Rotations of the most asymmetric molecules via 4-step and 1-step ladder operators

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Abstract. The symmetries of the free rotations of asymmetric molecules - at the levels of their respective Hamiltonians, spheroconal harmonic eigenfunctions, and eigenenergies - are reviewed in general. The situation of the most asymmetric molecules is analyzed in particular; their eigenstates with vanishing asymmetry-distribution eigenenergies are identified together with the Valdés and Piña 4-step ladder operators connecting them. Three sets of ladder operators identified by Méndez-Fragoso and Ley-Koo, connecting specific eigenstates of molecules with any symmetry, are also reviewed briefly. The successive applications of the 4-step ladder operators, to the lower eigenstates $1, y, xz, xyz$, of the most asymmetric molecules, lead to their respective angular momentum $\ell = 4N, 4N+1, 4N+2, 4N+3,$ for $N = 0,1,2,...$, companions of the same species with vanishing asymmetry-distribution energy; in turn, the successive application of the cartesian components of the angular momentum $L_x, L_y, L_z$ operators to the above states, for each value of $\ell$, lead to the respective companion states with the same angular momentum and companion species $[xy, xz, yz, 1], [z, xyz, x, y], [y, 1, xy, xz], [x, y, z, xyz]$ and complementary excitations, thus completing each set of $(2\ell+1)$ eigenstates, with symmetrically distributed energy levels.

1. Introduction
Kramers and Ittmann pioneered the study of the quantum rotations of asymmetric molecules using Lamé spheroconal harmonic polynomials [1], and Patera and Winternitz identified the corresponding representations of the rotational group [2]. This contribution is focused on the successive use of the 4-step ladder operators identified in [3], and of the angular momentum operators as one of the sets identified in [4], on the appropriate eigenstates of the most asymmetric molecules, exhibiting the respective connections among successive pairs of such states.

The article reviews in Sect. 2 the symmetries of the free rotations of asymmetric molecules, including the most asymmetric ones, at the levels of their Hamiltonians, eigenfunctions and eigenenergies, referring the readers to [5-8] for the details. Sections 3 and 4 describe the actions of the respective 4-step and 1-step ladder operators on the individual pairs of eigenstates. Section 5 provides the overall picture of the successive and combined actions of both types of operators, starting from the lower eigenstates with $\ell = 0, 1, 2, 3$ and vanishing asymmetry-distribution energy. Section 6 contains a discussion of the specific results of this investigation and its relevance for developing the theory of angular momentum in bases of Lamé spheroconal harmonics.

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2. Symmetries in the rotations of asymmetric molecules
The section reviews briefly and successively the symmetries of the Hamiltonians, their eigenfunctions and energy spectra for asymmetric molecules, including the most asymmetric ones.

2.1. Symmetries in the Hamiltonians
The starting point is the Hamiltonian for the free rotations of asymmetric molecules with moments of inertia $I_1 < I_2 < I_3$ in the body fixed reference frame with principal axes:
\[
H = \frac{1}{2} \left( \frac{L_x^2}{I_1} + \frac{L_y^2}{I_2} + \frac{L_z^2}{I_3} \right)
\]
in terms of the squares of the cartesian components of the angular momentum operators.

Piña introduced the reparametrization [5]:
\[
\frac{1}{I_i} = Q + P e_i
\]
in terms of the average of the trace of the matrix of inverses of moments of inertia,
\[
Q = \frac{1}{3} \left( \frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3} \right)
\]
the parameters of asymmetry-distribution, $e_1 > e_2 > e_3$, subject to the conditions of not contributing to the trace, and on their magnitudes
\[
e_1 + e_2 + e_3 = 0, \quad e_1^2 + e_2^2 + e_3^2 = \frac{3}{2} \]
and the magnitude of the asymmetry $P$, such that
\[
P^2 = \frac{2}{9} \left[ \left( \frac{1}{I_2} - \frac{1}{I_3} \right)^2 + \left( \frac{1}{I_1} - \frac{1}{I_3} \right)^2 + \left( \frac{1}{I_1} - \frac{1}{I_2} \right)^2 \right].
\]

In this way, the Hamiltonian $H = H^0 + P H^*$ is separated into its spherical rotor and asymmetry-distribution contributions
\[
H^0 = \frac{1}{2} Q L^2, \quad H^* = \frac{1}{2} \left( e_1 L_x^2 + e_2 L_y^2 + e_3 L_z^2 \right).
\]

The three pairs of Hamiltonians commute with each other and consequently share common eigenfunctions. Their invariance under the individual parity transformations $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$ lead also to eigenfunctions with the respective well-defined parities.

The two conditions on the asymmetry-distribution parameters indicate that only one of them can be chosen independently. An alternative parametrization with a single angle, $0 < \sigma < 60^\circ$, can also be used:
\[
e_1 = \cos \sigma, \quad e_2 = \cos(\sigma - 120^\circ), \quad e_3 = \cos(\sigma + 120^\circ).
\]

The particular cases of ($\sigma = 0$, $e_1 = 1$, $e_2 = e_3 = -0.5$) and ($\sigma = 60^\circ$, $e_1 = e_2 = 0.5$, $e_3 = -1$) correspond to prolate and oblate symmetric molecules with the respective $x$ and $z$ axes of rotational symmetry. The most asymmetric molecules are defined by ($\sigma = 30^\circ$, $e_1 = \sqrt{3}/2$, $e_2 = 0$, $e_3 = -\sqrt{3}/2$), for which $H^*$ loses its dependence on $L_x$, and becomes proportional to $L_x^2 - L_z^2$. Also, for molecules with values of $\sigma$ and $60^\circ - \sigma$, it is easy to establish the relationships $e_i(60^\circ - \sigma) = -e_i(\sigma)$, $e_i(60^\circ - \sigma) = -e_i(\sigma)$ and $e_i(60^\circ - \sigma) = -e_i(\sigma)$, with the corresponding changes of sign between $H^*(\sigma)$ and $H^*(60^\circ - \sigma)$, complemented with the exchange of $L_x^2$ and $L_z^2$. 

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2.2. Symmetries in the eigenfunctions in spheroconal coordinates

The spheroconal coordinates are expressed in terms of their transformation equations to cartesian coordinates: \( x = rd_n(x_1 | k_1^2) sn(x_2 | k_2^2), \quad y = r cn(x_1 | k_1^2) cn(x_2 | k_2^2), \quad z = rsn(x_1 | k_1^2) dn(x_2 | k_2^2) \) using the Jacobi elliptical integrals. Their parameters \( k_i^2 \) are subject to the condition that their sum is one, ensuring that the sum of the squares of the cartesian coordinates is equal to the square of the spherical radial coordinate. Fixed values of the angular coordinates \( x_1 = x_{10} \) and \( x_2 = x_{20} \) correspond to elliptical cones with axis along the \( z \)-axis and the \( x \)-axis, respectively. Notice that the change of the indices 1 and 2 in the coordinates and parameters is equivalent to the exchange of \( x \) and \( z \), while \( y \) remains the same.

The scale factors for these coordinates are readily obtained [3-8]:
\[
h_i = 1, \quad h_{x_1} = h_{x_2} = r \sqrt{1 - k_1^2 sn^2(x_1 | k_1^2) - k_2^2 sn^2(x_2 | k_2^2)}. \]
leading to the spheroconal coordinate representation of the operators of the square of the angular momentum and the asymmetry-distribution Hamiltonian,
\[
\hat{L}^2 = \frac{\hbar^2 r^2}{h_x^2} \left[ \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} \right],
\]
\[
\hat{E}^* = -\frac{\hbar^2 r^2}{2h_x^2} \left\{ [e_1 - (e_1 - e_2)sn^2(x_2 | k_2^2)] \frac{\partial^2}{\partial x_1^2} + [e_2 - (e_2 - e_1)sn^2(x_1 | k_1^2)] \frac{\partial^2}{\partial y_1^2} \right\}.
\]

The respective eigenvalue equations with eigenvalues \( \hbar^2 \ell(\ell + 1) \) and \( E^* \), respectively, admit common factorizable eigenfunctions \( \Lambda_i(x_i) \Lambda_j(x_j) \). Both equations can be simultaneously separated into ordinary Lamé differential equations, provided the geometric parameters and the asymmetry-distribution parameters are chosen to be connected by
\[
k_1^2 = \frac{e_2 - e_3}{e_1 - e_3}, \quad k_2^2 = \frac{e_1 - e_2}{e_2 - e_3}.
\]

In such a case, the symmetric prolate and oblate molecules are characterized by \((k_1^2 = 0, k_2^2 = 1)\) and \((k_1^2 = 1, k_2^2 = 0)\), respectively, and the most asymmetric by \(k_1^2 = k_2^2 = 0.5\).

In fact, the separated equations for \( i = 1, 2 \) have the common form
\[
\left[ -\frac{d^2}{dx_i^2} + \ell(\ell + 1) k_i^2 sn^2(x_i | k_i^2) \right] \Lambda_i(x_i) = \hbar_i \Lambda_i(x_i),
\]
with separation constants
\[
h_1 = -\frac{\ell(\ell + 1)e_1}{e_1 - e_3}, \quad h_2 = \frac{\ell(\ell + 1)e_2}{e_2 - e_3}, \quad \frac{2E^*}{h_1 h_2} - \frac{\ell(\ell + 1)e_i}{h_i^2 (e_i - e_j)}.
\]

After the Lamé equations are solved, their respective eigenvalues can be combined, so that
\[
h_1 + h_2 = \ell(\ell + 1), \quad e_1 h_1 + e_2 h_2 = 2E^* / h^2.
\]

The derivatives of the Jacobi elliptical functions \( sn, cn \) and \( dn \) equal the products of the other two: \( cn dn, -dn sn, -k^2 sn cn \), respectively. Consequently, the Lamé equation has removable singularities of eight different species \( A: [1, d, c, s, d, ds, cs, cd, scs] \) and \( B: [1, s, c, d, sc, sd, cd, scd] \) using only the initial of the respective functions, for the variables \( x_1 \) and \( x_2 \). Their corresponding products \( AB: [1, x, y, z, xy, xz, yz, xyz] \) allow the identifications of the respective \( x, y \) and \( z \) parities for the successive eigenfunctions, as well as their number and type of cartesian nodal planes: \( n^{AB} = 0, 1, 2 \) or \( 3 \).
The general form of the Lamé functions includes the product of the singularity removing factor and a polynomial in even powers of \( \text{sn}(\chi_i | k_i^2) \): 
\[
\Lambda^\alpha(\chi_i, h_i^\alpha) = A(\chi_i) \sum_{\ell=0}^{N_{\max}} a_{\ell}^\alpha(h_i^\alpha) \text{sn}^{2\ell}(\chi_i | k_i^2).
\]

Substitution in the Lamé differential equation leads to three term recurrence relations for the expansion coefficients, equivalent to a tridiagonal matrix eigenvalue problem; diagonalization of the latter yields the eigenvalues \( h_i^\alpha \), and the associated coefficients \( a_{\ell}^\alpha(h_i^\alpha) \). The subindices in the eigenvalues count the number of nodal elliptical cones in the eigenfunction which come in symmetrical pairs. The values of \( N_{\max} \) are: \((\ell + 2)/2 \) for \( \ell \) even and \( A=1 \), and \( \ell/2 \) for \( \ell \) odd and \( A=1 \), or \( (\ell + 1)/2 \) for \( \ell \) odd, and \( A=d, c, s \), and \((\ell - 1)/2 \) for \( \ell \) odd and \( A=dc, ds, cs \). In both cases the total number of states is \((2\ell + 1)\).

The matching of the eigenvalues, \( h_i^\alpha \) and \( h_i^\beta \), is guided by their species and parities, and also by the condition that their sum is \( \ell(\ell + 1) \). Additionally, the number of nodes for the product eigenstates with a given value of \( \ell \), using the notation \( \ell[AB]n_i n_j \), is such that: \( n_i^A + n_i^B = \ell \). Correspondingly, the combination \( \sum_i h_i^\alpha + \sum_i h_i^\beta \) yields the asymmetry-distribution energy \( E_{n_i n_j}^{\alpha \beta} \) for each eigenstate.

Figures 2 in [6] and 2 in [7] illustrate 3-dimensional polar graphs for the eigenfunctions with \( \ell = 4 \) and 5, respectively, for \( \sigma = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ \). The readers may examine them in order to recognize some of their properties as described in the previous paragraphs. Additionally, notice the same shapes in the first and fifth columns, second and fourth, as well as in the upper and lower parts of the third one, differing only in orientations. The latter follow from the symmetries in the last paragraph in Sect. 2.1 and in the first paragraph of this section.

### 2.3 Symmetries in the asymmetry-distribution energies

Figure 1 in [7] illustrates the asymmetry-distribution energy spectra \( E_{n_i n_j}^{\alpha \beta}(\sigma) \) for the values of \( \ell = 0,1,2, \ldots, 10, 20, 30 \), as functions of the asymmetry parameter in the interval \( [0,60^\circ] \). The doubly degenerate energy levels for the prolate and oblate symmetric molecules at the left and right of the individual figures, with energies such that \( E^{\ast}(\sigma = 0) = -E^{\ast}(\sigma = 60^\circ) \) can be recognized. The reader may interpolate or extrapolate, between or from them, following the energy lines from the left and the right with equal steps in \( \sigma \) accompanied by equal vertical displacements towards or away from the horizontal line with \( E = 0 \). The reasons mentioned in the closing paragraph of the previous section also explain the general connections \( E_{n_i n_j}^{\alpha \beta}(\sigma) = -E_{n_i n_j}^{\alpha \ast B}(60^\circ - \sigma) \) for species \([AB]\) and \([A^\ast B]\) in which \( x \) and \( z \) are exchanged, accompanied by the exchange of excitations in \( \chi_1 \) and \( \chi_2 \). The figures under consideration contain lines that are antisymmetric relative to the point \((\sigma = 30^\circ, E^{\ast} = 0)\); alternatively, a rotation of each figure around such a point by \( 180^\circ \) is self-mapping.

### 2.4 Symmetries in the most asymmetric molecules

The most asymmetric molecules defined by the parameters \( \sigma = 30^\circ \), \( k_1^2 = k_2^2 = 0.5 \), are described by the Hamiltonian \( H^{\ast} = (\sqrt{3}/4)[L_x^2 - L_z^2] \), which is antisymmetric under the exchange of \( L_x \) and \( L_z \). This allows us to expect that it may have eigenstates with vanishing asymmetry-distribution energy, \( E = 0 \).

The species of such eigenstates should be invariant under the exchange of \( x \) and \( z \). The favoured options are \( 1, y = cc, xz = ds \ sd, \) and \( xz = ds \ scd, \) with the common \([A] = [B]\). The vanishing of the
energy $E_{n_1,n_2}^{(Ab)}$, according with Sect. 2.2 requires that $h_{n_1}^0 = h_{n_2}^0$. Then the excitation of both degrees of freedom must also be the same $n_1 = n_2$. From the distribution of nodes for a given $\ell$, the states of our interest belong in the following categories: $|\ell = 4N[1,2N,2N]$, $|\ell = 4N+1[y2N,2N]$, $|\ell = 4N + 2[xz2N,2N]$, and $|\ell = 4N + 3[xyz2N,2N]$.  

3. Angular Momentum 4-step ladder operators for the most asymmetric molecules

Valdés and Piña investigated the rotational spectra of the most asymmetric molecules, identifying their eigenstates with vanishing energies as well as the 4-step ladder operators connecting them [3]. Here we simply borrow their equations describing the pertinent states and ladder operators.

In their notation, the Lamé polynomials $\Lambda_{\ell n} \equiv f_n(1/4,3/4,w)$ become the products of the singularity removing factors and Jacobi polynomials of degree $n$ with labels $\alpha, \gamma$ in the variable $w = c\tau^2 (\chi_i | k_i^2 = 0.5)$ squared:

$$f_n (1/4,3/4,w)$$

$$= \Lambda_{4n,0} = \sqrt{w} f_n (3/4,5/4,w)$$

$$= \Lambda_{4n,1,0} = \sqrt{1-w} f_n (5/4,3/4,w)$$

$$= \Lambda_{4n,2,0} = \sqrt{w(1-w)} f_n (7/4,5/4,w)$$

The 4-step ladder operators, connecting eigenstates of the same species, do it as follows:

$$\Lambda_{1,0} \equiv \frac{\sqrt{(\ell + 1)(\ell + 2)(\ell + 3)(\ell + 4)}}{2\ell + 5}$$

$$\Lambda_{1,4,0} \equiv \frac{\sqrt{(\ell + 1)(\ell + 2)(\ell + 3)(\ell + 4)}}{2\ell + 5}$$

in their up and down versions, respectively.

4. Three sets of ladder operators for molecules of any asymmetry

The ladder operators for the Lamé spheroidal harmonic polynomials, identified in [4], come in three sets: 1) For eigenstates with the same angular momentum $\ell$, same species $AB$, and different and complementary angular excitations $n_1 + n_2 = n'_1 + n'_2 = \ell - n^{(a)}$, $h_{n_1}^a + h_{n_2}^a = h_{n'_1}^a + h_{n'_2}^a = \ell + (l+1)$ according to Sect. 2.2. 2) For eigenstates with the same angular momentum $\ell$ and different species, corresponding to the cartesian components of the angular momentum operators $L_x$, $L_y$, $L_z$. 3) For eigenstates with neighbouring values of angular momentum $\ell' = \ell \pm 1$, different parities and different species, which correspond to the cartesian components of the linear momentum operators $p_x$, $p_y$, $p_z$.

![Figure 1.](image) Actions of angular momentum operators between pairs of eigenstates of companion species for a) even and b) odd values of $\ell$. 

Notice that both figures contain the operators $L_x$, $L_y$ and $L_z$ in the same positions. The species of the eigenstates on the lower left and upper right corners belong to the species symmetric under the exchange between $x$ and $z$, while the pairs in the upper left and lower right corners change one into the other under the same exchange.

5. Connections of successive rotational eigenstates of the most asymmetric molecules using the 4-step ladder and $L_x, L_y, L_z$ operators

This section exhibits graphically, via figures 2 and 3, the overall picture of the connections between the eigenstates with vanishing asymmetry-distribution energy and $\ell = 4N, 4N+1, 4N+2, 4N+3$ for $N = 0, 1, 2, 3$, provided by the 4-step ladder operators described in Sect. 3; as well as their companion eigenstates for each value of $\ell$ of different species and angular excitations, using the angular momentum operators as described in Sect. 4.

![Figure 2](image-url)

**Figure 2.** Actions of 4-step ladder operators between eigenstates of the same species with $E = 0$ for $\ell = 0, 1, 2, 3$ modulo 4.

The actions depicted in figure 2 combine the raising actions for both degrees of freedom described in Sect. 4, for $n_1 = n_2 = 0, 2, 4, 6$. The lowest eigenstates are the monomials $1, y, xz, xyz$ in their cartesian representation.
Figure 3a. Actions of angular momentum operators $L_x$, $L_y$, $L_z$ between eigenstates with a given value of $\ell = 4N, 4N+1, 4N+2, 4N+3$ and companion species for $N=0, 1$. 
Figure 3b. For N=2.
The actions depicted in figure 3 follow from the successive applications of the operators of figure 1, starting from the eigenstates with $E^* = 0$ of figure 2. In figure 3a the lower eigenstates 1 has zero eigenvalues for any component of the angular momentum; $y$ becomes $z$ and $x$ when $L_y$ and $L_z$ act on it, with positive and negative energies because $E_+ > 0$ and $E_- < 0$, respectively; $xz$, under the action of the same operators become $yz$ and $xy$ with the corresponding positive and negative energies, respectively, and under $L_y$ leads to the two states of species $|1\rangle$ with positive energy for $n_1=2$, $n_2=0$ and negative for $n_1=0$, $n_2=2$; and $xyz$ under the actions of $L_x$, $L_y$ and $L_z$ becomes the companions of species $x$, $y$, $z$ with $n_1=2$, $n_2=0$ above, and with $n_1=0$, $n_2=2$ in the order $z$, $y$, $x$ symmetrically below. The extensions for $N=1$, 2, 3 can be identified in the upper part of figure 3a, and figures 3b and 3c, with the successive applications of the same operators. In the last two figures, notice that the energy levels far
above and below $E^* = 0$ come in pairs with almost the same energy, including the connections of some of those pairs represented only by the tip of the respective arrows. The readers may also ascertain, for each value of $\ell$, the numbers of states for the respective species, as described in Sect. 2.2, as well as the matching and the types of their nodal surfaces when going from the lower to the higher energy levels, following the changes in the $\chi_1$ and $\chi_2$ excitations.

6. Discussion
The symmetries of the rotations of asymmetric molecules reviewed in Sect. 2 allow the identification of the commuting set of operators $H, H^Q, H^*$ and the individual $x, y$ and $z$ parity operators; with the corresponding labeling of their common eigenstates $\ell[AB]\eta_1\eta_2$ characterizing their angular momentum, species and excitations, and also of their respective eigenenergies, especially $E^*$. The 4-step angular momentum ladder operators in Sect. 3 provide the connections between the eigenstates of the most asymmetric molecules with vanishing asymmetry-distribution energy $E^* = 0, \ell = 0, 1, 2, 3$ modulo 4 as graphically illustrated in Sect. 5. The cartesian components of the angular momentum operators in Sect. 4 applied successively to each of the above eigenstates lead to their sets of $2\ell$ companion eigenstates with the common value of $\ell$, companion species, and complementary excitations and, with energies $\pm E^*$ of the same magnitude above and below the level $E^* = 0$, as illustrated also in Sect 5.

In addition to this specific investigation for the most asymmetric molecules, a few remarks about molecules of any asymmetry can be added to the discussion. First, we recall the connection between the Hamiltonians $H^*(\sigma)$ and $H^*(60^{\circ}-\sigma)$ involving the change of sign in their respective asymmetry-distribution parameters as well as the exchange of $L_x$ and $L_z$; and also the consequent antisymmetry of the lines in the $(\sigma, E^*)$ planes in figure 1 of [7] relative to the point $(\sigma = 30^{\circ}, E^* = 0)$. The labeling of the eigenstates of the most asymmetric molecules is also valid for the molecules with the other asymmetries, $0 < \sigma < 60^{\circ}$; for any of them with a fixed value of $\sigma$ and their respective energies $E^*(\sigma)$, the connections illustrated in figure 3 also hold, with the corresponding changes in the energy positions. While the present investigation involves only vertical displacements, the linear momentum operators in Sect. 4 produce horizontal displacements connecting states in different columns in figure 3, for molecules of any asymmetry; for the most asymmetric molecules, four successive applications should take us from $\ell$ to $\ell + 4$ making contact with Sect. 3. Our concluding remark is that these investigations contribute to the development of the theory of angular momentum in bases of Lamé spheroidal harmonic polynomials.

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