [67].

5. Hyperspherical expansion of the wave equation

The preliminary treatment of hyperspherical harmonics in section 3 suffices to formulate an expanded version of (1.2). On the left-hand side of this equation, the factors $R^{(3N-4)/2}$ have been separated out to allow setting a finite initial value of $\Psi(R, \hat{\boldsymbol{R}})$ at $R = 0$. The factors separated out take into account the centrifugal—actually, wave-mechanical—potential generated in polar coordinates with small values of R by compressing particles within short 'parallel circles'. We may then standardize wavefunctions that start at $R = 0$ with unit value in a *single hyperspherical channel* $(\lambda_0, \boldsymbol{\mu}_0)$, expanding as R increases into alternative channels $(\lambda, \boldsymbol{\mu})$, as indicated by

$$\begin{aligned} &\Psi_{\lambda_0\boldsymbol{\mu}_0}(\boldsymbol{R}) = \sum_{\lambda,\boldsymbol{\mu}} F_{\lambda_0\boldsymbol{\mu}_0,\lambda\boldsymbol{\mu}}(R)\, Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}}) \\ &F_{\lambda_0\boldsymbol{\mu}_0,\lambda\boldsymbol{\mu}} \to R^{\lambda_0}\delta_{\lambda_0\boldsymbol{\mu}_0,\lambda\boldsymbol{\mu}} \qquad \text{as} \quad R \to 0. \end{aligned} \tag{5.1}$$

Entering the expansion (5.1) in (1.2), and projecting the result onto the several harmonics $Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}})$, reduces (1.2) to the system of coupled radial Schrödinger equations

$$\frac{\mathrm{d}^2}{\mathrm{d}R^2} F_{\lambda_0\boldsymbol{\mu}_0,\lambda\boldsymbol{\mu}}(R) + \sum_{\lambda',\boldsymbol{\mu}'} F_{\lambda_0\boldsymbol{\mu}_0,\lambda'\boldsymbol{\mu}'} \langle \lambda'\boldsymbol{\mu}'|k^2(R)|\lambda\boldsymbol{\mu}\rangle = 0 \tag{5.2}$$

with the wavenumber matrix

$$\begin{aligned} \langle \lambda'\boldsymbol{\mu}'|k^2(R)|\lambda\boldsymbol{\mu}\rangle = &\left(2\mathcal{M}E - \frac{\lambda(\lambda+d-2)+[(d-2)^2-1]/4}{R^2}\right)\delta_{\lambda'\boldsymbol{\mu}',\lambda\boldsymbol{\mu}} \\ &+\frac{2\mathcal{M}\langle \lambda'\boldsymbol{\mu}'|Z(\hat{\boldsymbol{R}})|\lambda\boldsymbol{\mu}\rangle}{R} + \cdots . \end{aligned} \tag{5.3}$$

Here $Z(\hat{\boldsymbol{R}})/R$ represents the Coulomb potential energy of the interacting particles, evaluated at each hyper-radius R. The dots at the end of (5.3) stand for any additional terms of the k^2 matrix corresponding to Hamiltonian terms that represent spin–orbit or relativistic corrections not included explicitly. The ability of (5.2) to include such effects—thus far not exploited—may bypass the current need to treat such terms perturbatively rather than directly in the basic equation.

The system of coupled equations (5.2) is formally infinite, owing to the infinite range of its parameter λ, and thus seemingly impractical as noted in section 1. However, circumstances also described in section 1 reduce its size generally to a modest level.

5.1. Displaying the evolution toward fragmentation

Our approach to displaying this evolution derives from features of the fragmentation of nuclei that are held together by short-range interactions [86]. Beyond this range, r_0, energy eigenfunctions resolve into *fragmentation eigenchannels*, labelled here by ρ, each of them propagating at $r > r_0$ in force-free space with *unchanged structure*, i.e. with spherical

wavefronts, r-independent angular distributions $f_\rho(\theta,\varphi)$ and uniform phases $\phi_\rho(r)$. Here the parameter sets $\{f_\rho(\theta,\varphi)\}$ and $\{\phi_\rho(r)\}$ embody the effect of all particle interactions at $r < r_0$.

The opportunity occurred in [86] to utilize an analogous parametrization *regardless of interaction ranges*, by embodying the effect of *all* interactions at the ranges $0 \leqslant r \leqslant R$ into parameter sets $\{f_\rho(R;\hat{\boldsymbol{R}})\}$ and $\{\phi_\rho(R)\}$ to be evaluated *for successive values of* R. These sets' dependence on R displays each eigenchannel's evolution as R increases from its 0 value (at the system's centre of mass) towards ∞, i.e. disregarding all interactions at $r > R$ at each step of integration.

The hyperspherical channel functions (5.1), $\Psi_{\lambda_0\boldsymbol{\mu}_0}(\boldsymbol{R})$, of each multi-particle system serve here as a basis to calculate the $\{f_\rho(R;\hat{\boldsymbol{R}})\}$ and $\{\phi_\rho(R)\}$ parameters by casting them into superpositions

$$\Phi_\rho(\boldsymbol{R}) = \sum_{\lambda_0\boldsymbol{\mu}_0} \langle\rho(R)|\lambda_0\boldsymbol{\mu}_0\rangle \Psi_{\lambda_0\boldsymbol{\mu}_0}(\boldsymbol{R}) = \sum_{\lambda_0\boldsymbol{\mu}_0} \langle\rho(R)|\lambda_0\boldsymbol{\mu}_0\rangle \sum_{\lambda\boldsymbol{\mu}} F_{\lambda_0\boldsymbol{\mu}_0,\lambda\boldsymbol{\mu}}(R) Y_{\lambda\boldsymbol{\mu}}(\hat{\boldsymbol{R}}) \tag{5.4}$$

with initial values of the coefficients

$$\langle\rho(R)|\lambda_0\boldsymbol{\mu}_0\rangle \to 1 \qquad \text{i.e.} \quad \langle\rho| \to \langle\lambda_0\boldsymbol{\mu}_0| \qquad \text{as} \quad R \to 0. \tag{5.5}$$

Requiring each phase $\phi_\rho(R)$ of $\Phi_\rho(\boldsymbol{R})$, and its gradient $(\mathrm{d}\phi/\mathrm{d}R)$, to be uniform over each hyper-surface ($R =$ constant) identifies each superposition (5.4), $\Phi_\rho(\boldsymbol{R})$, as an *eigenchannel* of the propagating Schrödinger equation (1.2) at *each value* of R. It thus implies that the angular eigenfunction $f_\rho(R;\hat{\boldsymbol{R}})$, representing the aggregate's 'shape' at R, evolves 'in step' from each hyper-surface to the next. This requirement translates into a system of linear homogeneous equations for the coefficients $\langle\rho(R)|\lambda_0\boldsymbol{\mu}_0\rangle$.

Following the 'phase–amplitude' approach of [86], which replaces second-order wave equations with pairs of first-order equations, references [77, 78] introduced the eigenphase's $\tan\phi_{\rho(R)}$—without previous reference to (5.4)—as an eigenvalue of the 'R-matrix'

$$\begin{aligned}\langle\lambda\boldsymbol{\mu}|\mathcal{R}(R)|\lambda'\boldsymbol{\mu}'\rangle &= \sum_{\lambda_0\boldsymbol{\mu}_0} \left(\frac{\mathrm{d}F}{\mathrm{d}R}\right)^{-1}_{\lambda\boldsymbol{\mu},\lambda_0\boldsymbol{\mu}_0} F_{\lambda_0\boldsymbol{\mu}_0,\lambda'\boldsymbol{\mu}'}(R) \\ &= \sum_\rho \langle\lambda\boldsymbol{\mu}|\rho(R)\rangle \tan\phi_{\rho(R)} \langle\rho(R)|\lambda'\boldsymbol{\mu}'\rangle. \end{aligned} \tag{5.6}$$

Reference [79] proceeded then by taking the derivative of (5.6) with respect to R, replacing its element $(\mathrm{d}^2F/\mathrm{d}R^2)$ with its expression (5.2) in terms of the k^2 matrix (5.3), and finally transforming the result to the $\langle\rho(R)|$ basis by means of the coefficients $\langle\rho(R)|\lambda\boldsymbol{\mu}\rangle$ and their reciprocals.

Taking the $\mathcal{R}$ matrix as a stepping stone served thus to resolve the initial *second-order* equation (5.2) into the set of *first-order equations* corresponding to the diagonal and off-diagonal elements of (5.6), respectively,

$$\frac{\mathrm{d}\tan\phi_{\rho(R)}}{\mathrm{d}R} = 1 + \langle\rho(R)|k^2(R)|\rho(R)\rangle \tan^2\phi_{\rho(R)} \tag{5.7a}$$

$$\frac{\mathrm{d}\langle\rho(R)|\lambda\boldsymbol{\mu}\rangle}{\mathrm{d}R} = \sum_{\rho'\neq\rho} \frac{\sin\phi_{\rho(R)}\langle\rho(R)|k^2(R)|\rho'(R)\rangle \sin\phi_{\rho'(R)}}{\sin(\phi_\rho - \phi_{\rho'})} \langle\rho'(R)|\lambda\boldsymbol{\mu}\rangle \tag{5.7b}$$

with R expressed in units of $(\mathrm{d}R/\mathrm{d}\phi_\rho)$. This set of equations has been integrated numerically in [79] for the prototype example of doubly excited He, with conclusions described below.

5.2. Illustration and discussion

The numerical integration of (5.7*a*)–(5.7*b*) for He has been carried out with a device that accelerates the convergence of expansion into harmonics $\langle\lambda\boldsymbol{\mu}|$, by replacing these harmonics with eigenvectors of the k^2 matrix (5.3) at each R. These eigenvectors represent 'adiabatic' solutions of our problems, carried out earlier in the frame of [1, 2], i.e. disregarding the coupling between the radial and angular variables, R and $\hat{\boldsymbol{R}}$.

The sample results shown in figure 1 should be viewed as interconnecting each system's sets of compact (c) and fragmented (f) channels, outlined in [3, 79]. Quantum mechanical scattering theory represents this connection by 'Jost' matrices J_{fc} [87]. Each standing-wave eigenfunction of (1.2), identified by an initial boundary condition (c) at its compact limit, is represented asymptotically near its (f) limit by $\sum_f \sin(k_f R) J_{fc}$, or more conveniently in terms of its outgoing and incoming components

$$\sum_f \exp(\mathrm{i}k_f R) J^+_{fc} \qquad \sum_f \exp(-\mathrm{i}k_f R) J^-_{fc}. \tag{5.8}$$

The matrices $J^{\pm}_{fc}$ are complex conjugate for 'open' channels f, i.e. when the energy suffices to achieve the f limit; for energetically 'closed' channels the wavenumber k_f is imaginary, whereby one component converges to zero at discrete eigenvalues of the energy E and the other diverges as $R \to \infty$. The Jost matrices serve then to construct scattering matrices

$$S_{f'f} = \sum_c J^+_{f'c} \left(\frac{1}{J^-}\right)_{cf} \tag{5.9}$$

as detailed in [3, 4]. In this frame one views each amplitude $\langle\rho(R)|\lambda_0\boldsymbol{\mu}_0\rangle$ of (5.4), evaluated at a finite range R, as a partial construction of the Jost matrix element J_{fc} with f representing the limit of $\langle\rho(R)|$ as $R \to \infty$. Plots of the several bra symbols $\langle\rho(R)|$ achieve our objective of displaying the system's evolution from $R = 0$ toward ∞.

Figures 1(*a*) and (*b*) plot eigenphases $\phi_\rho(R)$ versus $\sqrt{R}$, modulo π, at energies straddling the $(2s)^2\ {}^1S$ resonance of He near 58 eV, for a number of $\langle\rho(R)|\lambda_0\boldsymbol{\mu}_0\rangle$ pairs. Each line's slope mirrors the rate of increase of $\phi_\rho(R)$, i.e. (loosely) the rate of expansion in R of the corresponding eigenfunction. (The first eigenphase's slope reflects the rapid motion of an electron ionized with approximately 33 eV kinetic energy; successive curves reflect the increasingly slower development of two-electron excitations in successively higher modes.) In the lower and upper ranges of the ordinate ϕ_ρ, corresponding to low values of $\sin[\phi_\rho(R)]$, pairs of curves appear to cross with minimal disturbance, owing to unresolved values of the coupling coefficient on the right of (5.7*b*), in spite of the singularity arising from the vanishing of its denominator at each crossing. Major effects of crossings emerge instead at middle ranges of $\phi_\rho(R)$, where pairs of curves appear to repel each other experiencing major deflections.

The localization of such major 'avoided crossings' within limited ranges of ordinates and abscissae, confirmed by analogous more dense plots, verifies our expectation that eigenfunctions propagate smoothly outside the limited parameter ranges where the coupling coefficients of (5.7*b*) diverge. The apparent 'repulsion' of curves at avoided crossings is a familiar aspect of the Landau–Zener phenomenon [88–90] occurring at points of 'degeneracy' where two alternative values of a parameter coincide, as the phases $(\phi_\rho, \phi_{\rho'})$ do here (modulo π).

An additional major manifestation of avoided crossings, namely, the hybridization of pairs $(\langle\rho|\lambda_0\boldsymbol{\mu}_0\rangle, \langle\rho'|\lambda'_0\boldsymbol{\mu}'_0\rangle)$, has, however, not been included in the calculations underlying figure 1. This hybridization might result by fitting parameters of the observed phenomena—slopes,

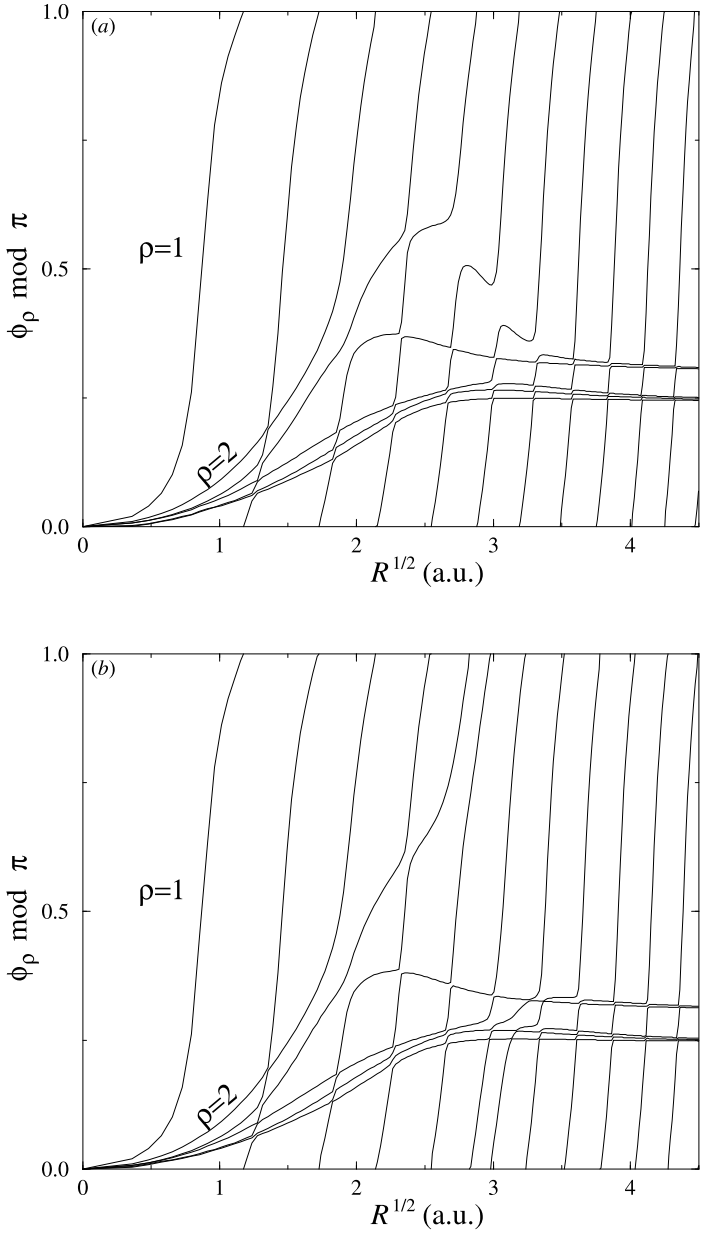


Figure 1. (*a*) Eigenphases ϕ_ρ modulo π versus the square root of the hyper-radius, calculated at the total energy $E = 57$ eV above the ground state, just below the '$(2s^2)\,{}^1S$' resonant state in helium. (*b*) Shows the same set of eigenphases, calculated at a total energy $E = 58$ eV above the ground state.

slope differences of the curves and their closest approaches—to the corresponding elements of the Landau–Zener theory. The relevance of the present $\langle\rho|\lambda_0\boldsymbol{\mu}_0\rangle$ coefficients to the Jost matrices of interest remains fragmentary pending further developments of Nakamura's recent analytical improvements on the Landau–Zener theory [91, 92].

5.3. Qualitative effects of Coulomb interactions

Equation (5.3)'s matrix $\langle\lambda'\boldsymbol{\mu}'|Z(\hat{\boldsymbol{R}})|\lambda\boldsymbol{\mu}\rangle$ consists of $N(N-1)/2$ terms for an aggregate of N charged particles. These terms, included sequentially in computer programs, serve to solve (5.7*a*) and (5.7*b*) numerically, yet warrant analysis aimed at visualizing their qualitative action. To this end one may resolve the Z-matrix' action on the wavefunction Ψ into its several aspects.

Subsets of terms acting between particles with equal (opposite) charges push corresponding particle subsets apart (together). Within this scope one notes that:

(a) Expressing the distance between each atomic nucleus and another particle in terms of their common mass weighted hyper-radius *R scales up* its charge by its mass' square root, thereby boosting its interactions' strength and thus favouring *molecular dissociation* as compared to ionization by electron ejection.

(b) The force acting on each particle pair depends on the pair's orientation. Combining the Coulomb forces between various particle pairs thus involves extensive geometrical transformations of the relevant position coordinates.

Coulomb interactions between subsets of *identical particles* may be grouped conveniently, particularly so following the symmetrization of relevant position coordinates outlined in section 4.4 and in appendix D. It would then become possible to combine Coulomb terms pertaining to such subsets to yield expressions of their electrical multipole moments and of their corresponding multipole fields. A semi-macroscopic view of each aggregate's mechanics should thus emerge, in terms of collective variables.

Within the context of initial combination of molecular nuclei with closed-shell electrons, one could then envisage treating all molecular valence electrons as forming a gas whose electric multipole moments are inflated by electronic mutual repulsions, yet contained by the attractive multipole fields of nuclei and closed-shell cores. The proton-nuclei of hydrocarbon molecules would be similarly viewed. This attractive containment would perform a twofold action: holding the molecule together as a unit and simultaneously smoothing out the distribution of opposite charges throughout its volume.

Appendix A. Construction of ladder operators

The generic infinitesimal operators (2.6) raise and lower the eigenvalues, m_i and m_j, of operator pairs (H_i, H_j) by mapping a single harmonic onto a *superposition* of harmonics with different m_i's and m_j's. We construct here linear combinations of those operators that raise *or* lower by unity these eigenvalues in a definite way, according to (4.5).

Casting for this purpose (H_i, H_j) in the form of the first two expressions in (2.2), i.e. as $(H_i \equiv J_{ii}^{xy}, H_j \equiv J_{jj}^{xy})$, restricts the solutions E_α of (4.5) to combinations of the four components

$$J_{ij}^{xx}, \quad J_{ij}^{yy}, \quad J_{ij}^{xy}, \quad J_{ij}^{yx}. \tag{A.1}$$

Identification of the proper linear combinations proceeds through analysis of their commutator

relations with the H_i's, namely,

$$[H_i, J_{ij}^{yx}] = +\mathrm{i}J_{ij}^{yx} \qquad [H_j, J_{ij}^{xx}] = +\mathrm{i}J_{ij}^{xy} \tag{A.2a}$$

$$[H_i, J_{ij}^{yx}] = -\mathrm{i}J_{ij}^{xx} \qquad [H_j, J_{ij}^{xy}] = -\mathrm{i}J_{ij}^{xx} \tag{A.2b}$$

$$[H_i, J_{ij}^{yy}] = -\mathrm{i}J_{ij}^{xy} \qquad [H_j, J_{ij}^{yy}] = -\mathrm{i}J_{ij}^{yx} \tag{A.2c}$$

$$[H_i, J_{ij}^{xy}] = +\mathrm{i}J_{ij}^{yy} \qquad [H_j, J_{ij}^{yx}] = +\mathrm{i}J_{ij}^{yy}. \tag{A.2d}$$

Combinations of the operators (A.1) symmetric and antisymmetric in their (x, y) variables, analogues of (2.7*b*)'s symmetry in (i, j) indices, yield

$$E_{\pm\boldsymbol{\alpha}_{ij}^{(++)}} = (J_{ij}^{xx} - J_{ij}^{yy}) \pm \mathrm{i}(J_{ij}^{xy} + J_{ij}^{yx}) \tag{A.3a}$$

$$E_{\pm\boldsymbol{\alpha}_{ij}^{(+-)}} = (J_{ij}^{xx} + J_{ij}^{yy}) \mp \mathrm{i}(J_{ij}^{xy} - J_{ij}^{yx}) \tag{A.3b}$$

satisfying the desired equations

$$[H_i, E_{\pm\boldsymbol{\alpha}_{ij}^{(++)}}] = \pm E_{\pm\boldsymbol{\alpha}_{ij}^{(++)}} \qquad [H_j, E_{\pm\boldsymbol{\alpha}_{ij}^{(++)}}] = \pm E_{\pm\boldsymbol{\alpha}_{ij}^{(++)}} \tag{A.4a}$$

$$[H_i, E_{\pm\boldsymbol{\alpha}_{ij}^{(+-)}}] = \pm E_{\pm\boldsymbol{\alpha}_{ij}^{(+-)}} \qquad [H_j, E_{\pm\boldsymbol{\alpha}_{ij}^{(+-)}}] = \mp E_{\pm\boldsymbol{\alpha}_{ij}^{(+-)}} \tag{A.4b}$$

with

$$\boldsymbol{\alpha}_{i,j}^{(++)} = (+1, +1) \tag{A.5a}$$

$$\boldsymbol{\alpha}_{i,j}^{(+-)} = (+1, -1) \tag{A.5b}$$

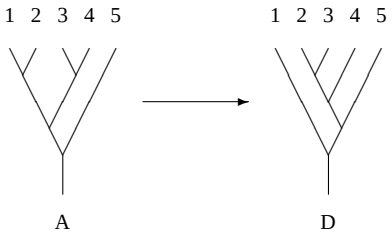
$$\boldsymbol{\alpha}_{k}^{(++)} = \boldsymbol{\alpha}_{k}^{(+-)} = 0 \qquad \text{for} \quad k \neq i, j. \tag{A.5c}$$

Note that the two operator sets $\{\frac{1}{2}(J_{ij}^{xx} \mp J_{ij}^{yy}), \frac{1}{2}(J_{ij}^{xy} \pm J_{ij}^{yx}), \frac{1}{2}(H_j \pm H_i)\}$ commute exactly like $\{l_x, l_y, l_z\}$ in three dimensions. The occurrence of (symmetric or antisymmetric) *pairs* of rotation operators in the role of both l_x and l_y, respectively, reflects the feature of the pairwise change of m_i and m_j. The symmetry of these operator pairs under interchange of the *first and second coordinates* $x_i \leftrightarrow y_i$ and $x_j \leftrightarrow y_j$ of the relevant H_i and H_j extends the present construction to ladder operators that change the m quantum numbers of H operators of the third type in (2.2), involving two z-coordinates.

For odd dimensions, ℓ ladder operator pairs pertaining to coordinate pairs $(i, 0)$ change only one of the m_i's. If again x_i, y_i make up the operator H_i pertaining to m_i, the two ladder operators acting on m_i are complex linear combinations of the two infinitesimal rotation operators which involve either of x_i or y_i, together with the single unpaired coordinate (denoted as x_0 in section 2, e.g. the z coordinate in the familiar case of $SO(3)$). In this case, the ladder operators are completely analogous to those in $SO(3)$.

Appendix B. Transformation between Jacobi trees

As an example of transformation between Jacobi trees, consider the two trees



The mass weighted relative coordinates for tree A result from independent-particle coordinates by the transformation

$$\boldsymbol{\xi}_1^A = \sqrt{\frac{M_1 M_2}{M_1 + M_2}}(\boldsymbol{r}_2 - \boldsymbol{r}_1) \tag{B.1a}$$

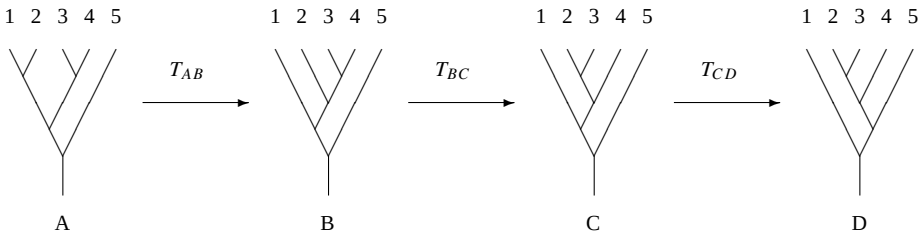
$$\boldsymbol{\xi}_2^A = \sqrt{\frac{M_3 M_4}{M_3 + M_4}}(\boldsymbol{r}_4 - \boldsymbol{r}_3) \tag{B.1b}$$

$$\boldsymbol{\xi}_3^A = \sqrt{\frac{(M_1 + M_2)(M_3 + M_4)}{M_1 + M_2 + M_3 + M_4}}\left(\frac{M_3\boldsymbol{r}_3 + M_4\boldsymbol{r}_4}{M_3 + M_4} - \frac{M_1\boldsymbol{r}_1 + M_2\boldsymbol{r}_2}{M_1 + M_2}\right) \tag{B.1c}$$

$$\boldsymbol{\xi}_4^A = \sqrt{\frac{(M_1 + M_2 + M_3 + M_4)M_5}{M_1 + M_2 + M_3 + M_4 + M_5}}\left(\boldsymbol{r}_5 - \frac{M_1\boldsymbol{r}_1 + M_2\boldsymbol{r}_2 + M_3\boldsymbol{r}_3 + M_4\boldsymbol{r}_4}{M_1 + M_2 + M_3 + M_4}\right) \tag{B.1d}$$

i.e. by first connecting particles 1 and 2, then 3 and 4, then the complex {12} to the complex {34}, and finally the complex {1234} to 5. The fifth Jacobi coordinate represents the centre of mass which remains the same for all trees consisting of the same particles, and is hence irrelevant to transformations of the four relative coordinates.

The transformation from A to D resolves into three elementary 'transplantations':



The transformation T_{AB} from A to B affects only the first and the third among the mass weighted Jacobi coordinates, since it transplants branch 2 from the complex {12} to the complex {234}. It is therefore represented by applying to the 4-vector $(\boldsymbol{\xi}_1^A, \boldsymbol{\xi}_2^A, \boldsymbol{\xi}_3^A, \boldsymbol{\xi}_4^A)$ the matrix

$$T_{AB} = \begin{pmatrix} \cos\phi_{AB} & 0 & -\sin\phi_{AB} & 0 \\ 0 & 1 & 0 & 0 \\ \sin\phi_{AB} & 0 & \cos\phi_{AB} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{B.2a}$$

i.e. by a 'kinematic rotation' through an angle

$$\phi_{AB} = \tan^{-1}\sqrt{\frac{M_2(M_1 + M_2 + M_3 + M_4)}{M_1(M_3 + M_4)}} \tag{B.2b}$$

according to (2.13). Note the general structure in the mass coefficients: transplanting branch q from the complex $\{pq\}$ to the complex $\{qr\}$ corresponds to a rotation by $\phi = \tan^{-1}\sqrt{M_q(M_p + M_q + M_r)/M_p M_r}$ (in the first quadrant, i.e. with positive signs for both the cosine and sine). The transformation T_{BC} transplants branch 3 from {34} to {23}, and T_{CD} transplants the complex branch {234} from {1234} to {2345}, with the respective transformation

matrices

$$T_{BC} = \begin{pmatrix} \cos\phi_{BC} & -\sin\phi_{BC} & 0 & 0 \\ \sin\phi_{BC} & \cos\phi_{BC} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$
$$T_{CD} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\phi_{CD} & -\sin\phi_{CD} \\ 0 & 0 & \sin\phi_{CD} & \cos\phi_{CD} \end{pmatrix} \tag{B.3a}$$

and rotation angles

$$\phi_{BC} = \tan^{-1}\sqrt{\frac{M_3(M_2+M_3+M_4)}{M_2M_4}}$$
$$\phi_{CD} = \tan^{-1}\sqrt{\frac{(M_2+M_3+M_4)(M_1+M_2+M_3+M_4+M_5)}{M_1M_5}}. \tag{B.3b}$$

The complete transformation for this sequence is represented by $T_{AD} = T_{CD} \cdot T_{BC} \cdot T_{AB}$ with

$$T_{AD} = \begin{pmatrix} \cos\phi_{AB}\cos\phi_{BC} & -\sin\phi_{BC} & -\sin\phi_{AB}\cos\phi_{BC} & 0 \\ \cos\phi_{AB}\sin\phi_{BC} & \cos\phi_{BC} & -\sin\phi_{AB}\sin\phi_{BC} & 0 \\ \sin\phi_{AB}\cos\phi_{CD} & 0 & \cos\phi_{AB}\cos\phi_{CD} & -\sin\phi_{CD} \\ \sin\phi_{AB}\sin\phi_{CD} & 0 & \cos\phi_{AB}\sin\phi_{CD} & \cos\phi_{CD} \end{pmatrix}. \tag{B.4}$$

Inserting the explicit expressions for the angles ϕ verifies that the coordinates $\boldsymbol{\xi}_i^D$, $1 \leqslant i \leqslant 4$, indeed describe the relative coordinates of tree D in terms of independent particles coordinates, namely

$$\boldsymbol{\xi}_1^D = \sqrt{\frac{(M_2+M_3)M_4}{M_2+M_3+M_4}}\left(\frac{M_2\boldsymbol{r}_2+M_3\boldsymbol{r}_3}{M_2+M_3} - \boldsymbol{r}_4\right) \tag{B.5a}$$

$$\boldsymbol{\xi}_2^D = \sqrt{\frac{M_2M_3}{M_2+M_3}}(\boldsymbol{r}_2-\boldsymbol{r}_3) \tag{B.5b}$$

$$\boldsymbol{\xi}_3^D = \sqrt{\frac{(M_2+M_3+M_4)M_5}{M_2+M_3+M_4+M_5}}\left(\frac{M_2\boldsymbol{r}_2+M_3\boldsymbol{r}_3+M_4\boldsymbol{r}_4}{M_2+M_3+M_4} - \boldsymbol{r}_5\right) \tag{B.5c}$$

$$\boldsymbol{\xi}_4^D = \sqrt{\frac{M_1(M_2+M_3+M_4+M_5)}{M_1+M_2+M_3+M_4+M_5}}\left(\frac{M_2\boldsymbol{r}_2+M_3\boldsymbol{r}_3+M_4\boldsymbol{r}_4+M_5\boldsymbol{r}_5}{M_2+M_3+M_4+M_5} - \boldsymbol{r}_1\right). \tag{B.5d}$$

Appendix C. Finite transformations of hyperspherical harmonics

Finite transformations of multi-dimensional harmonics (or operators) correspond to the infinitesimal ones considered in section 4 just as the prototype transformation (2.3) (pertaining to a physical-space rotation) corresponds to the infinitesimal (2.1). This correspondence holds generally, since all transformations relevant to this paper resolve into products of two-dimensional rotations, as stressed repeatedly in the text.

Section 4 has identified hyperspherical harmonics in the frame of a representation based on a vector $\boldsymbol{\lambda}$ in the ℓ-dimensional space of maximally commuting operator sets $\{H_i\}$. Within this scope, we might deal here just with ℓ-dimensional rotations of $\boldsymbol{\lambda}$. This space itself is,

however, subject to rotations of the $\{H_i\}$ induced by the $3(N-1)$-dimensional coordinate rotations considered in section 2 for N-particle aggregates. Generic infinitesimal operators on such spaces were indicated in (2.6) by J_{ij}^{xy}, whose label xy refers to a pair of coordinate axes, whereas ij refers to a pair of particles.

Viewing physical-space rotations, identified by three Euler angles, as our model, recall how two of these angles pertain to rotations about a z-axis (hence parallel to an xy-plane) and the third one to a shift of $\hat{z}$'s orientation to a new direction $\hat{z}'$, usually understood to lie on the previous xz-plane. Whereas rotations by an angle φ about $\hat{z}$ simply multiply eigenvectors of l_z with eigenvalue m by $\mathrm{e}^{\mathrm{i}m\varphi}$, rotations by an angle θ in the xz-plane transform it into a superposition of eigenvectors whose eigenvalues m' result by transforming the initial m with the Wigner matrix $d^{(l)}_{m'm}(\theta)$. (The index l stands here for the largest value ('highest weight') of m.)

Correspondingly, in a multi-dimensional space, we consider two distinct classes of two-dimensional rotations: (a) rotations about one of the $\{H_i\}$ operators' symmetry axes (i.e. in a plane orthogonal to that axis) which multiply a harmonic eigenvector of H_i with eigenvalue $|m_i| \leqslant \lambda_i$ by $\mathrm{e}^{\mathrm{i}m_i\varphi_i}$ and (b) orientation changes of an H_i's own axis, within a specified plane through that axis, yielding a superposition of harmonics with Wigner coefficients $D^{\lambda_i}_{\mu',\mu}$, whose subscripts differ only by replacing their m_i component with m'_i.

The multi-dimensional framework deals with transforming from one coordinate *basis*, including its operator set $\{H_i\}$, to a new *basis* with its operator set $\{H'_j\}$, each set of indices $\{i = 1, 2, \ldots\}$ and $\{j = 1, 2, \ldots\}$ being ordered. This framework affords articulating generic transformations through sequences of two-dimensional rotations by Euler angles $\{\varphi_\alpha\}$ and $\{\theta_\nu\}$: the initial $\varphi_{\alpha=1}$ equals the angle between the H_i's zero azimuth and the plane of the pair $\{H_{i=1}, H'_{j=1}\}$'s axes. The initial $\theta_{\nu=1}$ equals similarly the angle between the axes of $H_{i=1}$ and $H'_{j=1}$. The next $\varphi_{\alpha=2}$ shifts the plane of the $H_{i=1}$, $H'_{j=1}$ axes to $H'_{j=1}$'s zero azimuth. Corresponding angles $\{\varphi_{\alpha=3}, \theta_{\nu=2}, \varphi_{\alpha=4}\}$ pertain to the operator pair $\{H_{i=2}, H'_{j=2}\}$, a procedure to continue recursively.

Insofar as the $\{H_i\}$ operators are anchored to their coordinate systems, their two classes of rotations drag their coordinate axes along. Altogether, transformations of harmonics indices by coordinate rotations are thus seen to resolve into three elements: (a) rotation of the 'representation vector' $\boldsymbol{\lambda}$ in the ℓ-dimensional space of the $\{H_i\}$ set; (b) rotation of the $\{H_i\}$'s themselves, described above; (c) further rotations of coordinates with respect to the $\{H_i\}$.

Example: kinematic rotation of harmonics

Here we transform hyperspherical harmonics of two Jacobi vectors representing a three-particle system. Equations (2.12) and (2.13) have described the transformation of a Jacobi vector pair from tree A to tree B

$$A: \quad \begin{cases} \boldsymbol{\xi}_1^A = \sqrt{\dfrac{M_1M_2}{M_1+M_2}}(\boldsymbol{r}_1 - \boldsymbol{r}_2) \\ \boldsymbol{\xi}_2^A = \sqrt{\dfrac{(M_1+M_2)M_3}{M_1+M_2+M_3}}\left(\dfrac{M_1\boldsymbol{r}_1 + M_2\boldsymbol{r}_2}{M_1+M_2} - \boldsymbol{r}_3\right) \end{cases} \tag{C.1a}$$

$$B: \quad \begin{cases} \boldsymbol{\xi}_1^B = \sqrt{\dfrac{M_2M_3}{M_2+M_3}}(\boldsymbol{r}_2 - \boldsymbol{r}_3) \\ \boldsymbol{\xi}_2^B = \sqrt{\dfrac{M_1(M_2+M_3)}{M_1+M_2+M_3}}\left(\boldsymbol{r}_1 - \dfrac{M_2\boldsymbol{r}_2 + M_3\boldsymbol{r}_3}{M_2+M_3}\right) \end{cases} \tag{C.1b}$$

as a kinematic rotation by an angle $\beta = \tan^{-1}\sqrt{(M_1 + M_2 + M_3)M_2/(M_1M_3)}$,

$$\{\boldsymbol{\xi}_1^B, \boldsymbol{\xi}_2^B\} = \{\cos\beta\boldsymbol{\xi}_1^A - \sin\beta\boldsymbol{\xi}_2^A, \sin\beta\boldsymbol{\xi}_1^A + \cos\beta\boldsymbol{\xi}_2^A\}. \tag{C.2}$$

Since each vector $\boldsymbol{\xi}$ has three spatial components, we deal here with a six-dimensional coordinate transformation with components

$$\{\boldsymbol{\xi}_1^A, \boldsymbol{\xi}_2^A\} = \{(\xi_1^A)_x, (\xi_1^A)_y, (\xi_1^A)_z, (\xi_2^A)_x, (\xi_2^A)_y, (\xi_2^A)_z\} \equiv \{x_1, y_1, z_1, x_2, y_2, z_2\} \tag{C.3}$$

and similarly for $\boldsymbol{\xi}_i^B$. The x-component of $\boldsymbol{\xi}_1^B$ results from a rotation by the angle β in the x_1x_2-plane, the x-component of $\boldsymbol{\xi}_2^B$ by a rotation through $-\beta$ in the (oriented) x_2x_1-plane, and likewise for their y- and z-components. The corresponding transformation of three-particle harmonics $|\lambda, \boldsymbol{\mu}_A\rangle$, as represented, for example, by (3.3), is indicated according to section 3 by

$$|\lambda\boldsymbol{\mu}_B\rangle = T_{AB}(\beta)|\lambda\boldsymbol{\mu}_A\rangle = \sum_{\boldsymbol{\mu}'_A} |\lambda\boldsymbol{\mu}'_A\rangle D^{\lambda}_{\boldsymbol{\mu}'_A,\boldsymbol{\mu}_A}(\beta). \tag{C.4}$$

Dealing here with Cartesian coordinate rotations of the $\boldsymbol{\xi}$ vectors, at variance with the preceding polar coordinate description, our present operator T_{AB} factors into three separate (commuting) transformations of harmonics corresponding to rotations by β in each of the three coordinate planes x_1x_2, y_1y_2, and z_1z_2

$$T_{AB}(\beta) = \exp(\mathrm{i}\beta J_{12}^{xx})\exp(\mathrm{i}\beta J_{12}^{yy})\exp(\mathrm{i}\beta J_{12}^{zz}). \tag{C.5}$$

Convenient expressions of the three infinitesimal operators in this expression of T_{AB} appear in earlier parts of this paper. (a) Equation (2.2) identifies J_{12}^{zz} as the operator H_3 for our three-particle system, yielding immediately

$$\exp(\mathrm{i}\beta J_{12}^{zz})|\lambda\boldsymbol{\mu}_A\rangle = \exp(\mathrm{i}m_3\beta)|\lambda\boldsymbol{\mu}_A\rangle. \tag{C.6}$$

(b) Equation (A.3*b*) identifies the combination $J_{12}^{xx} + J_{12}^{yy}$ as the sum of the operator $E_{\boldsymbol{\alpha}_{12}^{(+-)}}$ and its reciprocal $E_{-\boldsymbol{\alpha}_{12}^{(+-)}}$, both acting on the eigenvalues m_1 and m_2 of the $\{H_1, H_2\}$ pair, the symbol $\boldsymbol{\alpha}_{12}^{(+-)}$ meaning 'raising m_1 and lowering m_2'. The combination $E_{\boldsymbol{\alpha}_{12}^{(+-)}} + E_{-\boldsymbol{\alpha}_{12}^{(+-)}}$ of two reciprocal (Hermitian conjugate) operators is itself Hermitian. The resulting matrix elements $\langle\lambda\boldsymbol{\mu}'_A|\exp(\mathrm{i}\beta\{E_{\boldsymbol{\alpha}_{12}^{(+-)}} + E_{-\boldsymbol{\alpha}_{12}^{(+-)}}\})|\lambda\boldsymbol{\mu}_A\rangle$ amount to Wigner $d^{(j)}_{m',m}$ elements, with parameters specified by the following observations. Projecting $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}'_A$ onto $\boldsymbol{\alpha}_{12}^{(+-)}$ generalizes the lower indices in $d^{(j)}_{m',m}$ to the present higher-dimensional setting:

$$m = \frac{\boldsymbol{\mu}_A \cdot \boldsymbol{\alpha}_{12}^{(+-)}}{\boldsymbol{\alpha}_{12}^{(+-)} \cdot \boldsymbol{\alpha}_{12}^{(+-)}} = \tfrac{1}{2}(m_1 - m_2) \tag{C.7}$$

and similarly $m' = (m'_1 - m'_2)/2$. Section 4.2 discussed in item (e) a succession, or *chain*, of harmonics labelled here by $\boldsymbol{\mu}_A + n\boldsymbol{\alpha}_{12}^{(+-)}$, with total length $2\lambda_s$, restricted, however, by (4.9). The 'multipole order' represented by the upper parameter in $d^{(j)}_{m',m}$ corresponds here to half the length of this chain of harmonics. Finally, the generalization of the 'triangular condition' familiar from three dimensions now requires $|\lambda\boldsymbol{\mu}_A\rangle$ and $|\lambda\boldsymbol{\mu}'_A\rangle$ to lie on the *same* chain of harmonics $|\lambda, \boldsymbol{\mu}_A + n\boldsymbol{\alpha}_{12}^{(+-)}\rangle$. Analogy to the relation $l_x = \frac{1}{2}(l_+ + l_-)$ suggests treating $\exp[\mathrm{i}\beta(E_{\boldsymbol{\alpha}_{12}^{(+-)}} + E_{-\boldsymbol{\alpha}_{12}^{(+-)}})]$ like a rotation about the x-axis in three dimensions. With the standard definition of Euler-angle rotations, the corresponding matrix element picks up an additional phase factor $\exp[\mathrm{i}(m' - m)\pi/2]$ resulting from rotating the y- onto the x-axis and back. Note also that the sum of reciprocal operators in our matrix element lacks the factor $\frac{1}{2}$, thereby effectively multiplying the angle β in the d-symbol's argument by a factor of 2. The procedure, outlined here for a three-particle example, extends similarly to larger aggregates.

Appendix D. Outline of procedures for treating large sets of identical particles

Constructing wavefunctions of a few (three or four) electrons, with the required antisymmetrization, is rather familiar, being extended to atomic shell filling, for example, in chapter 8 of [82]. Its extension to much larger sets remains problematic. Deceptively simple considerations, to be presented below, indicate that this extension may actually proceed along the same lines, essentially because successive steps prove independent of one another. Whether these considerations constitute more than just a 'solution in principle' for this fundamental problem of quantum many-body theory remains to be seen. The inevitable exponential proliferation of operations to be carried out hampers their actual implementation for all but the smallest sets of particles. Significant simplifications occur particularly for a system's ground state configuration owing to (in general) higher symmetry in this state. Even for this case, however, the antisymmetrization of sets with more than three identical particles still presents a formidable task. The most promising approach to this problem's systematic solution *and its implementation* is currently being developed by Barnea and Novoselsky [42], employing the concepts discussed in this topical review, namely, Jacobi coordinates and hyperspherical harmonics.

Coordinates and their symmetrization

Identity of particles implies that permutation of *any* pair of them leaves any function of the pair unchanged. Artificial labelling of such particles, by indices $i = 1, 2, 3, \ldots$, appears nevertheless generally desirable for purposes of 'book-keeping'. It is then necessary to 'symmetrize' any function of particle positions, $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$, to ensure its *invariance under permutation of each pair* of indices (i, j), by superposing sets of such functions differing by the whole set of relevant permutations. Spin and position coordinates should be combined, of course, in this construction that proves increasingly laborious with increasing number of particles.

Classification by seniority

The 'seniority' label ('v') of an atomic state indicates the number of its particle pairs characterized as ^{1}S and thus isolated from its remaining particles. This characterization means invariance under rotation of space coordinates of both spin and position variables. The spin part of this label applies equally regardless of the total number of particles in the system. The 'S' label implies a spherically symmetric matching of the pair's angular distribution, whose extension to multi-dimensional systems needs elaboration. Considering that this symmetry is attained by combining a pair of orbitals even and odd, respectively, under reflection through a plane—thus stretching in orthogonal directions—we suggest achieving the corresponding invariance in higher dimensions by combining pairs of hyperspherical harmonics pertaining to Jacobi trees constructed by selecting orthogonal space directions at each stepwise addition of one particle.

Introduction of 'triple tensors'

This operation, introduced by Judd in the 1960s and described in [82] (pp 209ff), yields a systematic classification of the shell-filling process for the electrons of each atomic shell. It rests on elementary applications of coordinate-rotation transformation pairs and of their 'reduction', which appear as equally serviceable regardless of their dimensionality.

Separation of particle subsets

This operation, familiar in atomic systems and leading there to the 'fractional parentage' procedure, has a major role in multi-particle settings where, typically, electron subsets perform varied functions forming 'closed shells' (or subshells) of different atoms as well as chemical bonds, *preserving the relevant symmetry and coherences*. The structure and flexibility of the Jacobi trees corresponding to alternative hyperspherical harmonics appear well suited to extension to multi-particle settings, with appropriate development of recursion techniques.

References

[1] Macek J H 1967 *Phys. Rev.* **160** 170
[2] Macek J H 1968 *J. Phys. B: At. Mol. Phys.* **1** 831
[3] Fano U 1981 *Phys. Rev.* A **24** 2402
[4] Fano U 1983 *Phys. Rev.* A **27** 1208
[5] Cartan E 1894 Sur la structure des groupes de transformations finis et continus *Thesis* (1952 reprint *Œuvres Complètes* (Paris: Vuibert) part I, vol I, p 127ff)
[6] Racah G 1965 *Group Theory and Spectroscopy* (*Ergebnisse der exacten Naturwissenschaften* vol 37) (Berlin: Springer) p 28
[7] Wybourne B G 1964 *Classical Groups for Physicists* (New York: Wiley)
[8] Cornwell J F 1984 *Group Theory in Physics* vol 2 (San Diego, CA: Academic) ch 13–16
[9] Morse P M and Feshbach H 1953 *Methods of Theoretical Physics* (New York: McGraw Hill) p 1730
[10] Fock V 1958 *Norske Vidensk. Selsk. Forh.* **31** 138
[11] Wannier G H 1953 *Phys. Rev.* **90** 817
[12] See, e.g., Smith F 1960 *Phys. Rev.* **120** 1058
[13] Tsipis C A, Popov V S, Herschbach D R and Avery J S (eds) 1996 *New Methods in Quantum Theory* (Dordrecht: Kluwer)
[14] Delves L M 1959 *Nucl. Phys.* **9** 391
[15] Delves L M 1962 *Nucl. Phys.* **20** 268
[16] Cobis A, Fedorov D V and Jensen A S 1998 *Phys. Lett.* B **424** 1
[17] Kievsky A 1998 *Nucl. Phys.* A **631** 669c
[18] Gorbatov A M and Khazov A Yu 1997 *Phys. At. Nucl.* **60** 1979
[19] Santopinto E, Iachello F and Giannini M M 1998 *Eur. Phys. J.* A **1** 307
[20] Smirnov Yu F and Shitikova K V 1978 *Sov. J. Part. Nucl.* **8** 344
[21] Ballot J L and Fabre de la Ripelle M 1980 *Ann. Phys., NY* **127** 62
[22] Zhukov M V, Danilin B V, Fedorov D V, Bang J M, Thompson I J and Vaagen J S 1993 *Phys. Rep.* **231** 151
[23] Kuppermann A and Kaye J A 1980 *Chem. Phys. Lett.* **74** 257
[24] Kaye J A and Kuppermann A 1981 *Chem. Phys. Lett.* **77** 573
[25] Kaye J A and Kuppermann A 1981 *Chem. Phys. Lett.* **78** 546
[26] Pack R T and Parker G A 1987 *J. Chem. Phys.* **87** 3888
[27] Linderberg J, Padkjær S B, Öhrn Y and Vessal B 1989 *J. Chem. Phys.* **90** 6254
[28] Launay J M and Le Dourneuf M 1989 *Chem. Phys. Lett.* **163** 178
[29] Launay J M and Le Dourneuf M 1990 *Chem. Phys. Lett.* **169** 473
[30] Lepetit B and Launay J M 1991 *J. Chem. Phys.* **95** 5159
[31] Honvault P and Launay J M 1998 *Chem. Phys. Lett.* **287** 270
[32] Groenenboom G C 1998 *J. Chem. Phys.* **108** 5677
[33] Yu H G 1997 *Chem. Phys. Lett.* **281** 312
[34] Wu Y M, Lepetit B and Kuppermann A 1991 *Chem. Phys. Lett.* **186** 319
[35] Adhikari S and Billing G D 1998 *Chem. Phys. Lett.* **284** 31
[36] See, e.g., Aquilanti V, Bonnet L and Cavalli S 1996 *Mol. Phys.* **89** 1
[37] Aquilanti V and Avery J 1997 *Chem. Phys. Lett.* **267** 1
[38] Aquilanti V, Cavalli S, Coletti C, De Fazio D and Grossi G 1996 *New Methods in Quantum Theory* ed C A Tsipis *et al* (Dordrecht: Kluwer)
[39] Aquilanti V, Cavalli S and Coletti C 1998 *Phys. Rev. Lett.* **80** 3209
[40] Novoselsky A, Katriel J and Gilmore R 1988 *J. Math. Phys.* **29** 1368
[41] Novoselsky A and Katriel J 1994 *Phys. Rev.* A **49** 833
[42] Barnea N and Novoselsky A 1998 *Phys. Rev.* A **57** 48

[43] Ovcharenko V I 1976 *Sov. J. Nucl. Phys.* **24** 483
[44] Lin C D 1981 *Phys. Rev.* A **23** 1585
[45] Lin C D 1982 *Phys. Rev.* A **25** 1535
[46] Lin C D 1984 *Phys. Rev.* A **29** 1019
[47] Chen Z and Lin C D 1990 *Phys. Rev.* A **42** 18
[48] Lin C D 1982 *Phys. Rev.* A **25** 76
[49] Lin C D 1982 *Phys. Rev.* A **26** 2305
[50] Lin C D 1983 *Phys. Rev.* A **27** 22
[51] Lin C D and Macek J H 1984 *Phys. Rev.* A **29** 2317
[52] Feagin J M and Briggs J S 1988 *Phys. Rev.* A **37** 4599
[53] Watanabe S and Lin C D 1986 *Phys. Rev.* A **34** 823
[54] Tolstikhin O I, Watanabe S and Matsuzawa M 1995 *Phys. Rev. Lett.* **74** 3573
[55] Christensen-Dalsgaard B L 1984 *Phys. Rev.* A **29** 2242
[56] Tang J, Watanabe S and Matsuzawa M 1992 *Phys. Rev.* A **46** 2437
[57] Sadeghpour H R and Greene C H *Phys. Rev. Lett.* **65** 313
[58] Sadeghpour H R *Phys. Rev.* A **43** 5821
[59] Qiu Y, Tang J-Z, Burdörfer J and Wang J 1998 *Phys. Rev.* A **57** R1489
[60] Greene C H 1981 *Phys. Rev.* A **23** 661
[61] Watanabe S 1982 *Phys. Rev.* A **25** 2074
[62] Clark C W and Greene C H 1980 *Phys. Rev.* A **21** 1786
[63] Bao C G, Yang X and Lin C D 1996 *Phys. Rev. Lett.* **76** 3096
[64] Yang X, Bao C G and Lin C D 1996 *Phys. Rev.* A **53** 3934
[65] Morishita T, Lin C D and Bao C G 1998 *Phys. Rev. Lett.* **80** 464
[66] Morishita T and Lin C D 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L209
[67] Cavagnero M 1984 *Phys. Rev.* A **30** 1169
[68] Cavagnero M 1986 *Phys. Rev.* A **33** 2877
[69] Cavagnero M 1987 *Phys. Rev.* A **36** 523
[70] Braun M, Schweizer W and Elster H 1998 *Phys. Rev.* A **57** 3739
[71] Braun M, Schweizer W and Elster H 1998 *Nucl. Phys.* A **631** 644c
[72] Aquilanti V and Avery J 1997 *Chem. Phys. Lett.* **267** 1
[73] Fano U 1983 *Rep. Prog. Phys.* **46** 97
[74] Lin C D 1986 *Adv. At. Mol. Phys.* **22** 77
[75] Lin C D 1995 *Phys. Rep.* **257** 1
[76] Chattopadhyay R and Das T K 1997 *Phys. Rev.* A **56** 1281
[77] Fano U and Sidky E 1992 *Phys. Rev.* A **47** 4776
[78] Bohn J L 1994 *Phys. Rev.* A **49** 3761
[79] Bohn J L and Fano U 1996 *Phys. Rev.* A **53** 4014
[80] Avery J 1989 *Hyperspherical Harmonics* (Dordrecht: Kluver)
[81] Erdélyi A, Magnus W, Oberhettinger F and Tricomi F G 1953 *Higher Transcendental Functions* vol II (New York: McGraw-Hill) ch 11, p 232ff
[82] Fano U and Rau A R P 1996 *Symmetries in Quantum Physics* (San Diego, CA: Academic)
[83] Abramowitz M and Stegun I A 1965 *Handbook of Mathematical Functions* (New York: Dover) (1972 9th printing) ch 22
[84] Heim T A and Green D 1999 *J. Math. Phys.* at press
[85] Cowan R D 1981 *Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press) ch 9
[86] Calogero F 1967 *Variable Phase Approach to Potential Scattering* (New York: Academic) ch 19
[87] Newton R G 1966 *Scattering Theory of Waves and Particles* (New York: McGraw Hill)
[88] Landau L D 1932 *Phys. Zts. Sowjet.* **2** 46
[89] Zener C 1932 *Proc. R. Soc.* A **137** 696
[90] Stückelberg E C G 1932 *Helv. Phys. Acta* **5** 369
[91] Zhu C and Nakamura H 1992 *J. Math. Phys.* **33** 2697
[92] Zhu C and Nakamura H 1995 *J. Chem. Phys.* **102** 7448