Properties of the spectra of asymmetric molecules: matrix evaluation in bases of spherical harmonics and common generating function

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The Schrödinger equation for the rotational states of asymmetric molecules is known to be separable in spheroconal coordinates and integrable in terms of Lamé functions. However, the numerical evaluation of the latter has not been developed efficiently, thereby limiting the practical application of such solutions. In this article, the matrix evaluation of the rotational states is formulated and implemented numerically for any asymmetric molecule, using the familiar bases of spherical harmonics. The matrix of the Hamiltonian - in a frame of reference fixed in the molecule and oriented along its principal axes - is constructed in the chosen basis and shown to separate into blocks of $(\ell+1)\times(\ell+1)$ and $\ell\times\ell$, for each value of the angular momentum quantum number ℓ. The diagonalization of the successive blocks leads to accurate values of eigenenergies and eigenvectors for all values of the asymmetry parameters. The connection between these rotational states and their Lamé function representation is also established, identifying at the same time a common generating function for spherical harmonics and spheroconal harmonics.

Keywords: Asymmetric molecules; rotation spectra; matrix evaluation; spherical harmonics; Lamé functions; spheroconal harmonics; generating function.

Se sabe que la ecuación de Schrödinger para los estados rotacionales de moléculas asimétricas es separable en coordenadas esferoconales e integrable en términos de funciones de Lamé. Sin embargo, la evaluación numérica de las últimas no se ha desarrollado eficientemente, limitando por lo tanto la aplicación práctica de tales soluciones. En este artículo, la evaluación matricial de los estados rotacionales se formula e implementa numéricamente para cualquier molécula asimétrica, usando la base familiar de armónicos esféricos. La matriz del Hamiltoniano - en un sistema de referencia fijo en la molécula y orientado a lo largo de los ejes principales - se construye en la base escogida y se muestra que se separa en bloques de $(\ell+1)\times(\ell+1)$ y $\ell\times\ell$, para cada valor del número cuántico de momento angular ℓ. La diagonalización de los bloques sucesivos conduce a valores precisos de las eigenenergías y los eigenvalores para todos los valores de los parámetros de asimetría. También se establece la conexión entre estos estados rotacionales y su representación en términos de funciones de Lamé, identificando al mismo tiempo una función generadora común para armónicos esféricos y armónicos esferoconales.

Descriptores: Moléculas asimétricas; espectro rotacional; evaluación matricial; armónicos esféricos; funciones de Lamé; armónicos esferoconales; función generadora.

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1. Introduction

The investigation and the results reported in this article have been motivated by and are complementary to the works in Refs. 1 to 3, as reflected by a comparison of their respective titles. In fact, in the notation of [1, 2] the rotational states of asymmetric molecules are described by the common eigenfunctions of the Schrödinger equation

$$\frac{1}{2}\left[\frac{\hat{L}_x^2}{I_1}+\frac{\hat{L}_y^2}{I_2}+\frac{\hat{L}_z^2}{I_3}\right]\Psi=E\Psi, \tag{1}$$

and the square and z-component of the angular momentum

$$\left(\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2\right)\Psi=\hbar^2\ell(\ell+1)\Psi, \tag{2}$$

$$\hat{M}_z\Psi=\hbar m\Psi, \tag{3}$$

where $\hat{L}_i$ and $\hat{M}_i$ are the components of the angular momentum in the body-fixed and laboratory fixed, or inertial, frames of reference respectively. Notice that our Eqs. (1) - (3) correspond to Eqs. (34)-(35) in Ref. 2.

The three Euler angles are the familiar variables for writing and connecting the descriptions of the rotational states in the body-fixed and inertial frames of reference. However, for the states with zero projection along the z-axis in the inertial frame of reference, the associated angle becomes ignorable in Eqs. (1) and (2), corresponding to the step from Eq. (32) to Eq. (37) in Ref. 2. In such a case, the problem depends only on the two other Euler angles, or any two alternative variables.

Kramers and Ittmann [1] chose the alternative of the spheroconal coordinates because Eqs. (1) and (2) become separable and integrable in terms the Lamé functions, while the third Euler angle associated with Eq.(3) becomes ignorable. Later authors [4–6] kept on working with the spherical Euler angles, and the subsequent work followed this usage [7–15]. While the solution of Ref. 1 is mathematically exact, in practical terms it was not applied because the numerical evaluation of the Lamé functions was not implemented. On the other hand, the development of the alternative description [4–15] took the perturbation approach route.

The investigations of Refs. 2 and 3 have retaken the route initated by Kramers and Ittmann [1], using spherical coordi-

nates (r,χ_1,χ_2) defined by the transformation equations to cartesian coordinates

$$\begin{aligned} x &= r\mathrm{dn}(\chi_1,k_1)\mathrm{sn}(\chi_2,k_2) \\ y &= r\mathrm{cn}(\chi_1,k_1)\mathrm{cn}(\chi_2,k_2), \\ z &= r\mathrm{sn}(\chi_1,k_1)\mathrm{dn}(\chi_2,k_2) \end{aligned} \tag{4}$$

in terms of Jacobian elliptic functions [16, 17], subject to the condition

$$k_1^2 + k_2^2 = 1. \tag{5}$$

The solutions of Eqs. (1) and (2) are separable

$$\Psi(\chi_1,\chi_2) = \Lambda(\chi_1)\Lambda(\chi_2), \tag{6}$$

in terms of Lamé functions, satisfying the ordinary differential equations:

$$\frac{d^2\Lambda_i}{d\chi_i^2} - \left[k_i^2\ell(\ell+1)\mathrm{sn}^2(\chi_i,k_i) + h_i\right]\Lambda_i = 0. \tag{7}$$

The lower order solutions for $\ell = 1, 2$ and 3 are presented explicitly in Ref. 2, including the respective eigenenergies in terms of the molecule asymmetry parameters. On the other hand, [3] includes higher order excited states for the most asymmetric molecules only.

It is still valid to say that the numerical evaluation of the Lamé functions of a higher order has not been developed efficiently, with the consequent limitations on the practical application of such solutions to characterize the spectra of any asymmetric molecule. The purpose of our investigation is to make up for such limitations, via the formulation of an alternative method to solve Eq. (1) - or some of its variations, already included in Ref. 2 - with reliable and accurate numerical values for the eigenenergies and eigenfunctions of any order of excitation.

It is convenient to describe now the two parametrizations included in Ref. 2, as alternatives to the use of the inverses of the moments of inertia in Eq. (1). The first one introduces the decomposition of the diagonal matrix of such inverses into its balanced-trace and traceless components [2]:

$$\begin{pmatrix} \frac{1}{I_1} & 0 & 0 \\ 0 & \frac{1}{I_2} & 0 \\ 0 & 0 & \frac{1}{I_3} \end{pmatrix} = \begin{pmatrix} Q & 0 & 0 \\ 0 & Q & 0 \\ 0 & 0 & Q \end{pmatrix} + P\begin{pmatrix} e_1 & 0 & 0 \\ 0 & e_2 & 0 \\ 0 & 0 & e_3 \end{pmatrix}. \tag{8}$$

It follows directly that

$$Q = \frac{1}{3}\left[\frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3}\right], \tag{9}$$

$$e_1 + e_2 + e_3 = 0, \tag{10}$$

$$\begin{aligned} Pe_i &= \frac{1}{3}\left[\frac{2}{I_i} - \frac{1}{I_j} - \frac{1}{I_k}\right], \\ (i,j,k) &= \mathrm{cyc}(1,2,3), \end{aligned} \tag{11}$$

and therefore

$$P^2(e_1^2+e_2^2+e_3^2) = \frac{1}{3}\left[\left(\frac{1}{I_1}-\frac{1}{I_2}\right)^2 + \left(\frac{1}{I_2}-\frac{1}{I_3}\right)^2 + \left(\frac{1}{I_3}-\frac{1}{I_1}\right)^2\right]. \tag{12}$$

By choosing

$$e_1^2 + e_2^2 + e_3^2 = \frac{3}{2}, \tag{13}$$

it follows that

$$P^2 = \frac{2}{9}\left[\left(\frac{1}{I_1}-\frac{1}{I_2}\right)^2 + \left(\frac{1}{I_2}-\frac{1}{I_3}\right)^2 + \left(\frac{1}{I_3}-\frac{1}{I_1}\right)^2\right]. \tag{14}$$

The change of the three parameters I_i to the five parameters Q, P and e_i, is subject to the conditions of Eqs. (10) and (13), so that a choice of one of the latter three determines the other two. The second alternative parametrization replaces the parameters e_i with a single angular parameter σ, [2]

$$e_1 = \cos\sigma,\ e_2 = \cos\left(\sigma - \tfrac{2\pi}{3}\right),\ e_3 = \cos\left(\sigma + \tfrac{2\pi}{3}\right), \tag{15}$$

ensuring that Eqs. (10) and (13) are satisfied.

The Hamiltonian in Eq. (1) takes and leads to the following alternative forms

$$\hat{H} = \frac{1}{2}Q\hat{L}^2 + \frac{1}{2}P\left[e_1\hat{L}_x^2 + e_2\hat{L}_y^2 + e_3\hat{L}_z^2\right], \tag{16}$$

$$\hat{H}^* = \frac{1}{2}\left[e_1\hat{L}_x^2 + e_2\hat{L}_y^2 + e_3\hat{L}_z^2\right], \tag{17}$$

$$\hat{H}^* = \frac{1}{2}\left[\cos\sigma\hat{L}_x^2 + \cos\left(\sigma - \tfrac{2\pi}{3}\right)\hat{L}_y^2 + \cos\left(\sigma + \tfrac{2\pi}{3}\right)\hat{L}_z^2\right]. \tag{18}$$

The trace component in Eq. (16) corresponds to the spherical molecule for which, $I_1 = I_2 = I_3$, so that $Q = 1/I_i$ and $P = 0$, with the well-known $\hbar^2\ell(\ell+1)/2$ energy spectrum and spherical harmonic $Y_{\ell m}$ eigenfunctions, for $m = \ell, \ell-1, \ldots, 1, 0, -1, \ldots, -(\ell-1), -\ell$ and $(2\ell+1)$-degeneracy. The traceless components correspond to the asymmetric contribution of magnitude P, Eq. (14), and distributions included in $\hat{H}^*$. By ordering the moments of inertia as $I_1 \leq I_2 \leq I_3$, the asymmetry distribution parameters may be restricted so that $e_1 \leq e_2 \leq e_3$ and $0 \leq \sigma \leq \pi/3$. Prolate symmetric molecules have $I_1 < I_2 = I_3$, $e_1 = 1$,

$e_2 = e_3 = -1/2$, and $\sigma = 0$. Oblate symmetric molecules have $I_1 = I_2 < I_3$, $e_1 = e_2 = 1/2$, $e_3 = -1$, and $\sigma = \pi/3$. The most asymmetric molecules have $e_1 = \sqrt{3}/2 = -e_3$, $e_2 = 0$, and $\sigma = \pi/6$.

In Sec. 2, the matrix evaluation of the eigenenergies and eigenfunctions of any of the equivalent Hamiltonians describing asymmetric molecules is formulated using the familiar bases of spherical harmonics. In Sec. 3 illustrative numerical results are reported for the energy spectra and eigenfunctions of different orders of excitation, for the different values of the molecule asymmetry parameters. Section 4 compares the solutions of the eigenvalue problem of asymmetric molecules developed in this work using spherical harmonics and that of Ref. 2 in terms of spheroconal harmonics. Consequently, the Coulomb potential and the addition theorem are identified as common generating functions for both types of spherical harmonics and spheroconal harmonics. The discussion in the final section emphasizes the exact nature of the matrix solution implemented in this work, for any asymmetry of the molecules, leading to accurate and reliable results for any order of excitation.

2. Matrix evaluation of asymmetric molecule rotational spectra using bases of spherical harmonics

The common feature of the operators in Eqs. (1), (2) and (16) - (18) is their quadratic dependence on the components of the angular momentum. Their differences and connections appear through the respective coefficients, as already established in Sec. 1. Consequently, the construction of the matrices of such operators requires the matrix elements of $\hat{L}_x^2$, $\hat{L}_y^2$ and $\hat{L}_z^2$ in the chosen bases. The general familiar basis of angular momentum eigenfunctions

$$\hat{L}^2 \left|\ell m_k\right\rangle = \hbar^2 \ell(\ell+1) \left|\ell m_k\right\rangle , \tag{19}$$

$$\hat{L}_k \left|\ell m_k\right\rangle = \hbar m_k \left|\ell m_k\right\rangle , \tag{20}$$

involves only diagonal elements for $\hat{L}^2$ and $\hat{L}_k$. For the other components, $\hat{L}_i$ and $\hat{L}_j$, $(i,j,k) = \mathrm{cyc}(x,y,z)$, we use their connections with the raising and lowering operators:

$$\begin{aligned} \hat{L}_i &= \tfrac{1}{2}(\hat{L}_+ + \hat{L}_-), \\ \hat{L}_j &= \tfrac{1}{2i}(\hat{L}_+ - \hat{L}_-), \end{aligned} \tag{21}$$

and their effects on the $|lm_k\rangle$ state:

$$\hat{L}_\pm \left|\ell m_k\right\rangle = \hbar C_\pm(\ell, m_k) \left|\ell m_k \pm 1\right\rangle , \tag{22}$$

$$C_\pm(\ell, m_k) = \sqrt{(\ell \mp m_k)(\ell \pm m_k + 1)}. \tag{23}$$

Correspondingly, their squares become

$$\hat{L}_i^2 = \tfrac{1}{4}\left(\hat{L}_+\hat{L}_+ + \hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+ + \hat{L}_-\hat{L}_-\right), \tag{24}$$

$$\hat{L}_j^2 = \tfrac{1}{4}\left(-\hat{L}_+\hat{L}_+ + \hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+ - \hat{L}_-\hat{L}_-\right), \tag{25}$$

and their effects on $|\ell m_k\rangle$ follows from the successive applications of Eqs. (22) - (23). The first terms raise m_k by 2, the next two terms leave m the same and the last terms lower m_k by 2. We illustrate the explicit form of the matrix elements of $\hat{H}^*$ for the specific cases of $k = x$, y and z:

$$\begin{aligned} \left\langle \ell m_x' \right| \hat{H}^* \left|\ell m_x\right\rangle =& \frac{\hbar^2}{2}\left\{\left[e_1 m_x^2 + \frac{e_2+e_3}{4}\left(C_+(\ell, m_x-1)C_-(\ell, m_x) + C_-(\ell, m_x+1)C_+(\ell, m_x)\right)\right]\delta_{m_x', m_x}\right. \\ &\left. + \frac{e_2-e_3}{4}\left[C_+(\ell, m_x+1)C_+(\ell, m_x)\delta_{m_x', m_x+2} + C_-(\ell, m_x-1)C_-(\ell, m_x)\delta_{m_x', m_x-2}\right]\right\}, \end{aligned} \tag{26}$$

$$\begin{aligned} \left\langle \ell m_y' \right| \hat{H}^* \left|\ell m_y\right\rangle =& \frac{\hbar^2}{2}\left\{\left[e_2 m_y^2 + \frac{e_3+e_1}{4}\left(C_+(\ell, m_y-1)C_-(\ell, m_y) + C_-(\ell, m_y+1)C_+(\ell, m_y)\right)\right]\delta_{m_y', m_y}\right. \\ &\left. + \frac{e_3-e_1}{4}\left[C_+(\ell, m_y+1)C_+(\ell, m_y)\delta_{m_y', m_y+2} + C_-(\ell, m_y-1)C_-(\ell, m_y)\delta_{m_y', m_y-2}\right]\right\}, \end{aligned} \tag{27}$$

$$\begin{aligned} \left\langle \ell m_z' \right| \hat{H}^* \left|\ell m_z\right\rangle =& \frac{\hbar^2}{2}\left\{\left[e_3 m_z^2 + \frac{e_1+e_2}{4}\left(C_+(\ell, m_z-1)C_-(\ell, m_z) + C_-(\ell, m_z+1)C_+(\ell, m_z)\right)\right]\delta_{m_z', m_z}\right. \\ &\left. + \frac{e_1-e_2}{4}\left[C_+(\ell, m_z+1)C_+(\ell, m_z)\delta_{m_z', m_z+2} + C_-(\ell, m_z-1)C_-(\ell, m_z)\delta_{m_z', m_z-2}\right]\right\}. \end{aligned} \tag{28}$$

Several conclusions can be drawn immediately. The selection rules $m_k' = m_k + 2$, m_k, $m_k - 2$ separate the matrix of order $(2\ell+1) \times (2\ell+1)$ into two tridiagonal blocks, one for even values of m_k and the other for odd values of m_k, of dimensions $(\ell+1) \times (\ell+1)$ and $\ell \times \ell$ for ℓ even, and the other way around for ℓ odd. Since $\hat{H}^*$ is Hermitian, its ma-

trices are symmetric with respect to the main diagonal. They are also symmetric with respect to the other diagonal, on account of Eq. (23) begins substituted in Eqs. (26) - (28), leading to combinations $|\ell, m_k\rangle \pm |\ell, -m_k\rangle$ with definite parities. Notice that both operators in Eqs. (1) - (2) are invariant under the individual parity transformations $x \to -x$, $y \to -y$ and $z \to -z$, accounting for the classification of the rotational states of asymmetric molecules of two kinds (ℓ even and odd), each one with four species of parity eigenstates $\{1, yz, xz, xy\}$ and $\{x, y, z, xyz\}$, respectively [2, 16].

Any of Eqs. (26) - (28) upon diagonalization may lead to the eigenenergies E^* and normalized eigenvectors

$$\Psi_{E^*\ell} = \sum_{m_k} a_{\ell m_k} |\ell m_k\rangle, \tag{29}$$

of $\hat{H}^*$ for any asymmetry. Of course, certain choices may lead to more transparency in certain cases. The choice of Eq. (26) is the natural one for prolate symmetric molecules with $e_2 = e_3$, since the non-diagonal terms vanish. Likewise, for the oblate symmetric case with $e_1 = e_2$, Eq. (28) takes the diagonal form. For the most asymmetric case, studied in Ref. 2 and more recently [3], $e_2 = 0$, $e_1 = -e_3 = \sqrt{3}/2$, Eq. (27) becomes:

$$\begin{aligned}\left\langle \ell m'_y \right| \hat{H}^* \left| \ell m_y \right\rangle = \\ - \hbar^2 \frac{\sqrt{3}}{4} \Big\{ C_+(\ell, m_y+1) C_+(\ell, m_y) \delta_{m'_y, m_y+2} \\ + C_-(\ell, m_y-1) C_-(\ell, m_y) \delta_{m'_y, m_y-2} \Big\}. \end{aligned} \tag{30}$$

Even though the diagonal terms drop out, the diagonalization effort is the same.

3. Illustrative numerical results

The diagonalization of Eqs. (26) - (28) was performed using Bunge's "Fast eigensolver for dense real-symmetric matrices" [18].

This section contains numerical and graphical results illustrating the energy eigenvalues and eigenfunctions of excited rotational states of molecules with different asymmetry distributions. The presentation of these results is accompanied by comments on their variations with the order of excitation for each type of molecule defined by a fixed value of its asymmetry parameter $\sigma = [0°, 60°]$, and also on their variations as the asymmetry changes.

3.1. Energy eigenvalues

Accurate and consistent values of the eigenenergies $E^*(\sigma)$ were obtained from the independent diagonalizations of the matrices in Eqs. (26) - (28), for the set of values of $\sigma = 0°$, $15°$, $30°$, $45°$, $60°$ and the respective values of e_i, Eq. (15).

Figure 1 presents the energy levels for the successive values of $\ell = 1, 2, \ldots, 7, 10, 20$ and 30 including their interpolations for all values of the asymmetry parameter σ.

The reader can ascertain the presence of $2\ell + 1$ energy levels for each value of ℓ. In particular, for the prolate and oblate symmetric molecules represented at the left and right end of each frame, respectively, the energies from Eqs. (26) and (28) become

$$E^*_{\ell m_x}(\sigma = 0°) = \frac{\hbar^2}{4} \left(3m_x^2 - \ell(\ell+1)\right), \tag{31}$$

$$E^*_{\ell m_z}(\sigma = 60°) = -\frac{\hbar^2}{4} \left(3m_z^2 - \ell(\ell+1)\right). \tag{32}$$

The double degeneracy of the energy levels with $m = \pm 1$, ± 2, ..., $\pm \ell$ is shared in both cases. Their reversed orders of excitation, starting and ending with the $m = 0$ state, respectively, involving the energies $\mp\hbar^2\ell(\ell+1)/4$, $\mp\hbar^2[\ell(\ell+1) - 3]/4, \ldots, \mp\hbar^2(\ell - 2\ell^2)/4$ of the same magnitude but opposite signs, should be noticed. For the asymmetric molecules, the removal of the degeneracy is appreciated as σ takes increasing values from $0°$ or decreasing values from $60°$. Since m_k is not a good quantum number in general, it is more meaningful to designate the energy levels as $E^*_{\ell n}$ where $n = 1, 2, \ldots, 2\ell + 1$ characterize the ordering of the energies. The symmetries of the Hamiltonian described at the end of the previous section explain the connection between the energies of molecules with "complementary" asymmetries and states $E^*_{\ell n_1}(\sigma_1) = E^*_{\ell n_2}(\sigma_2)$ for $\sigma_1 + \sigma_2 = 60°$ and $n_1 + n_2 = 2\ell + 1$, including the case of the most asymmetric molecule for which $E^*_{\ell n = \ell+1}(30°) = 0$.

Reference 2 presented the analytical forms for the lowest energy levels with $\ell = 1, 2, 3$. Here we quote only

$$\begin{aligned} E^*_{1,n} &= -\frac{\hbar^2}{2} e_n \qquad \text{for} \qquad n = 1, 2, 3, \\ E^*_{2,1} &= -\frac{3\hbar^2}{2}, \qquad\qquad E^*_{2,5} = \frac{3\hbar^2}{2}, \\ E^*_{2,n} &= -\frac{3\hbar^2}{2} e_{n-1} \qquad \text{for} \qquad n = 2, 3, 4. \end{aligned} \tag{33}$$

This allows us to recognize the cosine variations of the energy levels, according to Eqs. (15), as the asymmetry parameter changes in the frames for $\ell = 1$ and 2.

3.2. Eigenfunctions of rotational states

The diagonalizations of the matrices in Eqs. (26) - (28) also lead to accurate values of the eigenvectors $a_{\ell m_k}$ in the respective bases for $k = x, y, z$. The complete eigenfunctions in Eq. (29) $\Psi_{E^*\ell}$ are the same in the three bases, as constructed and illustrated in Fig. 2 for the specific case of $\ell = 4$. The forty-five entries are in correspondence with the energy levels in the associated part of Table I and Fig. 1.

For the prolate and oblate symmetric molecules, the eigenfunctions are directly the real and imaginary parts of respective spherical harmonics $|\ell m_x \pm\rangle$ and $|\ell m_z \pm\rangle$. They can be identified for $m = 0, 1, 2, 3, 4$ in ascending and decreasing

order in the left and right hand columns, respectively, recognizing the same shapes and the different orientations. Their circular-conical and meridian-plane nodes can be graphically identified.

Explicit numerical values of the energy eigenvalues $E^*_{\ell n}(\sigma)$ are included in Table II for the specific cases of $\ell = 4$ and 5, in order to illustrate the accuracy in their evaluation, as well as their variations and connections as functions of n and σ, as already discussed in the previous sections. The symmetries of the Hamiltonian are reflected in the "antisymmetry" in the energy-asymmetry parameter table relative to the most asymmetric molecule $n = \ell + 1$ state, and also in the invariance of the energy levels in the respective frames under a 180° degree rotation around the $(\sigma = 30^\circ, E^*_{\ell,n=\ell+1} = 0)$ center in the same plane. The evaluation of eigenenergies for higher values of ℓ well beyond those included in Refs. 2 and 3 can be done accurately and reliably.

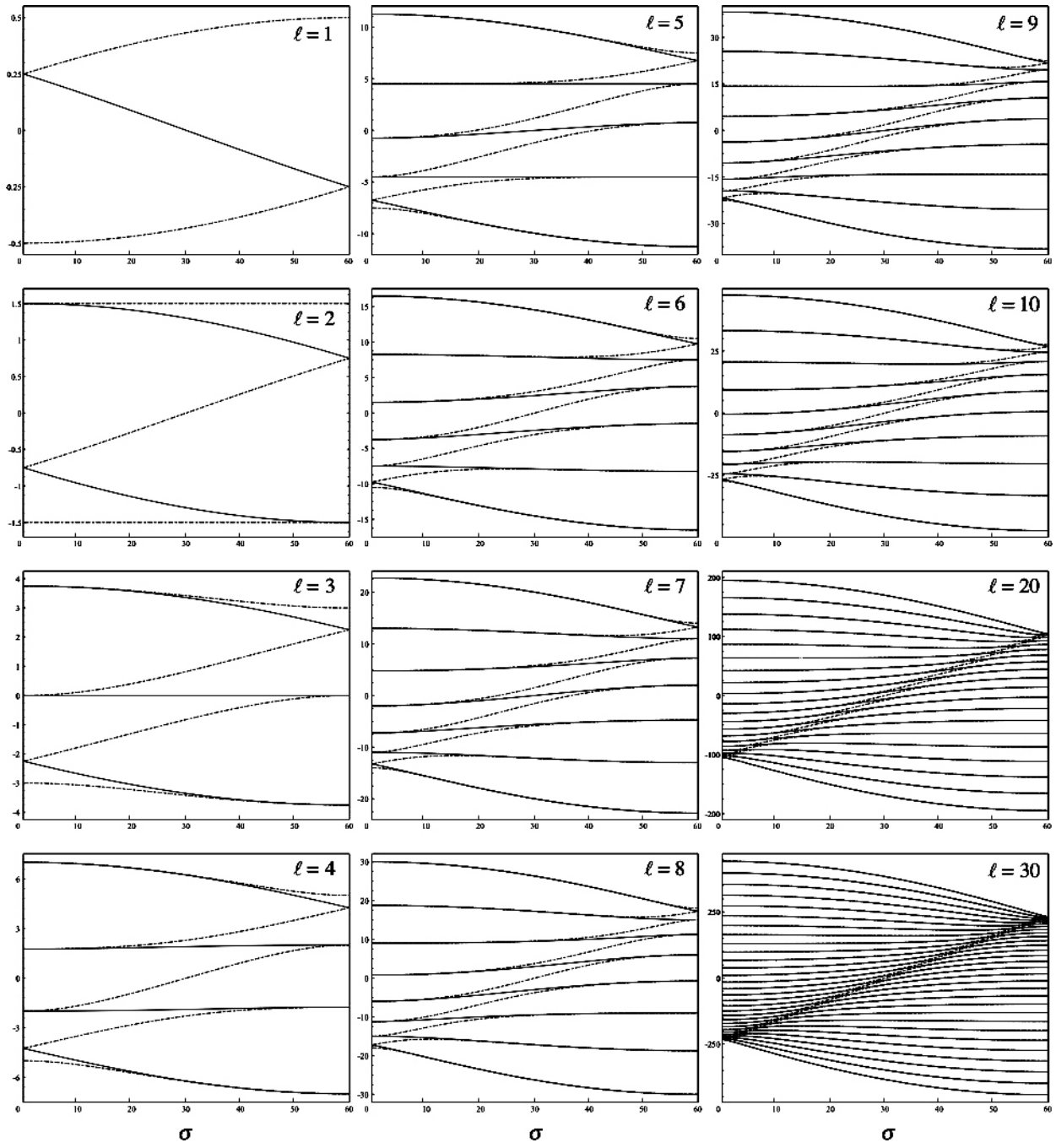

FIGURE 1. Energy spectra for states with $\ell = 0, 1, \ldots, 10, 20, 30$ and successive orders of excitation $n = 1, 2, \ldots, 2\ell + 1$, of molecules with different asymmetries $\sigma = [0^\circ, 60^\circ]$.

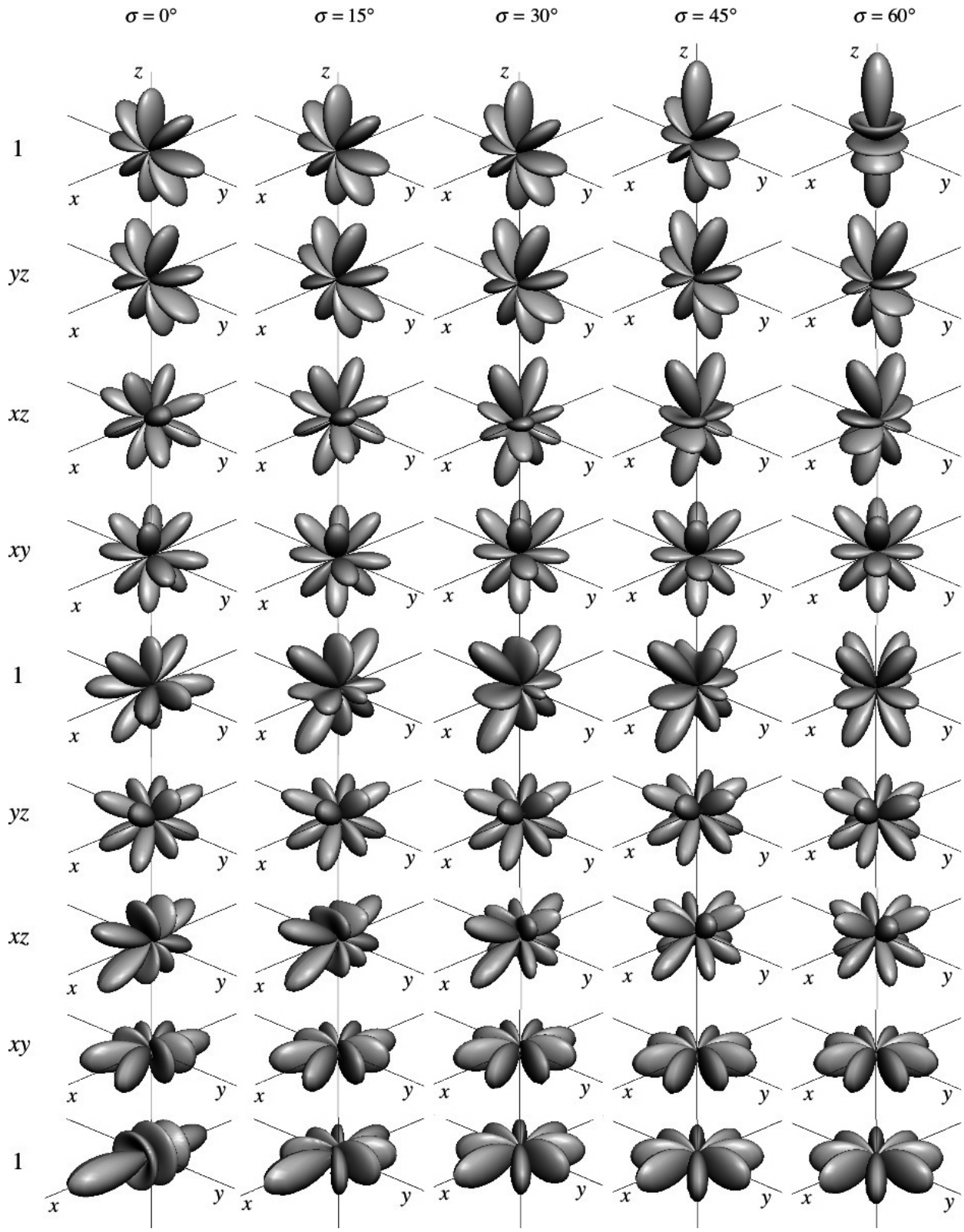

FIGURE 2. Eigenfunctions of rotational states with $\ell = 4$ and successive orders of excitation $n = 1, 2, \ldots, 9$ (from bottom to top) of molecules with asymmetries $\sigma = 0°, 15°, \ldots, 60°$. The entries on the left column describe the parity species of the respective wave functions in each row.

TABLE I. Energy eigenvalues $E^*_{\ell n}/\hbar^2$, for $\ell = 4$ and successive orders of excitation $n = 1, 2, \ldots, 9$ of molecules with different asymmetries $\sigma = 0^\circ, 15^\circ, \ldots, 60^\circ$.

σ	0°	15°	30°	45°	60°
$\ell = 4$					
1	-5	-5.47325098638820	-6.24499799839840	-6.80266075251004	-7
2	-4.25	-5.33848116723779	-6.22708271177908	-6.80174863502247	-7
3	-4.25	-3.14800932210267	-2.29128784747792	-1.85391409659007	-1.75
4	-2	-1.97211950357713	-1.89695569285688	-1.80294726130505	-1.75
5	-2	-1.32940976612184	0	1.32940976612184	2
6	1.75	1.80294726130506	1.89695569285688	1.97211950357713	2
7	1.75	1.85391409659007	2.29128784747792	3.14800932210267	4.25
8	7	6.80174863502247	6.22708271177908	5.33848116723779	4.25
9	7	6.80266075251004	6.24499799839840	5.47325098638820	5

TABLE II. Energy eigenvalues $E^*_{\ell n}/\hbar^2$, for $\ell = 5$ and successive orders of excitation $n = 1, 2, \ldots, 11$ of molecules with different asymmetries $\sigma = 0^\circ, 15^\circ, \ldots, 60^\circ$.

σ	0°	15°	30°	45°	60°
$\ell = 5\ n$					
1	-7.5	-8.53609003391197	-9.95422298349734	-10.9157869390600	-11.25
2	-6.75	-8.47438204173658	-9.94987437106620	-10.9156870109073	-11.25
3	-6.75	-5.30330085889910	-4.64443406791265	-4.50804116692859	-4.5
4	-4.5	-4.5	-4.5	-4.5	-4.5
5	-4.5	-3.21639483018463	-1.18540161279861	0.309185221261808	0.75
6	-0.75	-0.500162130901852	0	0.500162130901855	0.75
7	-0.75	-0.309185221261801	1.18540161279861	3.21639483018464	4.5
8	4.5	4.5	4.5	4.5	4.5
9	4.5	4.50804116692860	4.64443406791266	5.30330085889911	6.75
10	11.25	10.9156870109073	9.94987437106620	8.47438204173658	6.75
11	11.25	10.9157869390600	9.95422298349735	8.53609003391198	7.5

The eigenfunctions for the most asymmetric molecules are represented in the middle column. The fifth one at the center has parities $(+++)$, which it shares with its companions in the first and ninth rows, from top to bottom. The other states with parities $(+--)$, $(-+-)$, and $(--+)$ correspond to the second and sixth, third and seventh, and fourth and eighth rows, respectively.

The changes in the eigenfunctions of each species and excitation as the distribution of the asymmetry of the molecule changes can be followed by moving within each row. Notice that complementary rows $(n_1 + n_2 = 9)$ exhibit the same shapes with different orientations when moving in opposite directions. This behavior can be appreciated at the numerical level in Table I, giving the normalized eigenvectors in the basis $|\ell m_y\rangle$.

For the sake of space, the numerical results of Table II for $\ell = 5$ are not presented graphically, but they illustrate the corresponding behavior for the eigenfunctions for the negative parity states of species $(-++)$, $(+-+)$, $(++-)$, $(---)$.

4. Lamé functions, spheroconal harmonics and generating function

The rotational eigenenergies and eigenstates of asymmetric molecules - evaluated by the matrix method developed in Sec. 2, and illustrated by the Tables and Figures of Sec. 3 - are eigensolutions of the squares of the angular momentum, Eq. (2), and the related Hamiltonian operators of Eqs. (16) - (18).

The eigenfunctions of Eq. (29) can also be identified with the Lamé functions of Eq. (6), while the eigenvalues of ℓ and E^* may serve to evaluate the separation constants h_1 and h_2

associated with the respective Lamé differential Eqs. (7) expressed by the linear combinations [2]:

$$h_1 = \frac{\ell(\ell+1)e_3}{e_1-e_3} - \frac{2E^*}{\hbar^2(e_1-e_3)}, \tag{34}$$

$$h_2 = -\frac{\ell(\ell+1)e_1}{e_1-e_3} + \frac{2E^*}{\hbar^2(e_1-e_3)}. \tag{35}$$

In particular, the nodal surfaces of the wavefunctions illustrated in Fig. 2 can be identified as the elliptical cones with an axis along the z-axis or along the x-axis, defined by the fixed values of χ_1 or χ_2, respectively. More specifically, we make the explicit identification of the eigenfunctions in Eq. (29) with Their Lamé function product form:

$$\Psi(\chi_1,\chi_2) = \Lambda^A_{s_1}(\chi_1)\Lambda^B_{s_2}(\chi_2), \tag{36}$$

where

$$\begin{array}{rcccccccc} A & = & 1 & d & c & s & cs & ds & dc & dcs \\ B & = & 1 & s & c & d & cd & sd & sc & scd \\ AB & = & 1 & x & y & z & yz & xz & xy & xyz \end{array}$$

describe the classification of the parity eigenstates, consistent with Eqs. (4), and s_1 and s_2 count the number of nodes in the respective spheroconal angles, in such a way that $s_1+s_2=\ell$.

The spherical harmonics are eigenfunctions of the angular momentum operators $\hat{L}^2$ and $\hat{L}_k$. The rotational states of the asymmetric molecules are eigenfunctions of $\hat{L}^2$ and $\hat{H}^*$. The spherical harmonics are solutions of the Laplace equation

$$\nabla^2\phi(r,\theta,\varphi) = 0, \tag{37}$$

with complementary radial solutions

$$R(r) = Ar^{\ell} + Br^{-\ell-1}. \tag{38}$$

The Laplace equation is also separable into spheroconal coordinates, with solutions

$$\Phi(r,\chi_1,\chi_2) = R(r)\Psi_{E^*\ell}(\chi_1,\chi_2), \tag{39}$$

involving the same radial solutions of Eq. (38) and the spheroconal harmonics of Eq. (36).

The inverse of the distance between two points is known to be the generating function of the Legendre polynomials,

$$\frac{1}{|\vec{r}-\vec{r}'|} = \sum_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} P_\ell(\hat{\vec{r}}\cdot\hat{\vec{r}}'). \tag{40}$$

In turn, the Legendre polynomial via the addition theorem generates the spherical harmonics

$$P_\ell(\hat{\vec{r}}\cdot\hat{\vec{r}}') = \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{\ell} Y^*_{\ell m}(\theta',\varphi')Y_{\ell m}(\theta,\varphi). \tag{41}$$

The spherical harmonics $|\ell m\rangle$ and the spheroconal harmonics $\Psi_{E^*\ell}(\chi_1,\chi_2)$ are connected by Eq. (29), and by its inverse

$$|\ell m\rangle = \sum_A\sum_B\sum_{s_1}\sum_{s_2} \bar{a}^{\ell m}_{A,s_1,B,s_2}\Lambda^A_{s_1}(\chi_1)\Lambda^B_{s_2}(\chi_2). \tag{42}$$

Then it is straightforward to prove the addition theorem in terms of the spheroconal harmonics

$$P_\ell(\hat{\vec{r}}\cdot\hat{\vec{r}}') = \frac{4\pi}{2\ell+1} \times \sum_A\sum_B\sum_{s_1}\sum_{s_2} \Lambda^A_{s_1}(\chi_1')\Lambda^B_{s_2}(\chi_2')\Lambda^A_{s_1}(\chi_1)\Lambda^B_{s_2}(\chi_2), \tag{43}$$

for ℓ even, $AB = 1$, yz, xz, xy; and for ℓ odd, $AB = x$, y, z, xyz, using orthonormality of the transformations of Eqs. (29) and (42).

5. Discussion

This work provides a reliable and accurate method for evaluating the exact rotational eigenenergies and eigenstates of molecules with any asymmetry, using the matrix representation of the corresponding Hamiltonian in a basis of spherical harmonics Eqs. (26) - (28). This approach can be contrasted with the traditional treatments of the same problem using perturbation methods starting from the known results for prolate and oblate symmetric molecules [7–15]. A recent work has investigated the rotational states of the most asymmetric molecule obtaining very accurate numerical values, but still with the idea of making perturbation extensions from that case [3]. The method introduced in the present investigation supersedes in practice the need for perturbation treatments, providing accurate exact results for any asymmetry and any order of excitation, as illustrated in section 3..

Section 4 puts the spherical harmonics and the spheroconal harmonics on an equal footing. Both are useful in the description of rotations: the spherical ones when there is an axis of rotational symmetry, and the spherconal ones when there is no such an axis. Their harmonic nature also makes it possible to identify common generating functions for both of them. Here we have limited the discussion to the Coulomb potential, Eq. (40), and the addition theorem, Eqs. (41) and (43).

The connection with the Lamé functions has also been identified, including the accurate determination of the separation constants h_1 and h_2 Eqs. (34) - (35), which in turn permits the evaluation of the functions themselves. While doing this work, we have formulated an alternative and independent matrix method to evaluate the Lamé functions per se, and also identified other generating functions [19]. The corresponding results will be reported in a companion article.

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