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Quantum dynamics of kinematic invariants in tetra- and polyatomic systems

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Received 2nd December 1998, Accepted 8th February 1999

For the dynamical treatment of polyatomic molecules or clusters as n-body systems, coordinates are conveniently broken up into external (or spatial) rotations, kinematic invariants, and internal (or kinematic) rotations. The kinematic invariants are related to the three principal moments of inertia of the system. At a fixed value of the hyperradius (a measure of the total moment of inertia), the space of kinematic invariants is a certain spherical triangle, depending on the number of bodies, upon which angular coordinates can be imposed. It is shown that this triangle provides the 24-element (group O) octahedral tesselation of the sphere for $n = 4$ and the 48-element (group O_h) octahedral tesselation for $n \geqslant 5$. Eigenfunctions describing the kinematics of systems with vanishing internal and external angular momentum can be obtained in closed form in terms of Bessel functions of the hyperradius and surface spherical harmonics. They can be useful as orthonormal expansion basis sets for the hyperspherical treatment of the n-body particle dynamics.

I Introduction

A description of the internal dynamics of a four-atom system requires six coordinates, which are conveniently broken up into three quantities which are invariant under kinematic rotations (kinematic invariants) and three Euler angles specifying the kinematic rotation. In addition, the three usual (external) Euler angles are needed to specify the orientation of the system. Kinematic invariants include the three moments of inertia or any functions of them. Four-particle Hamiltonians have been written in terms of such coordinates since the time of Zickendraht,[1–6] and recently we have contributed to the subject by clarifying the ranges of the internal coordinates and by introducing convenient hyperspherical angles in the space of kinematic invariants.[7] In addition, we have recently provided a thorough analysis of body frames and their singularities in four-particle systems.[8]

Similarly, for systems of more than four atoms, the internal coordinates can be broken up into kinematic invariants and kinematic angles.[9–12] The kinematic invariants are the same as in the case of four atoms, with a reduction in the range of the variables when $n \geqslant 5$, while the kinematic angles grow in number to accommodate the $3n - 6$ dimensions of the internal space.

The organization of this paper is also follows. Section II deals with the case of four-atom systems, and contains the most detailed analysis of the paper. In this section we study the Schrödinger equation on the space of kinematic invariants for $n = 4$, we show that at fixed hyperradius this space is a highly symmetric, right spherical triangle, and we provide analytic expressions for the eigenvalues of the surface functions in the case $V = 0$, as well as for the low lying eigenfunctions. In Section III we discuss the most important changes which occur in the case $n \geqslant 5$. Finally, in Section IV we provide some conclusions and comments regarding future work.

II Four-atom systems

In this paper we adopt a model of the internal dynamics of four-atom systems which decouples the kinematic rotations and which works only with the kinematic invariants. In nuclear physics, this assumption is often made in the collective model.[1] This is a reasonable model for certain symmetry conserving processes, such as the ammonia inversion, where the prolate top configuration is approximately preserved as the system evolves along paths along which only the kinematic invariants change. Moreover, the model is a useful test case for more elaborate calculations in which other degrees of freedom are taken into account. We ignore the kinematic rotations by assuming that the wavefunction is an eigenstate of zero kinematic angular momentum (the internal angular momentum-like operator which generates kinematic rotations). Similarly, for simplicity, we assume that the wavefunction is an eigenfunction of (ordinary, external) angular momentum with $J = 0$. Under these circumstances, the wavefunction is independent of both the usual (or external) Euler angles and the kinematic (or internal) Euler angles, and depends only on the three kinematic invariants.

We choose our kinematic invariants in the following way. We let the three Jacobi vectors be $\{\boldsymbol{r}_\alpha\}$, $\alpha = 1, 2, 3$ which we arrange column-wise to form a 3×3 matrix $\boldsymbol{F}$. The singular value decomposition of $\boldsymbol{F}$ is $\boldsymbol{F} = \boldsymbol{RXK}^t$ where $\boldsymbol{R}$ is an $SO(3)$ rotation matrix specifying the usual (external) Euler angles in a principal axis frame, where $\boldsymbol{K}$ is another $SO(3)$ matrix specifying the kinematic rotation, and where $\boldsymbol{X}$ is the diagonal matrix of singular values, $\boldsymbol{X} = \mathrm{diag}\,(x_1, x_2, x_3)$. The singular values (x_1, x_2, x_3) are the kinematic invariants we use as coordinates. The moments of inertia of a four-atom system are given in terms of the x's by $I_1 = x_2^2 + x_3^2$, $I_2 = x_1^2 + x_3^2$, $I_3 = x_1^2 + x_2^2$ and the hyperradius by $\rho^2 = x_1^2 + x_2^2 + x_3^3$, and the signed volume of the tetrahedron spanned by the four particles is proportional to $V = x_1 x_2 x_3$. To achieve a one-to-one representation of configurations of the four-atom system, the internal Euler angles must be restricted to a certain subset of their usual ranges, a region we call the "kinetic cube". In addition, the kinematic invariants are restricted to the region $0 \leqslant |x_1| \leqslant x_2 \leqslant x_3$ of (x_1, x_2, x_3)-space. The chirality (and the sign of the volume) is determined by the sign of x_1, which can be positive or negative, but x_2 and x_3 are strictly non-negative. These constructions are explained in further detail in refs. 5–8 and 13.

An appealing feature of these coordinates is that the metric tensor on the space (x_1, x_2, x_3) of kinematic invariants is Euclidean.[1] Moreover, if the wavefunction is scaled to absorb the Jacobian volume element, then there are no first order derivatives in the expression for the kinetic energy. Specifically, if we denote the external (Cartesian) wavefunction by $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, and if we define the internal wavefunction by $\Phi(x_1, x_2, x_3) = \sqrt{D}\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, where D is the volume element $D = (x_2^2 - x_1^2)(x_3^2 - x_1^2)(x_3^2 - x_2^2)$, then the internal Schrödinger equation is

$$-\frac{\hbar^2}{2M}\nabla^2\Phi + V_2\Phi + V\Phi = E\Phi \quad (1)$$

where ∇^2 is the usual Euclidean Laplacian operator in the coordinates (x_1, x_2, x_3), where V is the potential and where V_2 is an "extra potential" term arising from commutators in the evaluation of the kinetic energy. This latter term is given by

$$V_2 = \frac{\hbar^2}{2M}\frac{1}{\sqrt{D}}\nabla^2\sqrt{D} \quad (2)$$

which is equivalent to

$$V_2 = -\frac{\hbar^2}{2M}\left[\frac{x_1^2 + x_2^2}{(x_2^2 - x_1^2)^2} + \frac{x_2^2 + x_3^2}{(x_3^2 - x_2^2)^2} + \frac{x_3^2 + x_1^2}{(x_3^2 - x_1^2)^2}\right] \quad (3)$$

The mass M in eqns. (1)–(3) is the total mass of the four-atom system. The normalization of the internal wavefunction Φ is simply $\langle\Phi|\Phi\rangle = \int dx_1\, dx_2\, dx_3 |\Phi|^2$. The general question of extra potential terms and their relation to the normalization convention for the wavefunction has been explored by Chapuisat, Belafhal and Nauts.[14]

In the hyperspherical approach to scattering calculations, it is necessary to determine the "surface functions", which are the eigenfunctions of the angular part of the Hamiltonian on the hypersphere in the internal space. In the present case, we will be interested in the surface functions on the two-dimensional sphere ρ = constant in (x_1, x_2, x_3)-space. The surface functions obviously depend on the potential V, but the case $V = 0$ is useful as a test case and for developing an expansion basis to use in the case $V \neq 0$. The surface functions when $V = 0$ are special cases of hyperspherical harmonics for the four-body problem in a symmetric representation. Hyperspherical harmonics form the basis of an attractive and efficient method for three-atom scattering calculations,[15,16] which we are interested in generalizing to the case of four atoms. Therefore we henceforth set $V = 0$ and study the equation

$$-\frac{\hbar^2}{2M}\nabla^2\Phi + V_2\Phi = E\Phi \quad (4)$$

Only a part of the sphere ρ = constant is physically realizable, due to the restriction $0 \leqslant |x_1| \leqslant x_2 \leqslant x_3$. The physically allowed region is illustrated in Fig. 1, in which the first octant of a sphere is cut by the two planes $x_1 = x_2$ and $x_2 = x_3$ to produce the spherical triangle SCB, with one corner at the "north pole" C. This triangle is one half of the physical region, containing shapes of positive chirality; a similar triangle of shapes of negative chirality lies behind the plane $x_1 = 0$. Taken together, these two triangles form a single spherical triangle constituting the physical region, illustrated in Fig. 2.

The physical region is bounded by arcs of three great circles. The arc SC is the line $x_1 = x_2$, which contains the prolate symmetric tops ($I_1 = I_2 > I_3$) of positive chirality. The arc S′C is the line $-x_1 = x_2$, containing the prolate symmetric tops of negative chirality. The arc SBS′ is the line $x_2 = x_3$, which contains the oblate symmetric tops ($I_2 = I_3 < I_1$). The arc CB is the line $x_1 = 0$ which divides the triangle into two equal triangles of opposite chirality, and which contains

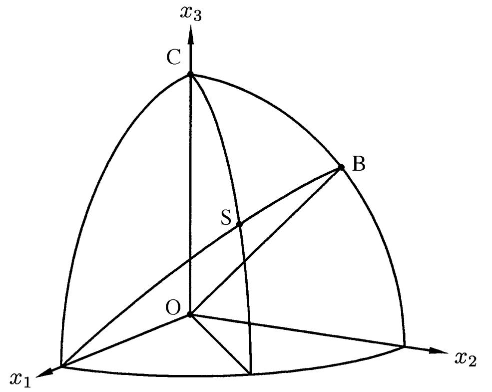

Fig. 1 The hypersphere ρ = constant is cut by the two planes $x_1 = x_2$ and $x_2 = x_3$ in (x_1, x_2, x_3)-space. The spherical triangle SCB is one half of the physical region on the hypersphere for the four-body problem, and the whole of the physical region for $n \geqslant 5$.

the planar shapes of zero volume. Points S and S′ are spherical tops of positive and negative chirality, respectively. Finally, the point C is the collinear shape.

Shapes of opposite chirality are mapped into one another by the parity operator. In the present case of vanishing external angular momentum ($J = 0$), the parity operator acts on the wavefunction by mapping (x_1, x_2, x_3) into $(-x_1, x_2, x_3)$, with no extra phase or rotation (which might be necessary in the case $J \neq 0$). Therefore states of even (odd) parity are even (odd) about the plane $x_1 = 0$.

Both the whole triangle SCS′ and triangle SCB of positive chirality are right spherical triangles with the rational angles (rational multiples of π) shown. The arc CB is $\pi/4$, the arc SB is $\cos^{-1}\sqrt{2/3}$ and the arc SC is $\cos^{-1}\sqrt{1/3}$, the latter being one half of the famous opening angle of 109.5° of the tetrahedral bond. The physical region is highly symmetrical on the sphere, being in fact one of 24 equivalent regions under a tesselation of the sphere by the 24-element octahedral group O.

Tesselations of the sphere are discussed by Magnus,[17] who calls the tesselation by 24 triangle with angles $\pi/2$, $\pi/3$ and $\pi/3$, such as our triangle SCS′, the "tetrahedral" tesselation (see Fig. 3). This name is given because the same tesselation as we produce in this paper by the action of the group O can also be produced by the group T_d. A different tesselation of the sphere is produced by the group O_h, this time with 48 triangles with angles $\pi/2$, $\pi/3$ and $\pi/4$ such as our triangle SCB. Magnus calls this the "octahedral" tesselation; it is illustrated in Fig. 4. The triangles SCS′ and SCB are examples of Moebius triangles.

The octahedral group O is the symmetry group of proper rotations of a certain cube inscribed in the sphere. The cube (not shown in the figures) is centered at the origin, with the

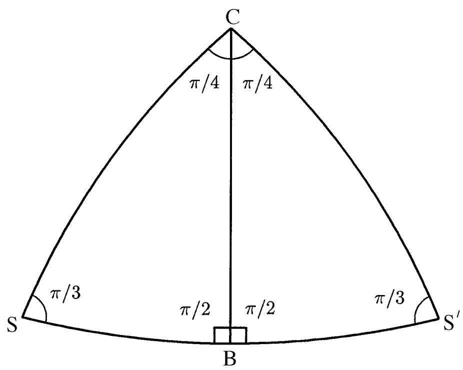

Fig. 2 The spherical triangle SCS′, the physical region for $n = 4$, is divided into two halves of opposite chirality.

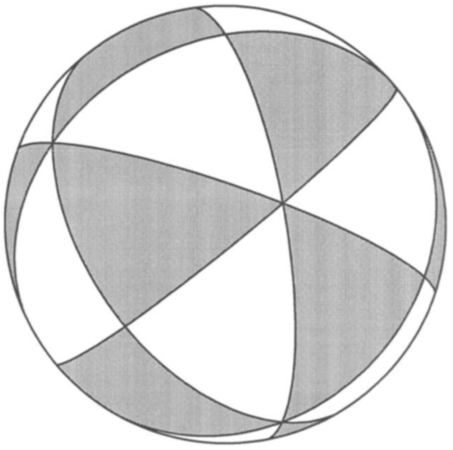

Fig. 3 The tesselation of the sphere by Moebius triangles of angles π/2, π/3 and π/3, such as the physical region SCS′ for $n = 4$. The replication of triangles is generated by either of the groups O or T_d.

three axes passing perpendicular to its six faces, and with one vertex at the point S in Fig. 1 (a second vertex is at S′). The cube is also invariant under inversion through the origin in (x_1, x_2, x_3) space; when combined with the proper rotations, the inversion produces the 48-element group O_h. One of the elements of O_h is a reflection in the plane $x_1 = 0$ (or the line CB), which is otherwise the parity operation (mapping shapes of opposite chirality into one another). When the physical region and the potential V_2 defined on it are replicated under the action of the group O, the result is a potential on the sphere with the symmetry group O_h. Therefore the surface eigenfunctions, or the eigenfunctions of the complete three-dimensional Hamiltonian, eqn. (1), in (x_1, x_2, x_3)-space can be classified by the irreducible representations (irreps) of O_h.

However, not all the irreps of O_h occur, due to the boundary conditions which the wave function much satisfy at the edge of the physical region. These boundary conditions can be determined in the following manner. We imagine a wavefunction with total internal (kinematic) and total external (ordinary) angular momentum set to zero. A point moves in the nine-dimensional configuration space on which the three Jacobi vectors are coordinates, and samples the values of the external wavefunction Ψ. Suppose the point passes through a prolate symmetric top of positive chirality. Then the equivalent point in the internal space bounces off the plane $x_1 = x_2$, or the line SC on the triangle in Fig. 2. One can concoct this motion so that the point on the internal space approaches and bounces perpendicularly off the wall $x_1 = x_2$. Very near but on opposite sides of the prolate symmetric top configuration, the singular values x_1 and x_2 have simply exchanged places. The shape has changed on crossing the prolate symmetric top (it is not symmetrical on the two sides), but since the shapes on opposite sides are related by a kinematic rotation and since Ψ is invariant under kinematic rotation, Ψ itself is even about the prolate symmetric top shape. This means that viewed as a function on the physical triangle, Ψ has vanishing normal derivative at the edges of the triangle (the value of Ψ at the edge is generally non-zero). This argument only applies to wavefunctions of vanishing total kinematic angular momentum.

The boundary conditions satisfied by the internal wavefunction Φ are different, because of the factor $\sqrt{D}$ which connects Φ with Ψ. If we set $x_2 = x_1 + \varepsilon$ and let $\varepsilon \to 0$, we see that D and hence Φ go to 0 as $\sqrt{\varepsilon}$ as we approach the boundary. Therefore the wavefunction Φ goes to zero at the edge of the triangle, but in a manner which is not analytic. In fact, Φ is rather singular at the edges; its first and all higher derivatives are infinite there. This singularity is obviously necessary to accommodate the singularities in V_2 seen in eqn. (3), which diverges as $-1/\varepsilon^2$ as the edge is approached.

The fact that wavefunctions may acquire singularities at the edges of their regions of definition, depending on normalization conventions, is well known. See, for example, Chapuisat *et al.*,[18] who examine singularities of wavefunctions for four-body problems in certain coordinate systems.

If a wavefunction Ψ which satisfies the Schrödinger equation and the boundary conditions is replicated around the sphere under the action of the octahedral group O, then the only irreps of O_h which are consistent with the boundary conditions are A_1 and A_2' (the latter being the A_2 irrep of O combined with the inversion). The A_1 irrep contains wavefunctions which are even under parity (reflection in the plane $x_1 = 0$), and the A_2' irrep those which are odd. A wavefunction Ψ extended in this way around the sphere is the natural analytic continuation of the wavefunction in the physical region. Similar statements can be made about the internal wavefunction Φ, but are more awkward because of the square root singularity in the factor $\sqrt{D}$ (if one replaces $\sqrt{D}$ by $\sqrt{|D|}$, then the same irrep labels and parity rules apply to Φ, but of course not the analytic continuation).

We turn now to solving the Schrödinger equation. First let us separate the dependence on the hyperradius from the Jacobian factor and the potential V_2, writing $\sqrt{D} = \rho^3 f(\Omega)$, where Ω represents any two coordinates on the sphere, and $V_2(x_1, x_2, x_3) = (\hbar^2/2M)(1/\rho^2)U_2(\Omega)$. Thus, in ordinary spherical coordinates (θ, ϕ) in (x_1, x_2, x_3)-space, we have

$$f(\Omega) = [(\sin^2\theta \cos 2\phi)(\cos^2\theta - \sin^2\theta\cos^2\phi) \times (\cos^2\theta - \sin^2\theta \sin^2\phi)]^{1/2} \quad (5)$$

and

$$U_2(\Omega) = -\left[\frac{1}{\sin^2\theta\cos^2 2\phi} + \frac{\cos^2\theta + \sin^2\theta\sin^2\phi}{(\cos^2\theta - \sin^2\theta\sin^2\phi)^2} + \frac{\cos^2\theta + \sin^2\theta\cos^2\phi}{(\cos^2\theta - \sin^2\theta\cos^2\phi)^2}\right] \quad (6)$$

Let us also write $\Phi(x_1, x_2, x_3) = R(\rho)Z(\Omega)$ to separate the Schrödinger equation (4). The hyperradial part of the Schrödinger equation becomes

$$-\frac{\hbar^2}{2M}\frac{1}{p^2}\frac{\mathrm{d}}{\mathrm{d}\rho}\left(\rho^2\frac{\mathrm{d}R}{\mathrm{d}\rho}\right) + \frac{\hbar^2\mu}{2M\rho^2}R(\rho) = ER(\rho) \quad (7)$$

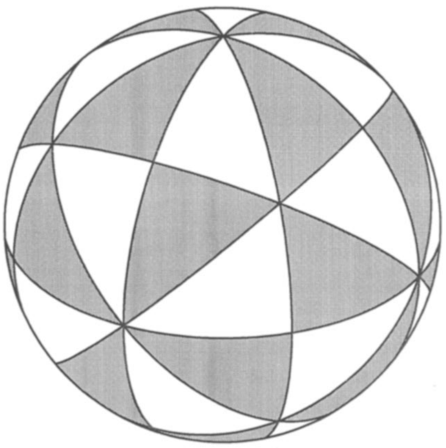

Fig. 4 The tesselation of the sphere by Moebius triangles of angles π/2, π/3 and π/4, such as the physical region SCB for $n \geqslant 5$. The replication is generated by the group O_h.

and the hyperangular part is

$$-\nabla_{\Omega}^2 Z(\Omega) + U_2(\Omega)Z(\Omega) = \mu Z(\Omega) \tag{8}$$

where $Z(\Omega)$ is the surface function and μ the surface eigenvalue. The eigenfunction $Z(\Omega)$ inherits its boundary conditions from $\Phi(x_1, x_2, x_3)$, and in particular, it goes to 0 at the boundaries as $\sqrt{\varepsilon}$. In eqn. (8) ∇_{Ω}^2 is the angular part of the Laplacian; for example in ordinary spherical coordinates, it is the usual operator,

$$\nabla_{\Omega}^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{9}$$

Actually, we will need to worry about explicit coordinates on the sphere, a fortunate circumstance since the ranges of the angles are awkward.

An apparently obvious approach to solving the surface equation (8) is to expand the unknown surface function $Z(\Omega)$ in the eigenfunctions of ∇_{Ω}^2, which otherwise are the Y_{lm}'s. The Y_{lm}'s must be symmetrized to satisfy the boundary conditions, but this can be done. Unfortunately, this expansion converges very slowly, because of the square root singularities in $Z(\Omega)$ at the boundaries. The well behaved Y_{lm}'s are suitable for expanding other well behaved functions. To overcome this problem, one could expand in other basis functions which have the correct $\sqrt{\varepsilon}$ behavior at the boundaries. Unfortunately, another problem then arises, since the matrix elements of the potential $U_2(\Omega)$ turn out to be infinite. For if we assume that $Z(\Omega) \sim \sqrt{\varepsilon}$ and use the behavior $U_2(\Omega) \sim 1/\varepsilon^2$ near the boundary, then a typical matrix element will have the behavior,

$$\int d\Omega Z(\Omega)^* U_2(\Omega)Z(\Omega) \sim \int d\varepsilon \sqrt{\varepsilon}\frac{1}{\varepsilon^2}\sqrt{\varepsilon} \sim \int \frac{d\varepsilon}{\varepsilon} = \infty \tag{10}$$

where the (logarithmic) divergence comes from the small region near the boundary. But how is it possible that the potential of a well behaved problem (we are setting $V = 0$, so the system consists of free particles) can have infinite matrix elements? The answer is that $U_2(\Omega)$, or equivalently, V_2, is not a real potential, but actually part of the kinetic energy. Indeed, if we compute the matrix elements of ∇_{Ω}^2 with respect to a wavefunction with the correct $\sqrt{\varepsilon}$ behavior at the boundary, we find that it too diverges logarithmically. Explicitly, we have

$$\int d\Omega Z(\Omega)^* \nabla_{\Omega}^2 Z(\Omega) \sim \int d\varepsilon \sqrt{\varepsilon}\frac{d^2}{d\varepsilon^2}\sqrt{\varepsilon} \sim \int \frac{d\varepsilon}{\varepsilon} = \infty \tag{11}$$

where it is the component of the Laplacian orthogonal to the boundary which causes the infinity. Thus, both the Laplacian and the "potential" $U_2(\Omega)$ give rise to infinite matrix elements with wavefunctions with the right boundary conditions. A more careful analysis shows, however, that the sum of the matrix elements of the Laplacian and $U_2(\Omega)$ is always finite and well behaved, as one would expect.

Alternatively, if one were to attempt a direct numerical evaluation of the surface eigenfunctions in the Φ or $Z(\Omega)$ form, with or without a true potential V, the singularities in Φ and $U_2(\Omega)$ would cause serious problems. The singularities would have a negative impact on the convergence of most common quadrature or basis expansion methods, including DVR methods, unless great care were taken.

The lessons we learn in this way are clearly also relevant to the case $V \neq 0$, and they suggest that the apparently simple form, eqn. (1), of the internal Schrödinger equation is misleading. Instead, there are advantages to working with the external wavefunction Ψ, which has no singularities and which satisfies a version of the Schrödinger equation without the V_2 term (although with first derivatives). This is

$$-\frac{\hbar^2}{2M}(\nabla^2 + 2\boldsymbol{K}\cdot\nabla)\Psi = E\Psi \tag{12}$$

where we have set $V = 0$ and where $\boldsymbol{K}$ is the vector in (x_1, x_2, x_3)-space given by

$$\boldsymbol{K} = \frac{1}{\sqrt{D}}\nabla\sqrt{D} \tag{13}$$

The norm of the external wavefunction is $\langle\Psi|\Psi\rangle = \int dx_1 dx_2 dx_3 D|\Psi|^2$ (including the Jacobian factor D). Eqn. (12) can also be separated into an angular and a hyperradial part, although we will not need to do this since it turns out that the solutions can be obtained analytically. The three-dimensional form, eqn. (12), is more convenient for this purpose. The problem of changing the normalization of the wavefunction and its relation to the form of the Schrödinger equation has been studied in a more general setting by Nauts and Chapuisat.[19]

We begin by finding the eigenvalues μ of the surface equation (8). We do this by noting that separation of variables on the original nine-dimensional Laplacian in the Jacobi coordinates $(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$ leads to solutions of the form

$$\Psi = \frac{1}{\rho^3} j_{\lambda+3}(k\rho)X_{\lambda}(\Omega) \tag{14}$$

where $\lambda = 0, 1, 2, \ldots$ is the quantum number of the grand angular momentum operator, where k is defined by $E = \hbar^2k^2/2M$, where $j_{\lambda+3}$ is a spherical Bessel function, and where $X_{\lambda}(\Omega)$ is a harmonic on the eight-dimensional sphere. In the present case, however, we are interested in wavefunctions which are invariant under both external and internal (or kinematic) rotations, so $X_{\lambda}(\Omega)$ becomes a function only on the two-dimensional sphere in (x_1, x_2, x_3)-space. The point for now is that the hyperradial part of the wavefunction is known. If we now write $\Phi = \sqrt{D}\Psi = \rho^3 f(\Omega)\Psi = R(\rho)Z(\Omega)$, then we have $R(\rho) = j_{\lambda+3}(k\rho)$ and $Z(\Omega) = f(\Omega)X_{\lambda}(\Omega)$. Then, substituting this form of $R(\rho)$ into eqn. (7) and using the standard differential equation satisfied by the Bessel functions, we find

$$\mu = (\lambda + 3)(\lambda + 4) \tag{15}$$

All surface eigenvalues have this form for some choice of the eigenvalue λ of the grand angular momentum, taken from the range $\lambda = 0, 1, 2, \ldots$. However, we note that not all eigenvalues of the grand angular momentum operator occur in the class of wavefunctions we are considering (those with vanishing external and internal angular momentum), and, as we will see, some occur more than once. Thus we have extra work to do to determine the allowed values of λ and their multiplicities.

For later purposes it will be useful to note the zero energy limit of the radial wavefunctions, eqn. (14). If we take $k \to 0$, we can replace $R(\rho)$ by the limiting value,

$$\lim_{k\to 0}\frac{R(\rho)}{k^{\lambda+3}} = \lim_{k\to 0}\frac{1}{\rho^3}\frac{j_{\lambda+3}(k\rho)}{k^{\lambda+3}} = (\text{constant})\rho^{\lambda} \tag{16}$$

On the other hand, the harmonics $X_{\lambda}(\Omega)$ are homogeneous polynomials in the components of the unit vector on the eight-dimensional hypersphere, so when they are multiplied by ρ^{λ}, they become homogeneous polynomials of degree λ in the nine Cartesian components of the three Jacobi vectors.

Thus, to find the surface harmonics, we can seek solutions of eqn. (12) with $E = 0$ which are homogeneous polynomials of degree λ in the Cartesian components of the Jacobi vectors. We can then just split off a factor of ρ^{λ}, and we will have the surface harmonics. However, the polynomials should be invariant under both external and internal rotations. The polynomials which are invariant under external rotations are functions only of the Jacobi dot products $\boldsymbol{r}_{\alpha}\cdot\boldsymbol{r}_{\beta}$ and the (one) Jacobi triple product $\boldsymbol{r}_1\cdot(\boldsymbol{r}_2\times\boldsymbol{r}_3)$, of which the dot products

Table 1 Eigenvalues λ of the grand angular momentum and $\mu = (\lambda + 3)(\lambda + 4)$ of the surface harmonics, in both symmetry classes A_1 (even) and A'_2 (odd)

	(A_1)		(A'_2)	
n	λ	μ	λ	μ
1	0	12	3	42
2	4	56	7	110
3	6	90	9	156
4	8	132	11	210
5	10	182	13	272
6	12	240	15	342
7	12	240	15	342
8	14	306	17	420
9	16	380	19	506
10	16	380	19	506
11	18	462	21	600
12	18	462	21	600
13	20	552	23	702
14	20	552	23	702
15	22	650	25	812
16	22	650	25	812
17	24	756	27	930
18	24	756	27	930
19	24	756	27	930
20	26	870	29	1056

are even under parity and the triple product odd. The triple product is otherwise the same as the volume $V = x_1 x_2 x_3$, and is automatically a kinematic invariant. On the other hand, the polynomials in the Jacobi dot products which are kinematic invariants are also polynomials in the squares of the singular values (x_1, x_2, x_3), which are the eigenvalues of the matrix of Jacobi dot products. Therefore the most general polynomials in the components of the nine Jacobi vectors which are invariant under both external and kinematic rotations are polynomials in the squares of the singular values, optionally multiplied by $V = x_1 x_2 x_3$. Thus, we seek solutions of eqn. (12) with $E = 0$ which are homogeneous polynomials of degree λ in the three kinematic invariants (x_1, x_2, x_3).

These polynomials must belong to the A_1 or A'_2 symmetry classes of the group O_h to satisfy the correct boundary conditions. The ground state $\lambda = 0$ can be obtained by inspection; here the solution is simply $\Psi = 1$, which belongs to the A_1 symmetry class (it has even parity). This is otherwise a plane wave back in the nine-dimensional (Cartesian) configuration space with $E = 0$. The corresponding surface eigenfunction is $Z(\Omega) = f(\Omega)$, and the surface eigenvalue is $\mu = 3 \times 4 = 12$.

One way to find the eigenfunctions in a systematic manner is to start with some set of hyperspherical harmonics with external angular momentum set of zero, and then to average these over the group of kinematic rotations. This projects out states of vanishing kinematic angular momentum. Since external and kinematic rotations commute, the resulting state is still a state of vanishing external angular momentum. This is a purely algebraic process, that is, there are no matrices to be diagonalized or roots of polynomials which must be determined. However, one should think carefully before beginning in order to shortcut the algebra. This approach is educational, for it shows how one might construct hyperspherical harmonics in a symmetric representation (a representation which transforms covariantly under kinematic rotations) for the four-body problem.

Table 2 Eigenfunctions Ψ for different values of λ

λ	$\Psi_\lambda(x_1, x_2, x_3)$
0	1
3	$x_1 x_2 x_3$
4	$2(x_1^4 + x_2^4 + x_3^4) - 7(x_1^2 x_2^2 + x_1^2 x_3^2 + x_2^2 x_3^2)$
6	$4(x_1^6 + x_2^6 + x_3^6) - 27(x_1^2 x_2^4 + x_1^4 x_2^2 + x_1^2 x_3^4 + x_1^4 x_3^2 + x_2^2 x_3^4 + x_2^4 x_3^2) + 570 x_1^2 x_2^2 x_3^2$
7	$x_1 x_2 x_3 [4(x_1^4 + x_2^4 + x_3^4) - 9(x_1^2 x_2^2 + x_1^2 x_3^2 + x_2^2 x_3^2)]$

A more direct route is to expand the angular part of the unknown polynomial Ψ in ordinary Y_{lm}'s. An eigenfunction Ψ with quantum number λ is a homogeneous polynomial in (x_1, x_2, x_3) of degree λ, and therefore its angular part can contain only Y_{lm}'s with $l \leqslant \lambda$. The Y_{lm}'s must of course be symmetrized under the group O_h to contain the correct irrep (A_1 if λ is even, A'_2 if λ is odd, since only an odd polynomial can be odd under $x_1 \to -x_1$). An example will illustrate the process. If we project out the A_1 class of wavefunctions from the Y_{lm}'s for $l = 0, 2, 4$, we find one function each for $l = 0$ and $l = 4$, and none for $l = 2$. The projection process involves summing over the octahedral group. Call these projected functions simply Y_0 and Y_4 (in fact, $Y_0 = 1$). Then a fourth order polynomial in (x_1, x_2, x_3) with A_1 symmetry is necessarily a linear combination of $\rho^4 Y_4$ and $\rho^4 Y_0$. Substituting such a linear combination into the wave equation (12) leads to linear equations for the coefficients which can be solved to find the eigenfunction. In this process, it is never actually necessary to work with the Y_{lm}'s in angular form; instead, one can work with the Euclidean coordinates (x_1, x_2, x_3) throughout. This process shows that the number of solutions of a given value of λ is the same as the number of Y_{lm}'s of the given symmetry class for $l = \lambda$. We note that this procedure effectively makes use of a non-orthonormal basis, since the Y_{lm}'s are not orthonormal when the Jacobian factor D is included in the normalization integral.

The number of eigenfunctions for given λ can be determined from a simple Clebsch–Gordan series for the group O, without the necessity of projecting wavefunctions. We can work with O instead of O_h because the parity is determined by λ. The method proceeds as follows. The group O has five irreps, A_1, A_2, E, T_1 and T_2. First, we note that the constant 1 and the monomials (x_1, x_2, x_3), which respectively span the same spaces as the Y_{lm}'s for $l = 0$ and $l = 1$, transform respectively according to the irreps A_1 and T_1 (the latter of which is three-dimensional) of O. Forming products of the $l = 1$ states with themselves we get $l = 0, 1, 2$; and forming products of T_1 states with themselves, we get the A_1, E, T_1 and T_2 irreps. Then subtracting A_1 and T_1 from the list to account for $l = 0$ and $l = 1$, we find that the $l = 2$ states contain the irreps E and T_2. Since an A_1 irrep is not in the list, there are no solutions to eqn. (12) with $\lambda = 2$. Continuing in this way, we find that $l = 3$ consists of $A_2 + T_1 + T_2$. The presence of A_2 indicates that there is one (odd parity) solution to eqn. (12) for $\lambda = 3$.

In this manner we have constructed Table 1, which contains the first twenty eigenvalues of both the even and odd parity classes. The integer n simply sequences the eigenvalues, and values of λ and $\mu = (\lambda + 3)(\lambda + 4)$ are given. We see that the first degeneracy occurs in the even eigenfunction with $\lambda = 12$; at higher values of λ, degeneracies of higher order become the rule. The table reveals a pattern, namely that every odd eigenvalue is matched by an even eigenvalue with λ replaced by $\lambda - 3$. This is because the only way to construct an odd polynomial is to multiply the odd function $V = x_1 x_2 x_3$ by an even polynomial of degree less by three. Thus the number of solutions for an odd value of λ is the number of even polynomials in the A_1 symmetry class for $\lambda - 3$.

It is also possible to find a closed expression for the order of degeneracy for a given value of λ. It is only necessary to do this for even λ, since the degeneracy for odd λ follows by the rule just mentioned. If we let $\lambda = 2\nu_1$ then the order of the degeneracy is

$$d(\lambda) = \tfrac{3}{8} + \tfrac{1}{3}\,[\mathrm{mod}\,(\nu - 1, 3) - 1] + \frac{(-1)^\nu}{4} + \frac{4\nu + 1}{24} \quad (17)$$

The quantity $d(\lambda)$ for even λ is always an integer; for example, we find $d(24) = 3$, indicating the 3-fold degeneracy for $\lambda = 24$ which is shown in Table 1. Eqn. (17) was derived by analyzing the two-term linear recurrence relation for the irreps of O, as explained above, and writing it in terms of a single 10×10, non-hermitian transfer matrix. By transforming the transfer matrix to Jordan normal form and imposing the required initial conditions, eqn. (17) results. The process is straightforward but not illuminating, so we will omit the somewhat lengthy details.

With somewhat more effort, the eigenfunctions can also be determined, as outlined above. We have listed the first several of these in Table 2; they are given in polynomial form, since to transform them into angular form on the sphere only obscures their structure and symmetry. Note the odd solution for $\lambda = 3$; the wavefunction Ψ is just the volume, $V = x_1 x_2 x_3$.

III The case $n \geqslant 5$

We now briefly discuss the case of five or more atoms. (For a different approach, see refs. 5 and 6.) The kinematic invariants can still be taken to be the singular values (x_1, x_2, x_3) of the $\boldsymbol{F}$ matrix when $n \geqslant 5$, but their ranges are now restricted to $0 \leqslant x_1 \leqslant x_2 \leqslant x_3$. That is, the smallest singular value x_1 is now required to be non-negative. This is because the parity operation is implemented by means of kinematic rotations when $n \geqslant 5$. This also means that if we look at the special class of wavefunctions which are invariant under kinematic rotations, then these will automatically have even parity. The physically allowed region of the hypersphere in (x_1, x_2, x_3)-space is now the triangle SCB in Fig. 1 (see Fig. 4 for the tesselation), and the boundary conditions on Ψ are even (vanishing normal derivative) at all edges. There are also restrictions on the ranges of the kinematic angles, which we will discuss in other publications since the kinematic angles do not concern us here.

In the case $n \geqslant 5$ the metric on the space (x_1, x_2, x_3) is still Euclidean, but the Jacobian factor D is different. For example, in the case of five atoms, $D = x_1 x_2 x_3 (x_2^2 - x_1^2)(x_3^2 - x_1^2)(x_3^2 - x_2^2)$. Thus, while V_2 is still given by eqn. (2), the expression (3) will change, as will the vector $\boldsymbol{K}$ appearing in eqn. (12). Thus, the eigenfunctions and eigenvalues in (x_1, x_2, x_3)-space will depend on the number of atoms, although they can be worked out by the methods explained here for the case $n = 4$.

IV Conclusions

In conclusion, we have found analytic solutions for four-particle dynamics on the space of kinematic invariants in the case $V = 0$, assuming both the external (ordinary) and internal (kinematic) angular momentum are zero, and we have outlined how these may be generalized for five or more particles. We have also elucidated the spaces involved in the dynamics of kinematic invariants, the boundary conditions satisfied by wavefunctions, and the action of parity in the various cases. In the future, we plan to examine in detail how motions such as the inversion in ammonia can be modelled in the space of kinematic invariants, how pseudorotational motions such as in PF_5 can be analyzed in terms of kinematic invariants and kinematic rotations, and how hyperspherical harmonics in the case $n = 4$, of which the eigenfunctions found in this paper are special cases, can be developed as a practical basis set for four-body scattering calculations.

Acknowledgements

We are grateful for gracious hospitality and many stimulating discussions with Aron Kuppermann. We also thank Professor Kuppermann and Dr Decheng Wang for kindly providing unpublished numerical results.

This work was supported by the US Department of Energy under Contract No. DE-AC03-76SF00098, by the Italian CNR and MURST, and by the EU under the TMR contract No. ERB-FMRX-CT96-0088.

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Paper 8/09417I