The rotational spectra of the most asymmetric molecules

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We consider the Schrödinger equation for the rotational spectra of the most asymmetric molecules. The energy eigenfunctions are also eigenfunctions of the square of the angular momentum vector and of one component of the angular momentum in the inertial frame. We follow our point of view in which the properties of the angular momentum spectra are used to delete, without loss of generality, one constant of motion and one of the Euler's angles. Then, instead of using Euler's angles, the Schrödinger equation and the energy eigenfunctions are expressed in terms of spheroconal coordinates in which that equation may be separable.

The most asymmetric case is specially analyzed. The characteristic symmetries of this problem are used to reduce the number of differential equations considered and the number of steps for a complete solution.

Keywords: Asymmetric molecule; rotation spectrum; spheroconal coordinates; Lamé equation.

Se considera la ecuación de Schrödinger de las moléculas más asimétricas. Las eigenfunciones de la energía son también funciones propias del cuadrado del momento angular y de una componente del momento angular en el sistema inercial. Seguimos nuestro punto de vista en que las propiedades del espectro del momento angular se usan para suprimir, sin pérdida de generalidad, una constante de movimiento y uno de los ángulos de Euler. La ecuación de Schrödinger y las eigenfunciones de la energía se expresan en función de coordenadas esferoconales en las cuales dicha ecuación es separable.

Se analiza en especial el caso más asimétrico. Las simetrías características de este caso se usan para reducir el número de ecuaciones diferenciales a considerar y el número de pasos para una solución completa.

Descriptores: Molécula más asimétrica; espectro rotacional; coordenadas esferoconales; ecuación de Lamé.

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1. Introduction

The study of the rigid body has a very old history that is still far from finished because of the incomplete knowledge of the analytical properties of the spectra of the quantum rigid body. The torque-free rigid body has been solved in Classical [1] and Quantum Mechanics [2], but the known solution is far from explicit. Our task has been to make explicit many aspects of this problem and its solutions.

The hamiltonian of the rigid motion of a molecule may be indicated by the same expression as that of classical kinetic energy

$$H = \mathbf{L}^{\mathrm{T}}\mathbf{I}^{-1}\mathbf{L}/2\,, \tag{1}$$

provided $\mathbf{L}$ is interpreted as the angular momentum vector operator in the fixed frame that has been generally expressed in terms of Euler angles.

The components of the angular momentum vector operator as a function of the three Euler angles in the body frame are

$$L_x = -\mathrm{i}\hbar\left[\cos\psi\frac{\partial}{\partial\theta} - \cot\theta\,\sin\psi\frac{\partial}{\partial\psi} + \frac{\sin\psi}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$L_y = -\mathrm{i}\hbar\left[-\sin\psi\frac{\partial}{\partial\theta} - \cot\theta\,\cos\psi\frac{\partial}{\partial\psi} + \frac{\cos\psi}{\sin\theta}\frac{\partial}{\partial\phi}\right] \tag{2}$$

$$L_z = -\mathrm{i}\hbar\frac{\partial}{\partial\psi},$$

and the components of the angular momentum vector in the inertial frame result in

$$M_x = -\mathrm{i}\hbar\left[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\,\sin\phi\frac{\partial}{\partial\phi} + \frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial\psi}\right]$$

$$M_y = -\mathrm{i}\hbar\left[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\,\cos\phi\frac{\partial}{\partial\phi} - \frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\psi}\right] \tag{3}$$

$$M_z = -\mathrm{i}\hbar\frac{\partial}{\partial\phi}.$$

These equations imply a definition of Euler angles where the angle of the second rotation is measured from the x axis, whereas it is the y axis that is used in Ref. 6. It follows that the α, β, γ, Euler angles of those authors correspond in our notation to $\alpha = \phi - \pi/2$, $\beta = \theta$, $\gamma = \psi + \pi/2$. These equations provide us with an easy comparison of corresponding quantities.

The physical information in Quantum Mechanics is obtained by solving the Schrödinger equation

$$H\Psi = E\Psi\,, \tag{4}$$

where H is the hamiltonian operator, E is a real constant and Ψ is a well-behaved complex function. Assuming a free top, the Hamiltonian operator is equal to the kinetic energy operator (1).

Actually, the Schrödinger equation has an infinite number of solutions which should be classified by the use of other operators, commuting with the Hamiltonian. Commutators in Quantum Mechanics correspond (except by a constant factor i$\hbar$) to the Poisson brackets of Classical Mechanics.

The useful operators commuting with the Hamiltonian are the $\mathbf{L}^2$ and M_z operators. These two also commute among themselves. We look for common eigenfunctions, by solving the Schrödinger equation and asking the eigenfunctions to be simultaneously solutions to the equations

$$\mathbf{L}^2\Psi = \hbar^2\ell(\ell+1)\Psi, \quad M_z\Psi = \hbar m\Psi, \tag{5}$$

where ℓ and m are integers, restricted by the condition

$$-\ell \leq m \leq \ell. \tag{6}$$

These are very well-known properties of Angular Momentum Theory [6].

The theory also includes the fact that operators $M_x \pm iM_y$ acting on a common solution of Eqs. (4) and (5) give a solution to the same equations with the same value E and ℓ but in which the integer m is increased or reduced by one unit. This useful property is used here to consider the common solutions having E and ℓ, with $m = 0$.

The remaining functions with $m \neq 0$ can then constructed by successive application of those operators.

Substitution of the explicit form of operator M_z in Euler variables (for $m = 0$) implies that the Ψ function will not be a function of angle ϕ; the $\mathbf{L}$ operator is also simplified since in this case derivatives with respect to ϕ can be deleted. The angular momentum operator in the body frame becomes

$$\begin{aligned} L_x &= -\mathrm{i}\hbar\left[\cos\psi\frac{\partial}{\partial\theta} - \cot\theta\sin\psi\frac{\partial}{\partial\psi}\right] \\ L_y &= -\mathrm{i}\hbar\left[-\sin\psi\frac{\partial}{\partial\theta} - \cot\theta\cos\psi\frac{\partial}{\partial\psi}\right] \\ L_z &= -\mathrm{i}\hbar\frac{\partial}{\partial\psi}. \end{aligned} \tag{7}$$

These operators are essentially the same as those found in the Quantum Mechanics of the hydrogen atom, except for the sign and the transformation $\psi = \pi/2 - \varphi$. The change of sign is irrelevant, as operators appear in the equations in quadratic form.

We ask the Ψ function to satisfy the following two equations in terms of the new $\mathbf{L}$ operator (7):

$$(L_x^2 + L_y^2 + L_z^2)\Psi = \hbar^2\ell(\ell+1)\Psi \tag{8}$$

and

$$(L_x^2/I_1 + L_y^2/I_2 + L_z^2/I_3)\Psi = 2E\Psi, \tag{9}$$

and some simplification of the problem is obtained when one takes a linear combination of these two equations to reduce the number of independent parameters. We define

$$1/I_j = Q + Pe_j, \tag{10}$$

and one imposes two restrictions on the e_j constants, namely

$$e_1 + e_2 + e_3 = 0 \tag{11}$$

$$e_1^2 + e_2^2 + e_3^2 = 3/2, \tag{12}$$

and the constants Q and P are determined by the inertia moments as

$$3Q = 1/I_1 + 1/I_2 + 1/I_3 \tag{13}$$

$$9P^2/2 = (1/I_1 - 1/I_2)^2 + (1/I_3 - 1/I_1)^2 + (1/I_2 - 1/I_3)^2. \tag{14}$$

The three parameters e_j can be written in terms of only one parameter σ:

$$\begin{aligned} e_1 &= \cos\sigma \\ e_2 &= \cos(\sigma - 2\pi/3) \\ e_3 &= \cos(\sigma + 2\pi/3) \qquad (0 \leq \sigma \leq \pi/3), \end{aligned} \tag{15}$$

where the value $\sigma = 0$ corresponds to the prolate symmetric top and the value $\sigma = \pi/3$ to the oblate symmetric case. The case $\sigma = \pi/6$ is the most asymmetric.

The energy value E becomes

$$2\,E = Q\hbar^2\ell(\ell+1) + 2\,PE^*, \tag{16}$$

where E^* is the constant eigenvalue of equation

$$2H^*\Psi = (e_1L_x^2 + e_2L_y^2 + e_3L_z^2)\Psi = 2E^*\Psi. \tag{17}$$

We look for simultaneous solutions to the Eq. (17) and (8).

In this system of equations, the three inertia moments have been replaced by only one parameter σ.

Many authors use a different asymmetry parameter κ introduced by Ray [7]. Our parameters are related to his by

$$e_1 = \cos\sigma = \frac{3-\kappa}{2\sqrt{3+\kappa^2}} \tag{18}$$

and Ray's energy $E(\kappa)$ can be expressed in terms of our reduced energy E^* as

$$E(\kappa) = \frac{\kappa}{3}\hbar^2\ell(\ell+1) + \sqrt{\frac{4}{3} + \frac{4}{9}\kappa^2}\,E^*. \tag{19}$$

The use of different parameters follows the use in mathematics where the parameters e_1, e_2 and e_3 are frequently found according to the masterly works of Weierstrass in the theory of elliptic functions.

The equations are separable by using the spheroconal coordinates χ_1, χ_2, defined [8] in terms of Jacobi elliptic functions

$$\mathbf{u} = \begin{pmatrix} \sin\theta\sin\psi \\ \sin\theta\cos\psi \\ \cos\theta \end{pmatrix} = \begin{pmatrix} \mathrm{dn}(\chi_1,k_1)\mathrm{sn}(\chi_2,k_2) \\ \mathrm{cn}(\chi_1,k_1)\mathrm{cn}(\chi_2,k_2) \\ \mathrm{sn}(\chi_1,k_1)\mathrm{dn}(\chi_2,k_2) \end{pmatrix}, \quad (20)$$

where $\mathbf{u}$ is the unit vector that is rotated by the rotation matrix in the constant vector

$$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

and where k_1 and k_2 are defined by

$$k_1^2 = \frac{e_2 - e_3}{e_1 - e_3}, \quad k_2^2 = \frac{e_1 - e_2}{e_1 - e_3}. \quad (21)$$

In these coordinates, when Ψ is factored into the product

$$\Psi = \Lambda_1(\chi_1)\Lambda_2(\chi_2), \quad (22)$$

Eq. (17) and (8) are separated into two Lamé's equations [9]

$$\frac{d^2\Lambda_j}{d\chi_j^2} - [k_j^2\ell(\ell+1)\mathrm{sn}^2(\chi_j,k_j) + h_j]\Lambda_j = 0 \quad (23)$$

$$(j = 1, 2),$$

written in terms of the separation constants

$$h_1 = -\frac{2E^*}{\hbar^2(e_1 - e_3)} + \frac{\ell(\ell+1)e_3}{e_1 - e_3}$$
$$h_2 = -\ell(\ell+1) - h_1 \,. \quad (24)$$

Lamé's equation has been studied for a long time, and many useful results are found in the last chapter of Whittaker and Watson's book of Analysis [9].

In particular, for $\ell = 2n$ (an even integer), the function Ψ can be written in terms of the unit vector $\mathbf{u}$ in (50) as one of four different classes of the form

$$\prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$$
$$u_y u_z \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$$
$$u_z u_x \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u} \quad (25)$$
$$u_x u_y \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u},$$

with $n+1$ functions of the first class and n functions of each of the other three classes.

For $\ell = 2n+1$ (an odd integer), one has n functions of the class

$$u_x u_y u_z \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$$

and $n+1$ functions of each of the classes

$$u_x \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$$
$$u_y \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u} \quad (26)$$
$$u_z \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u},$$

where matrix $\mathcal{A}(\alpha)$ is defined in terms of their inverse matrix,

$$\mathcal{A}^{-1}(\alpha) = \begin{pmatrix} e_1 & 0 & 0 \\ 0 & e_2 & 0 \\ 0 & 0 & e_3 \end{pmatrix} - \alpha \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (27)$$

and where the parameters α are computed to satisfy Lamé's differential equation.

Each term in the wave functions is a linear combination of an ℓ number of factors of components of the vector $\mathbf{u}$.

A direct calculation leads to

$$\mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha)\mathbf{u} = \frac{\{\mathcal{P}_1(\chi_1) - \alpha\}\{\mathcal{P}_2(\chi_2) - \alpha\}}{\{e_1 - \alpha\}\{e_2 - \alpha\}\{e_3 - \alpha\}}, \quad (28)$$

in terms of the functions

$$\mathcal{P}_1(\chi_1) = e_3 + (e_2 - e_3)\mathrm{sn}^2(\chi_1, k_1)$$
$$\mathcal{P}_2(\chi_2) = e_1 + (e_2 - e_1)\mathrm{sn}^2(\chi_2, k_2), \quad (29)$$

and therefore the α's are the roots of two polynomials in terms of functions $\mathcal{P}_1(\chi_1)$ and $\mathcal{P}_2(\chi_2)$.

The Hamiltonian is invariant with respect to a change of sign of each of the components of vector $\mathbf{u}$. These three changes of sign and the identity constitute the four-component group V that is basic [10] to the Quantum Mechanics of the rigid molecule. Each of these transformations allows us to classify the classes of wave functions according to the parity associated with the group elements [11].

The parity of the functions for ℓ an even number is collected in the Table I.

TABLE I. Classification of the eigenfunctions according to the V group for even ℓ.

name	Φ	u_x	u_y	u_z
symmetric	$\prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$	even	even	even
x type	$u_y u_z \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$	even	odd	odd
y type	$u_z u_x \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$	odd	even	odd
z type	$u_x u_y \prod_j \mathbf{u}^{\mathrm{T}}\mathcal{A}(\alpha_j)\mathbf{u}$	odd	odd	even

TABLE II. Classification of the eigenfunctions according to the V group for odd ℓ.

name	Φ	u_x	u_y	u_z
symmetric	$u_x u_y u_z \prod_j \mathbf{u}^{\mathrm{T}} \mathcal{A}(\alpha_j)\mathbf{u}$	odd	odd	odd
x type	$u_x \prod_j \mathbf{u}^{\mathrm{T}} \mathcal{A}(\alpha_j)\mathbf{u}$	odd	even	even
y type	$u_y \prod_j \mathbf{u}^{\mathrm{T}} \mathcal{A}(\alpha_j)\mathbf{u}$	even	odd	even
z type	$u_z \prod_j \mathbf{u}^{\mathrm{T}} \mathcal{A}(\alpha_j)\mathbf{u}$	even	even	odd

The parity of the functions for ℓ an odd number become Table II.

For the symmetric cases, the wave functions may be chosen to be the spherical harmonics $Y_{\ell\mathcal{M}}(\theta,\psi)$, with $-\ell \le \mathcal{M} \le \ell$, that are also found in the quantum solution of the hydrogen atom. But, because the Hamiltonian is quadratic in the angular momentum components one has, for the symmetric cases, a double degeneracy in the energy levels that are conveniently labelled with the integer $\pm\mathcal{M}$. In those cases it is better to use the wave functions $(Y_{\ell,\mathcal{M}} \pm Y_{\ell,-\mathcal{M}})/\sqrt{2}$, which are real functions and can be written in the forms (25) and (26), and classified by means of the elements of the group V into four types associated with the parity. This change of base functions was introduced by Wang [12] in one of the pioneer works on quantum theory of asymmetric molecules using matrix notation.

These wave functions in the oblate case ($\sigma = \pi/3$) are

$$\Psi^c_{\ell\mathcal{M}} = \left[\frac{(2\ell+1)(\ell-\mathcal{M})!}{8\pi(\ell+\mathcal{M})!}\right]^{1/2} P_\ell^{\mathcal{M}}(\cos\theta)\cos\mathcal{M}\psi \quad (30)$$

$$\Psi^s_{\ell\mathcal{M}} = \left[\frac{(2\ell+1)(\ell-\mathcal{M})!}{8\pi(\ell+\mathcal{M})!}\right]^{1/2} P_\ell^{\mathcal{M}}(\cos\theta)\sin\mathcal{M}\psi, \quad (31)$$

where $0 < \mathcal{M} \le \ell$, and

$$\Psi_{\ell 0} = \left[\frac{(2\ell+1)}{4\pi}\right]^{1/2} P_\ell(\cos\theta). \quad (32)$$

These real functions are easily classified according to the V group [11] as is shown in the Table III.

2. The most asymmetric molecule

The most asymmetric case occurs for the value $\sigma = \pi/6$, which is equidistant between the prolate and oblate symmetric cases. For this case $e_2 = 0$ and Ray's parameter is also $\kappa = 0$. The most asymmetric case is invariant under the transformation $\sigma \to \pi/3 - \sigma$, and one can expect some simplification vis-à-vis the general case. For example, the parameters k_1 and k_2 become the same:

$$k_1^2 = k_2^2 = 1/2. \quad (33)$$

We shall now study some properties of this case.

Making the change of variable

$$x = \mathcal{P}_1(\chi_1), \quad (34)$$

Lamé's equation (23) takes the algebraic form [9]

$$\frac{d^2\Lambda}{dx^2} + \left[\frac{1/2}{x-e_1} + \frac{1/2}{x-e_2} + \frac{1/2}{x-e_3}\right]\frac{d\Lambda}{dx} - \frac{\ell(\ell+1)x - 2E^*/\hbar^2}{4(x-e_1)(x-e_2)(x-e_3)}\Lambda = 0, \quad (35)$$

which in the most asymmetric case becomes

$$2w(1-w^2)\frac{d^2\Lambda(w)}{dw^2} + (1-3w^2)\frac{d\Lambda(w)}{dw} - \left(\frac{\ell(\ell+1)}{2}w + b\right)\Lambda(w) = 0, \quad (36)$$

where one makes the change of variable $x = \sqrt{3}w/2$ with $2E^*/\hbar^2 = -\sqrt{3}b$.

Solutions to this differential equation are found to be of eight types, seven of which are the product of a square root times a polynomial in w, whereas one of the eight is just a polynomial. See the Table IV, where $P(w)$ denotes different polynomials.

Given one solution to this equation $\Lambda(w)$ for particular values of the integer ℓ, and the separation constant b, then $\Lambda(-w)$ is also a solution, with the same ℓ, but separation constant $-b$. This property causes a simplification in obtaining the solutions to the Lamé equation in this most asymmetric case.

We found that for each of the type s and y functions, the separation constants with $b \neq 0$ come in a couple of the two allowed values $\pm b$. The corresponding polynomial is different only in the sign of the odd powers of w. For these two types of functions y and s, one finds the possibility of the value $b = 0$, occurring only once for each ℓ value. If the reminder after dividing ℓ by 4 is 1 or 2, then the function co-

TABLE III. Classification of the oblate functions according to the V group.

	$\Psi^c_{\ell\mathcal{M}}$	$\Psi^s_{\ell\mathcal{M}}$	$\Psi_{\ell 0}$
symmetric	even ℓ, even $\mathcal{M}$	odd ℓ, even $\mathcal{M}$	even ℓ
x type	odd ℓ, odd $\mathcal{M}$	even ℓ, odd $\mathcal{M}$	
y type	even ℓ, odd $\mathcal{M}$	odd ℓ, odd $\mathcal{M}$	
z type	odd ℓ, even $\mathcal{M}$	even ℓ, even $\mathcal{M}$	odd ℓ

TABLE IV. Classification of the most asymmetric functions according to the V group.

	$\Lambda(w)$, even ℓ	$\Lambda(w)$, odd ℓ
symmetric	$P(w)$	$\sqrt{w(1-w^2)}P(w)$
x type	$\sqrt{w(1-w)}P(w)$	$\sqrt{1+w}P(w)$
y type	$\sqrt{1-w^2}P(w)$	$\sqrt{w}P(w)$
z type	$\sqrt{w(1+w)}P(w)$	$\sqrt{1-w}P(w)$

rresponding to this value $b = 0$ is of type y. If the reminder after dividing ℓ by 4 is 3 or 0, then the function corresponding to the value $b = 0$ is of type s. The polynomials $P(w)$ when $b = 0$ are even functions, formed only by even powers of w.

On the other hand functions of type x and z never correspond to the null value of b. Moreover, for any eigenfunction of type x, with eigenvalue b and polynomial $P(w)$, there exists an eigenfunction of type z with eigenvalue $-b$ and polynomial $P(-w)$, having a sign difference for the coefficients of the odd powers. These characteristics of the most asymmetric case allow us to ignore the functions of type z since it is implicit in its partner of type x.

Let us consider first the particular solution belonging to the most asymmetrical Lamé equation with a zero value for constant b. In this case, the Lamé functions could be written in terms of Jacobi polynomials that obey the differential equation [13]:

$$y(1-y)\frac{d^2 f_n(y)}{dy^2} + [\gamma - y(1+\alpha)]\frac{df_n(y)}{dy} + n(n+\alpha)f_n(y) = 0. \quad (37)$$

When $\ell = 4n$, $(n = 0, 1, 2, \ldots)$, and $b = 0$, the solution to the Lamé equation is of type s. The associated equation (36 with $b = 0$) has also been considered in the context of Classical Mechanics as a particular case of Hill's equation [14], but without identifying it as a Jacobi equation with Jacobi polynomials as solutions for it.

When $\ell = 4n$, $(n = 0, 1, 2, \ldots)$, the solution to Lamé's equation (36 with $b = 0$) is of the form

$$\Lambda_{4n,0}(w) = f_n(1/4, 3/4, w^2), \quad (38)$$

When $\ell = 4n + 1$, $(n = 0, 1, 2, \ldots)$, the solution of Lamé's equation (36 with $b = 0$) is of the form

$$\Lambda_{4n+1,0}(w) = \sqrt{w} f_n(3/4, 5/4, w^2)\,. \quad (39)$$

In the case $\ell = 4n + 2$ $(n = 0, 1, 2, \ldots)$, the solution of Lamé's equation (36 with $b = 0$) is of the form

$$\Lambda_{4n+2,0}(w) = \sqrt{1-w^2} f_n(5/4, 3/4, w^2)\,. \quad (40)$$

And in the case $\ell = 4n + 3$ $(n = 0, 1, 2, \ldots)$, the solution of Lamé's equation (36 with $b = 0$) is of the form

$$\Lambda_{4n+3,0}(w) = \sqrt{w(1-w^2)} f_n(7/4, 5/4, w^2)\,. \quad (41)$$

The most asymmetrical Lamé's functions can be constructed by means of the ladder operators [15] with ℓ jumping by four:

$$\left[2w(1-w^2)\frac{d}{dw} + (\ell+4)\left(w^2 - \frac{\ell+2}{2\ell+5}\right)\right]\Lambda_{\ell+4,0} = \frac{\sqrt{(\ell+1)(\ell+2)(\ell+3)(\ell+4)}}{2\ell+5}\Lambda_{\ell,0} \quad (42)$$

and

$$\left[2w(1-w^2)\frac{d}{dw} - (\ell+1)\left(w^2 - \frac{\ell+3}{2\ell+5}\right)\right]\Lambda_{\ell,0} = -\frac{\sqrt{(\ell+1)(\ell+2)(\ell+3)(\ell+4)}}{2\ell+5}\Lambda_{\ell+4,0}, \quad (43)$$

where normalization factors were assumed so as to make the right hand side of these equations similar.

Below, we shall study the cases in which $b \neq 0$ and there are 6 types of functions occupying the upper positions in Table IV, excluding the type z. We shall write the differential equations for the polynomials without the root factor.

2.1. Type s, even ℓ

In the symmetric case, with even ℓ, the differential equation satisfied by the polynomial is the same (36):

$$2w(1-w^2)\frac{d^2P(w)}{dw^2} + (1-3w^2)\frac{dP(w)}{dw} + \left(\frac{\ell(\ell+1)}{2}w + b\right)P(w) = 0\,. \quad (44)$$

We substitute into it the polynomial

$$P(w) = \sum_{j=0}^{k} a_j w^j \quad (45)$$

setting the coefficients of all the powers of w equal to zero. We then find the following results:
1.1 The degree of the polynomial is $k = \ell/2$.
1.2 One has $k + 1$ homogeneous linear equations relating the $k + 1$ coefficients of the polynomial. The matrix of this system of linear equations is a function of the parameter b. The non-trivial solution exists only when the determinant is zero; this determines $k + 1$ different values of b. Each value provides a different polynomial. The coefficients of the polynomial can be found by recurrence, starting from b and a_0.
1.3 The explicit forms of the equations for the coefficients are

$$\begin{aligned}
&ba_0 + a_1 = 0\\
&(2m+1)(m+1)a_{m+1} + ba_m\\
&\qquad + (\ell/2 - m + 1)(\ell - 1 + 2m)a_{m-1} = 0\\
&\qquad\qquad (m = 1, 2, \ldots, k-1)\\
&(\ell/2 - k + 1)(2k - 1 + \ell)a_{k-1} + ba_k = 0.
\end{aligned} \quad (46)$$

1.4 The matrix of the above system of equations is tridiagonal. The determinant of this matrix produces the eigenvalues b. The tridiagonal form of the matrix allows us to obtain the determinant by recurrence [16], by means of a family of polynomials in b. Each of these polynomials of degree j is the determinant of the submatrix of dimension $j \times j$. We define $y_0 = 1$, $y_1(b) = b$, and

$$y_{j+1}(b) = by_j(b) - A_j y_{j-1}(b), \quad (j = 1, 2, \ldots, k) \quad (47)$$

where A_j is the product of two entries of the tridiagonal matrix at both sides of the main diagonal at positions $(j, j+1)$ and $(j+1, j)$

$$A_j = j(2j-1)\left[\frac{\ell(\ell+1)}{2} - (j-1)(2j-1)\right]. \qquad (48)$$

The characteristic polynomial for determining the values of b is $y_{k+1}(b)$.

In a similar way, one writes and solves the differential equations for the other 5 types of polynomials. The differential equation is different in each case since the root factor has been deleted. The set of linear equations for the coefficients is also different. But in every case we use the same method of solution, and in each case the matrix for the coefficients of the polynomial is tridiagonal, and therefore the algebraic equation for the eigenvalue b is obtained by a similar recurrence with different A_j constants.

2.2. Type y, even ℓ

The substitution of the case $\Lambda(w) = \sqrt{1-w^2}P(w)$ in (36) gives the following equation for the polynomial $P(w)$:

$$2w(1-w^2)\frac{d^2P(w)}{dw^2} + (1-7w^2)\frac{dP(w)}{dw} + \left(\frac{(\ell-2)(\ell+3)}{2}w + b\right)P(w) = 0. \qquad (49)$$

By substituting into (49) the polynomial (45)

$$P(w) = \sum_{j=0}^{k} a_j w^j \qquad (50)$$

and by setting the coefficients of all the powers of w equal to zero, we found that:

2.1 The degree of the polynomial is $k = \ell/2 - 1$.

2.2 There are $k+1$ homogeneous linear equations relating the $k+1$ coefficients of the polynomial. The matrix of this new system of linear equations is again a function of the parameter b. The non-trivial solution exists only when the determinant is zero; this determines $k+1$ different values of b. Each value provides a different polynomial, and as before the coefficients of the polynomial are obtained by recurrence starting from b and a_0.

2.3 The explicit form of the equations for the coefficients is

$$\begin{aligned}
&ba_0 + a_1 = 0\\
&(2m+1)(m+1)a_{m+1} + ba_m\\
&\qquad + (\ell/2-m)(\ell+1+2m)a_{m-1} = 0\\
&\qquad\qquad (m = 1, 2, ..., k-1)\\
&(\ell/2-k)(2k+1+\ell)a_{k-1} + ba_k = 0. \qquad (51)
\end{aligned}$$

2.4 This recurrence produces the family of polynomials of degree j equal to the determinant of the submatrix of dimension $j \times j$. We again define $y_0 = 1$, $y_1(b) = b$, and

$$y_{j+1}(b) = by_j(b) - A_j y_{j-1}(b), \quad (j = 1, 2, \ldots, k) \qquad (52)$$

where A_j is the product of the two entries of the tridiagonal matrix on both sides of the main diagonal at positions $(j, j+1)$ and $(j+1, j)$:

$$A_j = j(2j-1)[\frac{\ell(\ell+1)}{2} - j(2j+1)]. \qquad (53)$$

The characteristic polynomial for determining the values of b is $y_{k+1}(b)$.

2.3. Type x, even ℓ

The substitution of the case $\Lambda(w) = \sqrt{w(1-w)}P(w)$ in (36) gives the following equation for the polynomial $P(w)$:

$$2w(1-w^2)\frac{d^2P(w)}{dw^2} + (3-2w-7w^2)\frac{dP(w)}{dw} + \left(\frac{(\ell-2)(\ell+3)}{2}w + b - 3/2\right)P(w) = 0. \qquad (54)$$

In analogous way to the previous cases, take the polynomial (45)

$$P(w) = \sum_{j=0}^{k} a_j w^j \qquad (55)$$

to substitute in Eq. (54), set the coefficients of all the powers of w equal to zero. The following results are obtained:

3.1 The degree of the polynomial is $k = \ell/2 - 1$.

3.2 We have $k+1$ homogeneous linear equations relating the $k+1$ coefficients of the polynomial. The matrix of this system of linear equations is a function of the parameter b. The non trivial solution exists only when the determinant of the system is equal to zero; this determines $k+1$ different values of b. Each value of b provides a different polynomial. The coefficients of the polynomial can be found by recurrence, starting from b and a_0.

3.3 The explicit form of the equations for the coefficients is

$$\begin{aligned}
&(b-3/2)a_0 + 3a_1 = 0\\
&(2m+3)(m+1)a_{m+1} + [b - 3/2 - 2m]a_m\\
&\qquad + (\ell/2-m)(\ell+1+2m)a_{m-1} = 0\\
&\qquad\qquad (m = 1, 2, ..., k-1)\\
&(\ell/2-k)(2k+1+\ell)a_{k-1} + (b - 3/2 - 2k)a_k = 0. \qquad (56)
\end{aligned}$$

3.4 The recurrence produces the family of polynomials of degree j equal to the determinant of the submatrix of dimension $j \times j$. We define here $y_0 = 1$, $y_1(b) = b - 3/2$, and

$$y_{j+1}(b) = (b - 2j - 3/2)y_j(b) - A_j y_{j-1}(b), \quad (j = 1, 2, ..., k) \qquad (57)$$

where A_j is the product of the two entries of the tridiagonal matrix at both sides of the main diagonal at positions $(j, j+1)$ and $(j+1, j)$

$$A_j = j(2j+1)\left[\frac{\ell(\ell+1)}{2} - j(2j+1)\right]. \qquad (58)$$

The characteristic polynomial to determine the values of b is $y_{k+1}(b)$.

2.4. Type s, odd ℓ

The substitution of the case $\Lambda(w) = \sqrt{w(1-w^2)}P(w)$ in (36) gives the following equation for the polynomial $P(w)$:

$$2w(1-w^2)\frac{d^2P(w)}{dw^2} + (3-9w^2)\frac{dP(w)}{dw} + \left(\frac{(\ell-3)(\ell+4)}{2}w + b\right)P(w) = 0. \quad (59)$$

We substitute into it the polynomial (45)

$$P(w) = \sum_{j=0}^{k} a_j w^j, \quad (60)$$

setting the coefficients of all the powers of w equal to zero. We find the following results:

4.1 The degree of the polynomial is $k = (\ell-3)/2$.

4.2 A number of $k+1 = (\ell-1)/2$ homogeneous linear equations relate the $k+1$ coefficients of the polynomial. The matrix of this system of linear equations is a function of the eigenvalue b. The non trivial solution exists only when the determinant is zero; this leads $k+1$ different values of b. Each value determines a different polynomial. The coefficients of the polynomial can be found by recurrence, starting from b and a_0.

4.3 The explicit form of the equations for the coefficients is

$$\begin{aligned} &ba_0 + 3a_1 = 0 \\ &(2m+3)(m+1)a_{m+1} + ba_m \\ &\qquad + [\ell(\ell+1)/2 - (m+1)(2m+1)]a_{m-1} = 0 \\ &\qquad\qquad (m = 1, 2, \ldots, k-1) \\ &(\ell/2 + k + 1)(\ell - 2k - 1)a_{k-1} + ba_k = 0. \end{aligned} \quad (61)$$

4.4 A recurrence also produces a family of polynomials of degree j equal to the determinant of the submatrix of dimension $j \times j$. We again define $y_0 = 1$, $y_1(b) = b$, and

$$y_{j+1}(b) = by_j(b) - A_j y_{j-1}(b)\,, \quad (j = 1, 2, ..., k) \quad (62)$$

where A_j is the product of the two entries of the tridiagonal matrix on both sides of the main diagonal at the entries $(j, j+1)$ and $(j+1, j)$:

$$A_j = j(2j+1)[\frac{\ell(\ell+1)}{2} - (j+1)(2j+1)]\,. \quad (63)$$

The characteristic polynomial that determines the values of b is $y_{k+1}(b)$.

2.5. Type y, odd ℓ

The substitution of the case $\Lambda(w) = \sqrt{w}P(w)$ in (36) gives the following equation for the polynomial $P(w)$:

$$2w(1-w^2)\frac{d^2P(w)}{dw^2} + (3-5w^2)\frac{dP(w)}{dw} + \left(\frac{(\ell-1)(\ell+2)}{2}w + b\right)P(w) = 0. \quad (64)$$

Let us again make the substitution of the the polynomial

$$P(w) = \sum_{j=0}^{k} a_j w^j \quad (65)$$

in Eq. (64), setting the coefficients of all the powers of w equal to zero. We found the similar results:

5.1 The degree of the polynomial is $k = (\ell-1)/2$.

5.2 One has $k+1$ homogeneous linear equations relating the $k+1$ coefficients of the polynomial. The matrix of this system of linear equations is a function of the parameter b. The non trivial solution exists only when the determinant is zero; this determines $k+1$ different values of b. Each value produces a different polynomial. The coefficients of the polynomial can be found by recurrence, starting from b and a_0.

5.3 The explicit form of the equations for the coefficients is

$$\begin{aligned} &ba_0 + 3a_1 = 0 \\ &(2m+3)(m+1)a_{m+1} + ba_m \\ &\qquad + [\ell(\ell+1)/2 - m(2m-1)]a_{m-1} = 0 \\ &\qquad\qquad (m = 1, 2, ..., k-1) \\ &(\ell+2k)(\ell-2k+1)a_{k-1}/2 + ba_k = 0\,. \end{aligned} \quad (66)$$

5.4 A new recurrence provides a family of polynomials of degree j, equal to the determinant of the submatrix of dimension $j \times j$ of the system: we again define $y_0 = 1$, $y_1(b) = b$, and

$$y_{j+1}(b) = by_j(b) - A_j y_{j-1}(b)\,, \quad (j = 1, 2, ..., k) \quad (67)$$

where A_j is the product of the two entries of the tridiagonal matrix on both sides of the main diagonal at positions $(j, j+1)$ and $(j+1, j)$

$$A_j = j(2j+1)[\frac{\ell(\ell+1)}{2} - j(2j-1)]\,. \quad (68)$$

The characteristic polynomial for determining the values of b is $y_{k+1}(b)$.

2.6. Type x, odd ℓ

The substitution of the case $\Lambda(w) = \sqrt{1+w}P(w)$ in (36) gives the following equation for the polynomial $P(w)$:

$$2w(1-w^2)\frac{d^2P(w)}{dw^2} + (1+2w-5w^2)\frac{dP(w)}{dw} + \left(\frac{(\ell-1)(\ell+2)}{2}w + b + 1/2\right)P(w) = 0. \quad (69)$$

We substitute into it the polynomial (45)

$$P(w) = \sum_{j=0}^{k} a_j w^j \tag{70}$$

setting the coefficients of all the powers of w equal to zero. We find the following results:

6.1 The degree of the polynomial is $k = (\ell - 1)/2$.

6.2 One has $k + 1 = (\ell + 1)/2$ homogeneous linear equations relating the $k + 1$ coefficients of the polynomial. The matrix of this system of linear equations is a function of the parameter b. The non trivial solution exists only when the determinant is zero; this determines $k + 1$ different values of b. Each value provides a different polynomial. The coefficients of the polynomial can be found by recurrence, starting from b and a_0.

6.3 The explicit form of the equations for the coefficients is

$$\begin{aligned}
&(b+1/2)a_0 + a_1 = 0\\
&(2m+1)(m+1)a_{m+1} + [(b+1/2)+2m]a_m\\
&\qquad + (\ell-2m+1)(\ell+2m)a_{m-1}/2 = 0\\
&\qquad\qquad (m = 1,2,...,k-1)\\
&(\ell-2k+1)(2k+\ell)a_{k-1}/2 + (b+1/2+2k)a_k = 0\,.
\end{aligned} \tag{71}$$

6.4 The recurrence produces the family of polynomials of degree j equal to the determinant of the submatrix of dimension $j \times j$. We define $y_0 = 1$, $y_1(b) = b + 1/2$, and

$$y_{j+1}(b) = (b + 2j + 1/2)y_j(b) - A_j y_{j-1}(b), \qquad (j = 1, 2, ..., k) \tag{72}$$

where A_j is the product of the two entries of the tridiagonal matrix on both sides of the main diagonal at positions $(j, j + 1)$ and $(j + 1, j)$:

$$A_j = j(2j-1)[\frac{\ell(\ell+1)}{2} - j(2j-1)]. \tag{73}$$

The characteristic polynomial for determining the values of b is $y_{k+1}(b)$.

Below the b values are tabulated for all the polynomials up to $\ell = 15$ (See Tables V to VIII).

When writing the eigenvalues b in the table of values, for each value of ℓ we find that they are ordered by the type of a function corresponding to the classification of the group V. For ℓ an even number, the greater value of b is always of symmetric type (s). The order from largest to smallest is s, x, y, z; which repeats cyclically. For ℓ an odd number, the greater value of b is of type z. The order is inverted to z, y, x, s, which repeats itself cyclically.

Another interesting property of the spectra is observed when we note that the b eigenvalues have almost a degeneration. As ℓ becomes larger, the b eigenvalues are grouped in couples of values that become closer in value. This happens for the different types of group V. Since this corresponds to

TABLE V. Eigenvalues b according to $\ell = 2 - 7$, and type of the V group for the most asymmetric case.

ℓ	Type	b
2	s	±1.7320508075689
2	x, z	±1.5
2	y	0
3	z, x	±3.949489742783
3	y	±3.8729833462074
3	x, z	±0.949489742783
3	s	0
4	s	±7.211102550928
4	x, z	±7.1904157598234
4	y	±2.6457513110646
4	z, x	±2.19041575982343
4	s	0
5	z, x	±11.49414663819150
5	y	±11.4891252930761
5	x, z	±5.36293051868569
5	s	±5.1961524227066
5	z, x	±1.368783880494185
5	y	0
6	s	±16.78391092456886
6	x, z	±16.78276990032108
6	y	±9.1651513899117
6	z, x	±9.11432541791537
6	s	±3.50718321108808
6	x, z	±2.83155551759430
6	y	±]0
7	z, x	±23.0755805845594
7	y	±23.0753326277447
7	x, z	±14.0138380013389
7	s	±14
7	z, x	±6.70803965346415
7	y	±6.4443016781448
7	x, z	±1.76978223668465
7	s	0

TABLE VI. Eigenvalues b according to $\ell = 8, 9, 10$, and type of the V group for the most asymmetric case.

ℓ	Type	b
8	s	±30.3678275070123
8	x, z	±30.3677753371381
8	y	±19.8799558776245
8	z, x	±19.8764578561354
8	s	±11.0360795803739
8	x, z	±10.949286970928

8	y	± 4.33443817624644
8	z, x	± 3.44060445193073
8	s	0
9	z, x	± 38.6602918232738
9	y	± 38.6602811125303
9	x, z	± 26.7521663013226
9	s	± 26.7513277147715
9	z, x	± 16.4384418576797
9	y	± 16.4128810481322
9	x, z	± 8.00461661312847
9	s	± 7.63979485960849
9	z, x	± 2.1580492334976
9	y	0
10	s	± 47.9528649646037
10	x, z	± 47.9528628075232
10	y	± 34.6267329990633
10	z, x	± 34.6265398453568
10	s	± 22.8721621755032
10	x, z	± 22.8651867293832
10	y	± 12.8448184810677
10	z, x	± 12.7179634066876
10	s	± 5.13682188750577
10	x, z	± 4.02645371505514
10	y	0

TABLE VII. Eigenvalues b according to $\ell = 11, 12, 13$, and type of the V group for the most asymmetric case.

ℓ	Type	b
11	z, x	± 58.2455056491701
11	y	± 58.245505221429
11	x, z	± 43.5024224454497
11	s	± 43.502379328453
11	z, x	± 30.3184753280879
11	y	± 30.3166758473324
11	x, z	± 18.7890799018142
11	s	± 18.7494797998074
11	z,x	± 9.26422979269084
11	y	± 8.79546969003276
11	x, z	± 2.5367084226849
11	s	0
12	s	± 69.5381933887331
12	x, z	± 69.5381933049892
12	y	± 53.3787715124891
12	z, x	± 53.3787621276328
12	s	± 38.7704174638424
12	x, z	± 38.7699730516097
12	y	± 25.7810284091082
12	z, x	± 25.7695705527514
12	s	± 14.6046016690127
12	x, z	± 14.4345829402282
12	y	± 5.91990928868307
12	z, x	± 4.59441661644294
12	s	0
13	z, x	± 81.83091588023716
13	y	± 81.830915864016
13	x, z	± 64.255565603662
13	s	± 64.2555636029947
13	z, x	± 48.2253783140692
13	y	± 48.2252723291192
13	x, z	± 33.7940412829763
13	s	± 33.7909105594589
13	z, x	± 21.0799222455574
13	y	± 21.0243743697317
13	x, z	± 10.4943386986705
13	s	± 9.91952164290954
13	z, x	± 2.90772914544503
13	y	0

TABLE VIII. Eigenvalues b according to $\ell = 14, 15$, and type of the V group for the most asymmetric case.

ℓ	Type	b
14	s	± 95.1236649296825
14	x, z	± 95.123664926568928
14	y	± 76.132683413936
14	z, x	± 76.132682994804036
14	s	± 58.6822486303082
14	x, z	± 58.6822240700879
14	y	± 42.8173767363793
14	z, x	± 42.8165591447652
14	s	± 28.620990959129427
14	x, z	± 28.6041510322987
14	y	± 16.3244223667596
14	z, x	± 16.1087758357521
14	s	± 6.68737187193915
14	x, z	± 5.14797794636587
14	y	0
15	z, x	± 109.4164347698555773
15	y	± 109.41643476926258
15	x, z	± 89.010046827009155
15	s	± 89.0100467404952
15	z, x	± 70.140462054122614
15	y	± 70.14045649788885
15	x, z	± 52.846648689261596
15	s	± 52.8464429052577

15	z, x	± 37.19316897069773
15	y	± 37.1883478499097996
15	x, z	± 23.321012881185754
15	s	± 23.2479042392256
15	z, x	± 11.7000964582398
15	y	± 11.0175745445891
15	x, z	± 3.27245385545921
15	s	0

(almost) the same root for two polynomials, this root is obtained by the Euclidean algorithm, also valid for polynomials, producing as the first approximation for the largest value of the eigenvalues b the prediction

$$b = \frac{\ell(2\ell - 1)}{4}\,. \tag{74}$$

This prediction gives a value smaller that the maximum eigenvalue by 1%. The next couple is well aproximated by the value $\ell(\ell - 3)/2$ larger that the actual value by 1%.

3. Applicability of the Theory

In general, the cases of rotational spectrum of very asymmetric molecules are not considered by most authors studying the rotational spectrum. Referring to this case, H.W. Kroto has written pages 99-100 of Ref. [11] "*In the high asymmetric case, as you might guess, the levels may not form an obvious simple pattern and the resulting spectrum can be quite a mess.*"

On the other hand, it is possible to find examples of symmetric oblate and prolate molecules, but not of exactly asymmetric molercules. Looking at the table of Molecular Constants involved in Microwave Spectrum [17], we found one case that is close to the more asymmetric molecule. It is ethylene oxide, when the hydrogen has been replaced by Deuterium C D_3 $-$C = O D, and the Carbon is the isotope C^{12}. It is also called deuterated acetaldehyde.

For this molecule the inverses of the moments of inertia are proportional to the numbers 20399, 15457, 11544, which correspond to a value of the σ angle of $26.16°$, near the $30°$ value of the most asymmetric case.

It is evident that the most asymmetric case studied in this paper will be only the first step in a perturbation theory starting with the exact case of most asymmetric molecules, since a very asymmetric molecule can only be approximated by this case.

However, perturbation theory is very similar to the one when the molecule is close to the symmetric oblate and prolate cases. See for example Sec. 3.10c of Ref. [11].

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