Rotational states of asymmetric molecules revisited: matrix evaluation and generating function of Lamé functions

E. Ley-Koo and R. Méndez-Fragoso

Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20 364, 01000 México, D.F., México,
e-mail: eleykoo@fisica.unam.mx, rmf@fisica.unam.mx

The solutions of the Schrödinger equation describing rotational states of asymmetric molecules are known to be separable as products of Lamé functions in spheroconal coordinates. However, the numerical evaluation of such solutions has not been implemented in efficient and practical ways. This paper overcomes this deficiency by presenting a matrix method for evaluating the needed Lamé functions, in their two kinds and eight species, to obtain accurate energy eigenvalues and eigenfunctions for the rotational states of molecules with any asymmetry. A generating function for these eigenfunctions, including its series expansions for any asymmetry, is also presented.

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

Se sabe que las soluciones de la ecuación de Schrödinger que describen estados rotacionales de moléculas asimétricas son separables como productos de funciones de Lamé en coordenadas esferoconales. Sin embargo, la evaluación numérica de tales soluciones no ha sido implementada en formas eficientes y prácticas. Este trabajo elimina tal deficiencia presentando un método matricial para evaluar las funciones de Lamé necesarias, en sus dos tipos y ocho especies, para obtener valores precisos de los eigenvalores de la energía y de las eigenfunciones para los estados rotacionales de moléculas con cualquier asimetría. También se presenta una función generadora para tales eigenfunciones incluyendo su desarrollo en serie para cualquier asimetría.

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

PACS: 33.20Sn; 33.15.Mt: 33.20.-t; 31.15.Hz

1. Introduction

This is a companion and complementary article of Ref. 1, concerning the accurate evaluation of rotational spectra of asymmetric molecules [2–5]. While [1] is based on the use of spherical harmonics to evaluate the energy eigenvalues and the intrinsic eigenfunctions of the rotational states of asymmetric molecules, the present investigation is focused on the numerical evaluation of the corresponding exact and separable Lamé function solutions. Indeed, Kramers and Ittmann introduced and analyzed such solutions [2], but their approach was not implemented in practice because the numerical methods for evaluating Lamé functions were not developed efficiently. On the other hand, the line of work pioneered by [3,4], using the basis of eigenfunctions of symmetric molecules later known as the Wigner D functions, became a practical tool for interpreting rotational spectra within the limiting framework of perturbation theory [7–17]. Recently, the investigations in Refs. 5 and 6 started the revisiting of Ref. 2, but the numerical results of the former are still limited to the lower excited states, while the later - focused on the most asymmetric molecules - still aims at taking the latter as a reference to do perturbation theory extensions for molecules with neighboring asymmetries.

Our revisiting of Refs. 2, 5, and 6 targets the construction of the exact and separable Lamé function solutions for molecules with any asymmetry and states of any excitation,

providing spectroscopically accurate numerical results. Section 2 reviews the simultaneous separation of the Schrödinger equation and the square of the angular momentum equation, in spheroconal coordinates, into two Lamé ordinary differential equations. We follow the notation of Refs. 5 and 6, including in the Appendix the details about the coordinates and operators for completeness sake. The separation constants are identified as well defined linear combinations of the eigenvalues of the energy E^* and the square of the angular momentum $\ell(\ell + 1)$. Section 3 studies the solutions to the Lamé differential equation, characterizing them by their parity and singularity properties, which lie behind their classification into two kinds, each with four species. Consequently, the Lamé functions can be expressed as the product of a singularity-removing factor and a series expansion in even powers of $\mathrm{sn}(\chi, k)$. The expansion coefficients are found to satisfy three-term recurrence relations, which can be rewritten in a single square tridiagonal matrix of finite dimension, for each kind and species of Lamé function and each value of ℓ. The diagonalization of such matrices yields accurate numerical values of the expansion coefficients and the separation constants for each Lamé function. Section 4 explains how to assemble the eigenfunctions of the rotational states of the asymmetric molecule, as products of matching Lamé functions according to kind and species, and also according to matching separation constants h_1 and h_2, which also yield accurate eigenenergies for the chosen value of ℓ.

The eigenfunctions turn out to be also of two kinds and four species. Numerical results for the respective functions and eigenvalues are illustrated in both Secs. 3 and 4. The discussion in Sec. 5 centers around the identification of generating functions for spheroconal harmonics, and their applications in quantum mechanics beyond the rotations of asymmetric molecules.

2. Separation of the Schrödinger equation and the square of the angular momentum eigenvalue equation into Lamé ordinary differential equations

The rotational states of an asymmetric molecule are determined by the common eigenfunctions of the Hamiltonian,

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

where I_1, I_2, I_3 are the moments of inertia and $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ are the angular momentum components in the reference frame fixed in the body and oriented along the principal axes; of the square of the angular momentum,

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

and of the z-component of the angular momentum in the laboratory, or inertial, reference frame,

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

borrowing Eqs. (34) and (35) of [5]. The $\hat{L}_i$ and $\hat{M}_i$ operators, where $i = x, y, z$, are expressed in terms of the three familiar Euler angles, Eqs. (32) and (33) of [5], but the eigenvalues E and $\ell(\ell+1)$ do not depend on m because the angle defining the orientation of the free molecule in the laboratory is ignorable. References 1 and 5 choose to describe the states with $m = 0$, for which the $\hat{L}_i$ become the familiar angular momentum operators depending on the other two Euler angles, Eq. (37) of Ref. 5.

For completeness, we also review the alternative parametrizations of the Hamiltonian, described by Eqs. (46) and (47) in Ref. 5:

$$\hat{H} = \frac{1}{2}Q\hat{L}^2 + P\hat{H}^*, \tag{4}$$

$$\hat{H} = \frac{1}{2}Q\hat{L}^2 + \frac{1}{2}P\left[e_1\hat{L}_x^2 + e_2\hat{L}_y^2 + e_3\hat{L}_z^2\right], \tag{5}$$

where the matrix of the inverses of the moments of inertia is separated into its trace and traceless contributions. Indeed, Eqs. (40)-(44) of Ref. 5 provide the relationships between the respective sets of parameters:

$$\frac{1}{I_i} = Q + Pe_i, \tag{6}$$

$$Q = \frac{1}{3}\left[\frac{1}{I_1}+\frac{1}{I_2}+\frac{1}{I_3}\right], \tag{7}$$

$$e_1 + e_2 + e_3 = 0, \tag{8}$$

$$e_1^2 + e_2^2 + e_3^2 = \frac{3}{2}, \tag{9}$$

$$P^2 = \frac{2}{9}\left[\left(\frac{1}{I_1}-\frac{1}{I_2}\right)^2+\left(\frac{1}{I_2}-\frac{1}{I_3}\right)^2+\left(\frac{1}{I_3}-\frac{1}{I_1}\right)^2\right]. \tag{10}$$

The parameter Q is the average trace of the matrix and provides the spherical top contribution $\hbar^2 Q\ell(\ell+1)$ to the energy eigenvalue in Eq. (4). The parameter P is a measure of the magnitude of the asymmetry of the molecule, while e_1, e_2, e_3 quantify the distribution of the asymmetry in the directions of the principal axes. The three asymmetry distribution parameters in Eqs. (8) and (9) can also be replaced by one single angular parameter, $0 \leq \sigma \leq \pi/3$, of Eq. (45) in Ref. 5:

$$e_1 = \cos\sigma, \quad e_2 = \cos(\sigma - \tfrac{2\pi}{3}), \quad e_3 = \cos(\sigma + \tfrac{2\pi}{3}), \tag{11}$$

the symmetric prolate and oblate molecules correspond to $\sigma = 0$ and $\sigma = \pi/3$, respectively, while the most asymmetric molecules have $\sigma = \pi/6$. In summary, the three moments of inertia are replaced by the three independent parameters Q, P and one e_i. By choosing $I_1 \leq I_2 \leq I_3$, the complete equalities lead to $Q = 1/I_1$ and $P = 0$, for the spherical molecule; the partial equality $I_1 < I_2 = I_3$ corresponds to the symmetric prolate molecule with $e_1 = 1$, $e_2 = e_3 = -1/2$ and rotational invariance around the x-axis; the other partial equality $I_1 = I_2 < I_3$ describes the symmetric oblate molecule with $e_1 = e_2 = 1/2$, $e_3 = -1$ and rotational invariance around the z-axis; and the most asymmetric molecule is characterized by $e_1 = -e_3 = \sqrt{3}/2$, $e_2 = 0$.

It is convenient to illustrate at once numerically, the corresponding values of the alternative asymmetry distribution parameters σ, e_1, e_2, e_3, k_1^2 and k_2^2, related by Eqs. (11) and (A.19), via Table I. We refer to it in Secs. 3 and 4 when reporting the numerical values for the successive functions and eigenvalues.

TABLE I. Corresponding values of asymmetry distribution parameters, related by Eqs. (11) and (A.19).

σ	$0°$	$15°$	$30°$	$45°$	$60°$
e_1	1	$\frac{\sqrt{6}+\sqrt{2}}{4}$	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$
e_2	$-\frac{1}{2}$	$\frac{\sqrt{2}-\sqrt{6}}{4}$	0	$\frac{\sqrt{6}-\sqrt{2}}{4}$	$\frac{1}{2}$
e_3	$-\frac{1}{2}$	$-\frac{1}{\sqrt{2}}$	$-\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{6}+\sqrt{2}}{4}$	-1
k_1^2	0	$\frac{3-\sqrt{3}}{3+\sqrt{3}}$	$\frac{1}{2}$	$\frac{2\sqrt{3}}{3+\sqrt{3}}$	1
k_2^2	1	$\frac{2\sqrt{3}}{3+\sqrt{3}}$	$\frac{1}{2}$	$\frac{3-\sqrt{3}}{3+\sqrt{3}}$	0

Next, we analyze the common eigensolutions of the Schrödinger equation for $\hat{H}^*$, Eq. (4), and the square of the angular momentum Eq. (2). Their explicit forms in spheroconal coordinates are written by using Eqs. (A.14) and (A.18), respectively:

$$-\frac{\hbar^2}{2\left(1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)\right)}$$

$$\times\left(\left(e_1 - (e_1 - e_2)\mathrm{sn}^2(\chi_2, k_2)\right)\frac{\partial^2}{\partial\chi_1^2} + \left(e_3 + (e_2 - e_3)\mathrm{sn}^2(\chi_1, k_1)\right)\frac{\partial^2}{\partial\chi_2^2}\right)\Psi = E^*\Psi, \tag{12}$$

$$-\frac{\hbar^2}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\left(\frac{\partial^2}{\partial\chi_1^2} + \frac{\partial^2}{\partial\chi_2^2}\right)\Psi = \hbar^2\ell(\ell+1)\Psi. \tag{13}$$

In fact, they can have factorizable solutions of the form

$$\Psi(\chi_1, \chi_2) = \Lambda_1(\chi_1)\Lambda_2(\chi_2), \tag{14}$$

which upon subtitution in Eqs. (12) and (13), and using Eq. (A.20) lead to

$$\frac{1}{(e_3 + (e_2 - e_3)\mathrm{sn}^2(\chi_1, k_1))}\left(\frac{1}{\Lambda_1}\frac{d^2\Lambda_1}{d\chi_1^2} + \frac{2E^*}{\hbar^2(e_1 - e_3)}\right)$$

$$+\frac{1}{(e_1 - (e_1 - e_2)\mathrm{sn}^2(\chi_2, k_2))}\left(\frac{1}{\Lambda_2}\frac{d^2\Lambda_2}{d\chi_2^2} - \frac{2E^*}{\hbar^2(e_1 - e_3)}\right) = 0, \tag{15}$$

$$\left(\frac{1}{\Lambda_1}\frac{d^2\Lambda_1}{d\chi_1^2} - \ell(\ell+1)k_1^2\mathrm{sn}^2(\chi_1, k_1) - \frac{\ell(\ell+1)e_3}{e_1 - e_3}\right)$$

$$+\left(\frac{1}{\Lambda_2}\frac{d^2\Lambda_2}{d\chi_2^2} - \ell(\ell+1)k_2^2\mathrm{sn}^2(\chi_2, k_2) + \frac{\ell(\ell+1)e_1}{e_1 - e_3}\right) = 0. \tag{16}$$

Simultaneous separation of Eqs. (15) and (16) can be achieved by equating the respective terms of Eq. (15) to $\pm\ell(\ell+1)/(e_1 - e_3)$ and correspondingly in Eq. (16) to $\mp2E^*/\hbar^2(e_1 - e_3)$, with the resulting ordinary differential equations

$$\frac{d^2\Lambda_1}{d\chi_1^2} - \left(\ell(\ell+1)k_1^2\mathrm{sn}^2(\chi_1, k_1) + \frac{\ell(\ell+1)e_3}{e_1 - e_3} - \frac{2E^*}{\hbar^2(e_1 - e_3)}\right)\Lambda_1 = 0, \tag{17}$$

$$\frac{d^2\Lambda_2}{d\chi_2^2} - \left(\ell(\ell+1)k_2^2\mathrm{sn}^2(\chi_2, k_2) - \frac{\ell(\ell+1)e_1}{e_1 - e_3} + \frac{2E^*}{\hbar^2(e_1 - e_3)}\right)\Lambda_2 = 0. \tag{18}$$

Both are of the Lamé equation form

$$\frac{d^2\Lambda_i}{d\chi_i^2} - \left(\ell(\ell+1)k_i^2\mathrm{sn}^2(\chi_i, k_i) + h_i\right)\Lambda_i = 0, \tag{19}$$

with the respective eigenvalues:

$$h_1 = \frac{\ell(\ell+1)e_3}{e_1 - e_3} - \frac{2E^*}{\hbar^2(e_1 - e_3)}, \tag{20}$$

$$h_2 = -\frac{\ell(\ell+1)e_1}{e_1 - e_3} + \frac{2E^*}{\hbar^2(e_1 - e_3)}. \tag{21}$$

Their combinations

$$e_1h_1 + e_3h_2 = -\frac{2E^*}{\hbar^2}, \tag{22}$$

$$h_1 + h_2 = -\ell(\ell+1), \tag{23}$$

yield the eigenvalues of Eqs. (12) and (13).

3. Matrix Evaluation of Lamé functions

This section is devoted to the analysis and construction of the solutions of the Lamé equation (19). The derivatives of the Jacobian elliptical functions, Eqs. (A.4), permit the identification of the removable singularities in the Lamé functions. The series expansion solutions in even powers of $\mathrm{sn}(\chi, k)$, after removal of the respective singularity factors, lead to three-term recurrence relations for the expansion coefficients; such relations can be expressed in a matrix form, which permits the accurate evaluation of the expansion coefficients and the eigenvalues h. The reader is referred to Whittaker and Watson [18] for the standard treatment of Lamé functions and to [19,20] for the spheroconal coordinates and Jacobi elliptic functions.

The removable singularities are identified as the factors $A = 1$, s, c, d, sc, sd, cd, scd in the eight species of Lamé

functions:

$$\Lambda^1 = \sum_p a_p^1 \text{sn}^{2p}(\chi, k), \tag{24}$$

$$\Lambda^s = \text{sn}(\chi, k) \sum_p a_p^s \text{sn}^{2p}(\chi, k), \tag{25}$$

$$\Lambda^c = \text{cn}(\chi, k) \sum_p a_p^c \text{sn}^{2p}(\chi, k), \tag{26}$$

$$\Lambda^d = \text{dn}(\chi, k) \sum_p a_p^d \text{sn}^{2p}(\chi, k), \tag{27}$$

$$\Lambda^{sc} = \text{cn}(\chi, k)\text{sn}(\chi, k) \sum_p a_p^{sc} \text{sn}^{2p}(\chi, k), \tag{28}$$

$$\Lambda^{sd} = \text{dn}(\chi, k)\text{sn}(\chi, k) \sum_p a_p^{sd} \text{sn}^{2p}(\chi, k), \tag{29}$$

$$\Lambda^{cd} = \text{dn}(\chi, k)\text{cn}(\chi, k) \sum_p a_p^{cd} \text{sn}^{2p}(\chi, k), \tag{30}$$

$$\Lambda^{scd} = \text{dn}(\chi, k)\text{cn}(\chi, k)\text{sn}(\chi, k) \sum_p a_p^{scd} \text{sn}^{2p}(\chi, k) . \tag{31}$$

Substitution of the successive functions of Eqs. (24) - (31) in the Lamé Eq. (19) leads to the respective three-term recurrence relations for the power expansion coefficients a_N^A:

$$(2N+1)(2N+2)a_{N+1}^1 - \left[(1+k^2)(2N)^2 + h\right] a_N^1 + k^2 \left[(2N-2)(2N-1) - \ell(\ell+1)\right] a_{N-1}^1 = 0, \tag{32}$$

$$(2N+2)(2N+3)a_{N+1}^s - \left[(1+k^2)(2N+1)^2 + h\right] a_N^s + k^2 \left[(2N-1)(2N) - \ell(\ell+1)\right] a_{N-1}^s = 0, \tag{33}$$

$$(2N+1)(2N+2)a_{N+1}^c - \left[(2N+1)^2 + k^2(2N)^2 + h\right] a_N^c + k^2 \left[((2N-1)(2N) - \ell(\ell+1)\right] a_{N-1}^c = 0, \tag{34}$$

$$(2N+1)(2N+2)a_{N+1}^d - \left[(2N)^2 + k^2(2N+1)^2 + h\right] a_N^d + k^2 \left[(2N-1)(2N) - \ell(\ell+1)\right] a_{N-1}^d = 0, \tag{35}$$

$$(2N+2)(2N+3)a_{N+1}^{sc} - \left[k^2(2N+1)^2 + (2N+2)^2 + h\right] a_N^{sc} + k^2 \left[2N(2N+1) - \ell(\ell+1)\right] a_{N-1}^{sc} = 0, \tag{36}$$

$$(2N+2)(2N+3)a_{N+1}^{sd} - \left[k^2(2N+2)^2 + (2N+1)^2 + h\right] a_N^{sd} + k^2 \left[2N(2N+1) - \ell(\ell+1)\right] a_{N-1}^{sd} = 0, \tag{37}$$

$$(2N+1)(2N+2)a_{N+1}^{cd} - \left[(1+k^2)(2N+1)^2 + h\right] a_N^{cd} + k^2 \left[(2N(2N+1) - \ell(\ell+1)\right] a_{N-1}^{cd} = 0, \tag{38}$$

$$(2N+2)(2N+3)a_{N+1}^{scd} - \left[(1+k^2)(2N+2)^2 + h\right] a_N^{scd} + k^2 \left[(2N+1)(2N+2) - \ell(\ell+1)\right] a_{N-1}^{scd} = 0. \tag{39}$$

These recurrence relations can be cast into tridiagonal matrix forms with expansion coefficients a_N^A as eigenvectors and h as eigenvalues, following the method introduced in connection with the evaluation of the electronic states of the hydrogen molecular ion [21], and Mathieu functions [22].

Notice that the matrices turn out to be finite dimensional. Consequently, the series solutions in Eqs. (32) - (39) become Lamé polynomials. The last term of the recurrence relations indicates that the respective matrices have finite dimension $N_{max} \times N_{max}$. In fact, for ℓ even Eq. (32) and Eqs. (36) - (38) determine, respectively,

$$N_{max}^1 = \frac{\ell}{2} + 1 \quad \text{and} \quad N_{max}^{sc} = N_{max}^{sd} = N_{max}^{cd} = \frac{\ell}{2}, \tag{40}$$

leading to a total of $\ell/2 + 1 + 3\ell/2 = 2\ell + 1$ independent solutions. Likewise, for ℓ odd Eqs. (33) - (35) and Eq. (39) lead respectively, to

$$N_{max}^s = N_{max}^c = N_{max}^d = \frac{\ell+1}{2} \quad \text{and} \quad N_{max}^{scd} = \frac{\ell-1}{2}, \tag{41}$$

also with a total of $2\ell + 1$ independent solutions. Consequently, the sums in Eqs. (24) - (31) include terms with $p = 1, 2, \ldots, N_{max}^A$, and are thereby identified as Lamé polynomials.

Notice that the matrices in Eqs. (32) - (39) are not symmetric and the appropriate LAPACK routine is used for their diagonalization, [23]. Their finite dimensions allow accurate evaluations of the eigenvalues h^A and eigenvectors a_p^A as illustrated in Table II and Fig. 1.

Table II contains the eigenvalues $h^A(k)$ for $\ell = 4$ and 5, for the respective kinds and species A, and for the values of the asymmetry distribution parameter k in the chosen molecule. The nine values for $\ell = 4$ are obtained from one 3×3 matrix for $A = 1$, and three 2×2 matrices for $A = sc$, sd, cd. Correspondingly, the eleven values for $\ell = 5$ follow from three 3×3 matrices for $A = s, c, d$ and one 2×2 matrix for $A = scd$.

Figure 1 illustrates the Lamé functions $\Lambda_n^A(\chi, k)$ for $\ell = 5$ of the species $A = s, c, d, scd$, Eqs. (25) - (27) and (31), in the interval $0 \leqslant am\chi \leqslant 90°$, for the values of the parameter k^2 in the successive rows from top to bottom. Notice the common node at $\chi = 0$ and the common zero slope at $am\chi = 90°$ for the Λ^s in the first column; the zero slope and the node at the respective ends for the Λ^c in the second column; the vanishing slopes at both ends for the Λ^d in the third column, except for the bottom $k = 1$ case in which $\Lambda^d = \Lambda^c$; and the nodes at both ends for the Λ^{scd} in the fourth column.

TABLE II. Eigenvalues h^A of Lamé Eq. (19) for chosen values of $0 \leq k^2 \leq 1$, $\ell = 4$ ($A = 1, sc, sd, cd$) and $\ell = 5$ ($A = s, c, d, scd$).

k^2	0	0.2679491924311	0.5	0.7320508075688	1
1	-16	-16.5851262965012	-17.2111025121022	-18.0899154478468	-20
sc	-16	-16.5840359204396	-17.1904157236340	-17.9288070427514	-19
sd	-9	-10.6692264277499	-12.6457511848807	-15.3102425028777	-19
cd	-9	-10.6082989483587	-12.1904156698290	-13.9045439338914	-16
1	-4	-6.8637729178446	-10	-13.1362268286893	-16
sc	-4	-6.0954559153276	-7.8095841501821	-9.3917009234711	-11
sd	-1	-4.6897572437845	-7.3542485627514	-9.3307734295673	-11
cd	-1	-2.0711928874085	-2.8095842039871	-3.4159640323311	-4
1	0	-1.9100844571886	-2.7888974102462	-3.4148736559090	-4

k^2	0	0.2679491924311	0.5	0.7320508075688	1
s	-25	-25.7285943365901	-26.4941465914849	-27.5248399518695	-30
c	-25	-25.7284748791048	-26.4891252471910	-27.4510721308369	-29
d	-16	-18.0685573651675	-20.3629303726905	-23.6602538501924	-29
scd	-16	-18.0589446825257	-20.1961522965227	-22.6999607822317	-26
s	-9	-12.3098812782257	-16.3687836315523	-21.1654954654817	-26
c	-9	-12.0815810174275	-15	-17.918418739595	-21
d	-4	-8.8345041215966	-13.6312158705639	-17.6901184271086	-21
scd	-4	-7.3000389890087	-9.8038474511094	-11.9410551502134	-14
s	-1	-6.3397458103695	-9.6370693353190	-11.9314424644276	-14
c	-1	-2.5489277750021	-3.5108746610388	-4.2715250620129	-5
d	0	-2.4751599384210	-3.5058533151019	-4.2714056044777	-5

The reader may also count the number of nodes in the open interval $0 < am\chi < 90°$, n, for the respective Λ_n^A and their variations in position as k^2 takes its successive values. Specifically, $n = 0, 1, 2$ for $A = s, c, d$, and $n = 0, 1$ for $A = scd$, as determined by the sizes of the matrices from which they are evaluated. The Lamé eigenvalues and functions constructed in this section are used for χ_1 and χ_2 in a complementary form in the following section.

The conclusion of this section is that an exact matrix method for the evaluation of Lamé polynomials and eigenvalues has been described and implemented, yielding accurate values for both, as illustrated by Fig. 1 and Table II. The method is in the Refs. 21 and 22 shows.

4. Rotational eigenstates and eigenvalues of asymmetric molecules

The eigenfunctions of Eq. (14) are constructed by multiplying the Lamé function solution to Eqs. (17) and (18), evaluated by the method described in Sec. 3, and chosen to be of complementary species within the two kinds of parity ($x \to -x, y \to -y, z \to -z$) eigenstates.

$$\Psi^1 = \Psi_{n_1 n_2}^{+++}(\chi_1, \chi_2) = \Lambda_{n_1}^1(\chi_1)\Lambda_{n_2}^1(\chi_2) , \qquad (42)$$

$$\Psi^{yz} = \Psi_{n_1 n_2}^{+--}(\chi_1, \chi_2) = \Lambda_{n_1}^{cs}(\chi_1)\Lambda_{n_2}^{cd}(\chi_2) , \qquad (43)$$

$$\Psi^{xz} = \Psi_{n_1 n_2}^{-+-}(\chi_1, \chi_2) = \Lambda_{n_1}^{ds}(\chi_1)\Lambda_{n_2}^{sd}(\chi_2) , \qquad (44)$$

$$\Psi^{xy} = \Psi_{n_1 n_2}^{--+}(\chi_1, \chi_2) = \Lambda_{n_1}^{dc}(\chi_1)\Lambda_{n_2}^{sc}(\chi_2) , \qquad (45)$$

$$\Psi^{x} = \Psi_{n_1 n_2}^{-++}(\chi_1, \chi_2) = \Lambda_{n_1}^{d}(\chi_1)\Lambda_{n_2}^{s}(\chi_2) , \qquad (46)$$

$$\Psi^{y} = \Psi_{n_1 n_2}^{+-+}(\chi_1, \chi_2) = \Lambda_{n_1}^{c}(\chi_1)\Lambda_{n_2}^{c}(\chi_2) , \qquad (47)$$

$$\Psi^{z} = \Psi_{n_1 n_2}^{++-}(\chi_1, \chi_2) = \Lambda_{n_1}^{s}(\chi_1)\Lambda_{n_2}^{d}(\chi_2) , \qquad (48)$$

$$\Psi^{xyz} = \Psi_{n_1 n_2}^{---}(\chi_1, \chi_2) = \Lambda_{n_1}^{dcs}(\chi_1)\Lambda_{n_2}^{scd}(\chi_2) . \qquad (49)$$

Notice that the combinations of A and B species for the Lamé functions in χ_1 and χ_2, respectively

A	1	cs	ds	dc	d	c	s	dcs
B	1	cd	sd	sc	s	c	d	scd
AB	1	yz	xz	xy	x	y	z	xyz

are associated with the reproduction of the removable singularity factors in Eqs. (42) - (49). The number of nodes of the respective Lamé functions are chosen to match the condition:

$$n_1 + n_2 = \ell , \qquad (50)$$
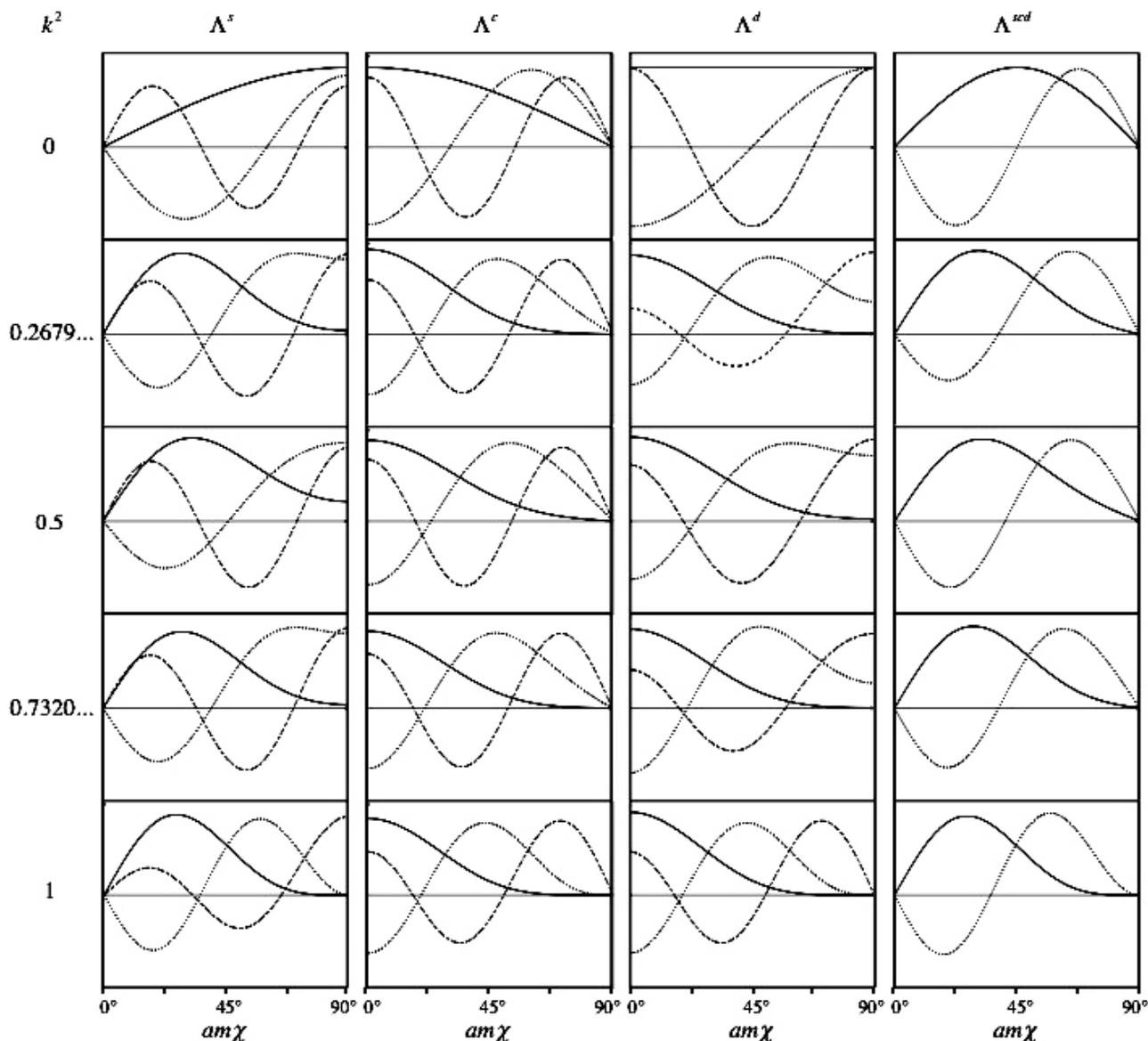
FIGURE 1. Lamé functions, Eqs. (25) - (27) and (31), for chosen values of $0 \leq k^2 \leq 1$ and $\ell = 5$ ($A = s, c, d, scd$), as functions of $0 \leq am\chi \leq 90°$, Eqs. (A.2) - (A.3).

counting the total number of nodal surfaces of the corresponding spheroconal harmonics of order ℓ, even or odd.

The eigenvalues $h_{n_1}^A$ and $h_{n_2}^B$ of the Lamé functions determine the energy eigenvalues $E_{n_1 n_2}^{*AB}$ via Eq. (22), and their sum satisfies Eq. (23).

The energy eigenvalues $E_{n_1 n_2}^{*A}$ may be evaluated numerically using Eq. (11) with the matching asymmetry distribution parameters of Table I, for $\ell = 4$ ($AB = 1, yz, xz, xy$) and $\ell = 5$ ($AB = x, y, z, xyz$), and also the values of $h^A(k1)$ and $h^B(k2)$ taken from Table II. It is no surprise that the numerical results coincide with those reported in Ref. 1, as the reader can check directly. Of course, these results hold in general for all values of ℓ, obviating the inclusion of the corresponding numerical Tables and Figures for the energy levels in this article, by referring the reader to Ref. 1.

On the other hand, the rotational eigenfunctions for the asymmetric molecules with $\ell = 4$ and 5 also follow from the diagonalizations of the matrices of Eqs. (32) - (39), yielding the respective expansion coefficients $a_N^A(k_1)$ and $a_N^B(k_2)$ to be used in the construction of the Lamé polynomials, Eqs. (24) -(31), and then the latter are matched in turn to lead to the product solutions of Eqs. (42) - (49). The eigenfunctions for $\ell = 4$ were graphically reported in [1], and here Fig. 2 does the complementary counterpart for $\ell = 5$. Again, the eigenfunctions obtained by the alternative methods of [1] and this work are numerically accurate and equivalent. The discussion of the individual and global properties of the eigenfunctions presented in [1] is also valid for any value of the magnitude of the angular momentum, including $\ell = 5$ as illustrated here. Specifically, the five cartesian-plane or elliptic-cone nodal surfaces for each eigenfunction

of the asymmetric molecules can be identified in the three middle columns, including their degeneration into circular-cone and meridian-plane nodes for the symmetric molecules in the outer columns.

It is also important to compare the advantages and disadvantages of the methods of Ref. 1 and this work. The framework of Ref. 1, using spherical harmonics, is more familiar for most people; but the Schrödinger equation is not separable into spherical coordinates. The spheroconal coordinates and the Lamé functions are not so familiar; but they are the natural tools behind the separabilty and integrability of the problem. The motivation to learn about them, including developing methods to evaluate them, is physically justified and long overdue. Both methods yield equally accurate numerical results. Of course, becoming familiar with both is most advantageous. On the practical side, for a given value of ℓ, the sizes of the matrices $\ell \times \ell$ and $(\ell+1) \times (\ell+1)$ in Ref. 1 and the smaller sizes of Eqs. (40) - (41) in this article tilt the scales in favor of the latter. The matrix evaluation of the Lamé functions in Sec. 3, for matching values of the asymmetry distribution parameters, in accord with Table I, leads in a natural way to the construction of the complete eigensolutions studied in this section.

The rotational states obtained in Refs. 1, 2, 5, and 6 and the present work are restricted to those with $m = 0$ in the laboratory-fixed frame. The states with m = ± 1, ± 2, follow from the successive applications of the ladder operators $\hat{M}_\pm$ to the state with $m = 0$. In practice, the familiar theory of angular momentum favors the representation of the corresponding states in terms of spherical harmonics [1] over the one constructed here in terms of Lamé functions. On the other hand, it may be worthwhile exploring the extension of the theory of angular momentum based on spheroconal harmonics.

We conclude this section by underlining the fact that the separable and integrable eigenfunctions and eigenenergies of asymmetric-molecule rotational states can be reliably constructed via the matrix evaluation of the Lamé polynomials.

The method is direct and simple, leading to accurate values for molecules with any asymmetry and for states of any excitation.

5. Common generating function for complete wave functions of rotational states and discussion

In the companion article [1], it was recognized that the complete wave functions for the rotational states of asymmetric molecules are spheroconal harmonics, *i.e.*, solutions of the angular part of the Laplace equation. Consequently, it was also possible to identify the Coulomb potential as the common generating function for the Legendre polynomials, and at the same time for both the spherical harmonics and the spheroconal harmonics via the addition theorem.

While the initial motivation of the work reported in Ref. 1 and this paper was the evaluation of the rotational states of asymmetric molecules, its results are valid and applicable to other quantum systems. Indeed, it is also known that the Schrödinger equation is separable and integrable for the hydrogen atom not only in spherical coordinates but also in spheroconal coordinates [24, 25]. Actually, this also holds for any central potential, since the corresponding operators

$$\hat{H}, \quad \hat{L}^2, \quad \hat{L}_z \quad \text{and} \quad \hat{H}, \quad \hat{L}^2, \quad a\hat{L}_x^2 + b\hat{L}_y^2 + c\hat{L}_z^2$$

form complete and commuting alternative sets; of course, the third members of each set do not commute with each other. Consequently, any generating function for spherical harmonics is also a generating function for spheroconal harmonics involving Lamé functions, Eqs. (24) - (31). As an example, we consider the Rayleigh expansion of the plane wave into spherical waves [19]:

$$e^{(i\vec{\kappa}\cdot\vec{r})} = \sum_\ell i^\ell (2\ell+1) j_\ell(\kappa r) P_\ell(\hat{\kappa}\cdot\hat{r}) \quad, \qquad (51)$$

and the addition theorem [1]:

$$P_\ell(\hat{\kappa}\cdot\hat{r}) = \frac{4\pi}{2\ell+1} \sum_m Y_\ell^{*m}(\theta_\kappa, \phi_\kappa) Y_\ell^m(\theta, \phi) = \frac{4\pi}{2\ell+1} \sum_{A,B} \sum_{n_1, n_2} \Lambda_{n_1}^A(\chi_{1_\kappa}, k_1) \Lambda_{n_2}^B(\chi_{2_\kappa}, k_2) \Lambda_{n_1}^A(\chi_1, k_1) \Lambda_{n_2}^B(\chi_2, k_2) \quad,$$

$$(52)$$

where $\chi_{1\kappa}$ and $\chi_{2\kappa}$ are the spheroconal coordinates defining the orientation of $\hat{\kappa}$, and where the k_1 and k_2 parameters are restricted by Eqs. (A.6) and (A.19), and the parity-singularity labels A and B and the number of nodes n_1 and n_2 are subject to the restrictions before and in Eq. (50), respectively.

The harmonic oscillator and the hydrogen atom in three dimensions have common generating functions for their respective complete wave functions in different coordinates [25] and [26], including spherical coordinates and also

spheroconal coordinates, as it follows from the application of Eq. (52).

In conclusion, the matrix evaluation of the Lamé functions introduced and developed in this work is useful to describe the rotational states of asymmetrical molecules, as well as alternative rotational states of any central potential quantum system.
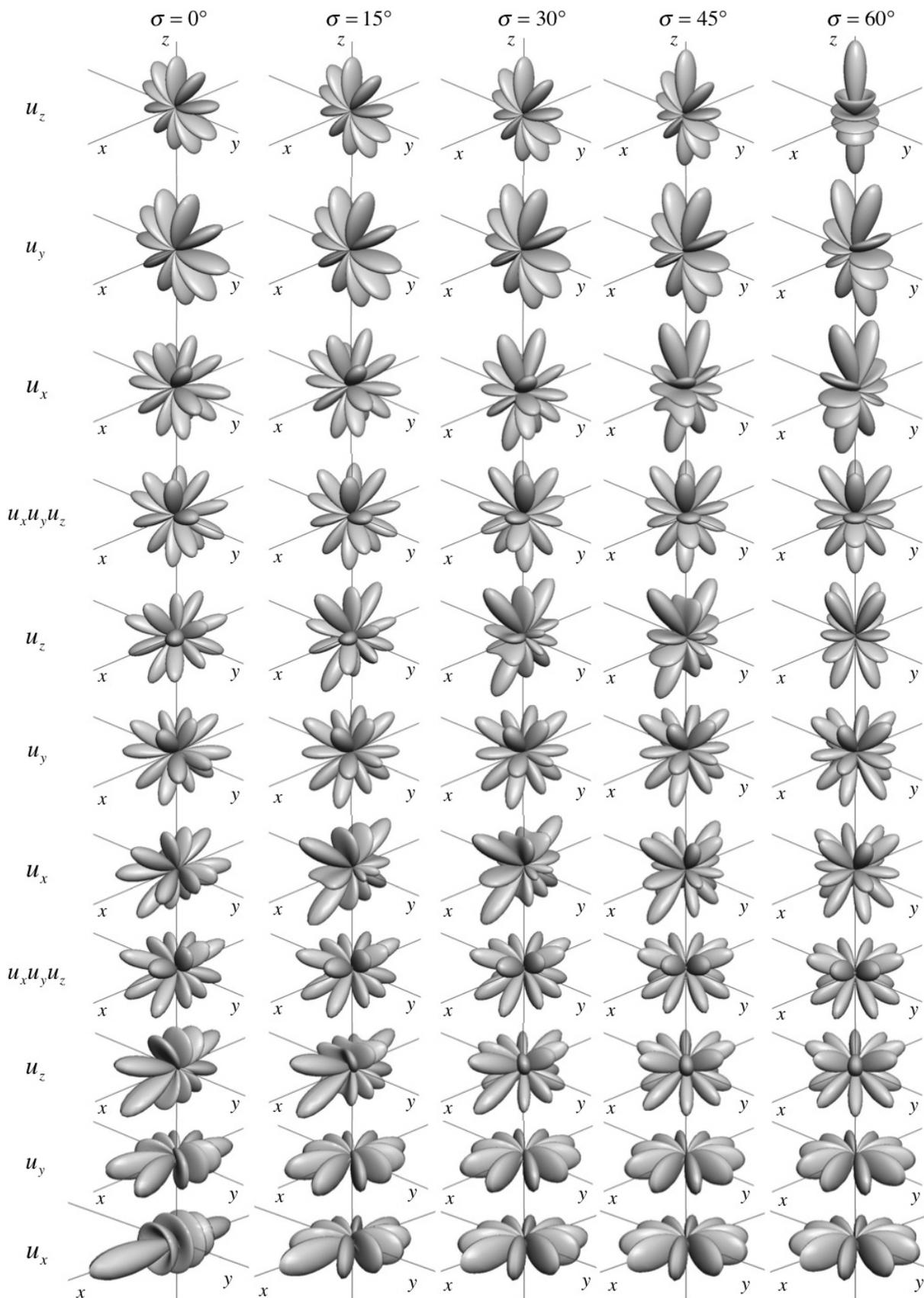
FIGURE 2. Lamé function rotational eigenstates $\Psi_{n_1 n_2}^{AB}$, Eqs. (46) - (48), in xyz space as functions of the asymmetry distribution parameter σ, Eq. (11).

Appendix

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

$$x = r\, \mathrm{dn}(\chi_1, k_1)\, \mathrm{sn}(\chi_2, k_2);$$

$$y = r\, \mathrm{cn}(\chi_1, k_1)\, \mathrm{cn}(\chi_1, k_1),$$

$$z = r\, \mathrm{sn}(\chi_1, k_1)\, \mathrm{dn}(\chi_2, k_2) \qquad (A.1)$$

involving Jacobian elliptic functions sn, cn and dn, [20]. The latter are defined and related in the following way:

$$u = \int\limits_0^{\varphi} \frac{d\alpha}{\sqrt{1 - k^2 \sin^2 \alpha}}, \qquad (A.2)$$

where φ is called the amplitude of u, and

$$\mathrm{sn}(u, k) = \sin\varphi,$$

$$\mathrm{cn}(u, k) = \cos\varphi = \sqrt{1 - \mathrm{sn}^2(u, k)},$$

$$\mathrm{dn}(u, k) = \sqrt{1 - k^2 \mathrm{sn}^2(u, k)} = \sqrt{1 - k^2 \sin^2 \varphi}. \quad (A.3)$$

Their derivatives are given by

$$\frac{d}{du}\mathrm{sn}(u, k) = \mathrm{cn}(u, k)\mathrm{dn}(u, k),$$

$$\frac{d}{du}\mathrm{cn}(u, k) = -\mathrm{sn}(u, k)\mathrm{dn}(u, k),$$

$$\frac{d}{du}\mathrm{dn}(u, k) = -k^2 \mathrm{sn}(u, k)\mathrm{cn}(u, k). \qquad (A.4)$$

The squares of Eqs. (A.1), upon summation and use of Eqs. (A.3), lead to

$$x^2 + y^2 + z^2 = r^2, \qquad (A.5)$$

provided that

$$k_1^2 + k_2^2 = 1. \qquad (A.6)$$

Therefore, the coordinate $0 < r < \infty$ defines families of concentric spheres.

The succesive elimination of the coordinate χ_1 or χ_2 between Eqs. (A.1), using Eqs. (A.3), leads to the respective equations:

$$\frac{x^2}{r^2 \mathrm{dn}^2(\chi_1, k_1)} + \frac{y^2}{r^2 \mathrm{cn}^2(\chi_1, k_1)} = 1, \qquad (A.7)$$

$$\frac{y^2}{r^2 \mathrm{cn}^2(\chi_2, k_2)} + \frac{z^2}{r^2 \mathrm{dn}^2(\chi_2, k_2)} = 1. \qquad (A.8)$$

Equation (A.7) for fixed values of r and χ, defines the intersection of the corresponding sphere and the surface defined by the value of the angular variable χ_1. Equation (A.8) does the same for fixed values of r and χ_2. Equations (A.7) and (A.8) can be rewritten, with the help of Eq. (A.5), in terms of only χ_1 and χ_2, respectively:

$$\frac{x^2 k_1^2 \mathrm{sn}^2(\chi_1, k_1)}{z^2 \mathrm{dn}^2(\chi_1, k_1)} + \frac{y^2 \mathrm{sn}^2(\chi_1, k_1)}{z^2 \mathrm{cn}^2(\chi_1, k_1)} = 1, \qquad (A.9)$$

$$\frac{y^2 \mathrm{sn}^2(\chi_2, k_2)}{x^2 \mathrm{cn}^2(\chi_2, k_2)} + \frac{z^2 k_2^2 \mathrm{sn}^2(\chi_2, k_2)}{x^2 \mathrm{dn}^2(\chi_2, k_2)} = 1. \qquad (A.10)$$

Equation (A.9), for fixed values χ_1, describes an elliptic cone with vertex at the origin ($x = 0, y = 0, z = 0$), its axis coinciding with the z-axis, and elliptical intersections with the succesive $z = z_0$ planes with major its semi-axis $z_0 \mathrm{dn}(\chi_1, k_1)/k_1 \mathrm{sn}(\chi_1, k_1)$ along the x-direction, and minor semi-axis $z_0 \mathrm{cn}(\chi_1, k_1)/\mathrm{sn}(\chi_1, k_1)$ along the y-direction. In the same way, Eq. (A.10) for fixed value of χ_2 describes elliptical cones with the succesive $x = x_0$ planes with minor axis along the y-axis and major axis along the z-axis.

The evaluation of the vector displacement using Eqs. (A.1) and (A.4):

$$d\vec{r} = \hat{i}dx + \hat{j}dy + \hat{k}dz = \Big(\hat{i}\mathrm{dn}(\chi_1, k_1)\mathrm{sn}(\chi_2, k_2) + \hat{j}\mathrm{cn}(\chi_1, k_1)\mathrm{cn}(\chi_2, k_2) + \hat{k}\mathrm{sn}(\chi_1, k_1)\mathrm{dn}(\chi_2, k_2)\Big) dr$$

$$+ \Big(-\hat{i}k_1^2 \mathrm{sn}(\chi_1, k_1)\mathrm{cn}(\chi_1, k_1)\mathrm{sn}(\chi_2, k_2) - \hat{j}\mathrm{sn}(\chi_1, k_1)\mathrm{dn}(\chi_1, k_1)\mathrm{cn}(\chi_2, k_2)$$

$$+ \hat{k}\mathrm{cn}(\chi_1, k_1)\mathrm{dn}(\chi_1, k_1)\mathrm{dn}(\chi_2, k_2)\Big) r d\chi_1$$

$$+ \Big(\hat{i}\mathrm{dn}(\chi_1, k_1)\mathrm{cn}(\chi_2, k_2)\mathrm{dn}(\chi_2, k_2) - \hat{j}\mathrm{cn}(\chi_1, k_1)\mathrm{sn}(\chi_2, k_2)\mathrm{dn}(\chi_2, k_2)$$

$$- \hat{k}\mathrm{sn}(\chi_1, k_1)k_2^2 \mathrm{sn}(\chi_2, k_2)\mathrm{cn}(\chi_2, k_2)\Big) r d\chi_2, \qquad (A.11)$$

permits the identification of the scale factors using Eqs. (A.3):

$$h_r = 1, \quad h_{\chi_1} = h_{\chi_1} = h_\chi,$$

$$h_\chi = r\sqrt{1 - k_1^2 \mathrm{sn}^2(\chi_1, k_1) - k_2^2 \mathrm{sn}^2(\chi_2, k_2)}. \qquad (A.12)$$

The reader can also identify the unit vectors $\hat{r}$, $\hat{\chi}_1$ and $\hat{\chi}_2$, and their ortogonality from Eq. (A.11).

The Laplace operator can be constructed by using Eq. (A.12):

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\left(1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)\right)}\left(\frac{\partial^2}{\partial\chi_1^2} + \frac{\partial^2}{\partial\chi_2^2}\right), \tag{A.13}$$

allowing the immediate identification of the square of the angular momentum operator of Eq. (38) in Ref. 5,

$$\hat{L}^2 = -\frac{\hbar^2}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\left(\frac{\partial^2}{\partial\chi_1^2} + \frac{\partial^2}{\partial\chi_2^2}\right). \tag{A.14}$$

The reader may notice the presence of only the second derivatives with respect to χ_1 and χ_2 in Eqs. (A.13) and (A.14), due to the equality of the scale factors in Eq. (A.12), in contrast with the corresponding operator in spherical coordinates.

The cartesian components of the angular momentum operator are necessary in order to construct the Hamiltonian operator. They take the forms:

$$\hat{L}_x = -i\hbar\left[\frac{\mathrm{cn}(\chi_2, k_2)\mathrm{dn}(\chi_1, k_1)\mathrm{dn}(\chi_2, k_2)}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\frac{\partial}{\partial\chi_1} + \frac{k_1^2\mathrm{sn}(\chi_1, k_1)\mathrm{sn}(\chi_2, k_2)\mathrm{cn}(\chi_1, k_1)}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\frac{\partial}{\partial\chi_2}\right], \tag{A.15}$$

$$\hat{L}_y = -i\hbar\left[\frac{\mathrm{sn}(\chi_1, k_1)\mathrm{cn}(\chi_2, k_2)\mathrm{dn}(\chi_1, k_1)}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\frac{\partial}{\partial\chi_2} - \frac{\mathrm{cn}(\chi_1, k_1)\mathrm{sn}(\chi_2, k_2)\mathrm{dn}(\chi_2, k_2)}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\frac{\partial}{\partial\chi_1}\right] \tag{A.16}$$

$$\hat{L}_z = i\hbar\left[\frac{k_2^2\mathrm{sn}(\chi_1, k_1)\mathrm{sn}(\chi_2, k_2)\mathrm{cn}(\chi_2, k_2)}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\frac{\partial}{\partial\chi_1} + \frac{\mathrm{cn}(\chi_1, k_1)\mathrm{dn}(\chi_1, k_1)\mathrm{dn}(\chi_2, k_2)}{1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)}\frac{\partial}{\partial\chi_2}\right]. \tag{A.17}$$

The Hamiltonian operator of Eq. (47) in [5] in spherical coordinates becomes

$$\hat{H}^* = \frac{1}{2}\left(e_1\hat{L}_x^2 + e_2\hat{L}_y^2 + e_3\hat{L}_z^2\right) = -\frac{\hbar^2}{2\left(1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2)\right)}$$
$$\times\left[\left(e_1 - (e_1 - e_2)\mathrm{sn}^2(\chi_2, k_2)\right)\frac{\partial^2}{\partial\chi_1^2} + \left(e_3 + (e_2 - e_3)\mathrm{sn}^2(\chi_1, k_1)\right)\frac{\partial^2}{\partial\chi_2^2}\right]. \tag{A.18}$$

It also involves only the second derivatives with respect to χ_1 and χ_2. Actually the original presence of the second derivative with respect to χ_1 and χ_2, and also the first derivatives, are eliminated by the choice

$$k_1^2 = \frac{e_2 - e_3}{e_1 - e_3}, \quad k_2^2 = \frac{e_1 - e_2}{e_1 - e_3}, \tag{A.19}$$

which is consistent with Eq. (A.6). Then the angular part of the square of the scale factor, Eq. (A.12), takes the alternative form:

$$1 - k_1^2\mathrm{sn}^2(\chi_1, k_1) - k_2^2\mathrm{sn}^2(\chi_2, k_2) = \frac{1}{e_1 - e_3}$$
$$\times\left[-e_3 - (e_2 - e_3)\mathrm{sn}^2(\chi_1, k_1)\right.$$
$$\left. + e_1 - (e_1 - e_2)\mathrm{sn}^2(\chi_2, k_2)\right], \tag{A.20}$$

which is the Weierstrass form of elliptical functions.

Acknowledgments

1. E. Ley-Koo and R. Méndez-Fragoso, *Properties of the spectra of asymmetric molecules: matrix evaluation in bases of spherical harmonics and common generating function.* (submitted for publication).

2. H.A. Kramers and G.P. Ittmann, *Z Phy.* **53** (1929) 553.

3. E.E. Witmer, *Proc. Nat. Acad.* **13** (1927) 60.

4. C. Wang, *Phys. Rev.* **34** (1929) 243.

5. E. Piña, *J. Mol. Struct. (THEOCHEM)* **493** (1999) 159.

6. M.T. Valdéz and E. Piña, *Rev. Mex. Fís.* **52** (2006) 220.

7. B.S. Ray, *Z. Phy.* **78** (1932) 74.

8. R. Mecke, *Z. Phy.* **81** (1933) 313.

9. G.W. King, R.M. Hainer, and P.C. Cross, *J. Chem. Phy.* **11** (1943) 27.

10. G.W. King, R.M. Hainer, and P.C. Cross, *J. Chem. Phy.* **12** (1944) 210.

11. G.W. King, R.M. Hainer, and P.C. Cross, *J. Chem. Phy.* **15** (1947) 820.

12. C. Van Winter, *Physica* **20** (1954) 274.

13. J.M. Bennett, I.G. Ross, and E.J. Wells, *J. Mol. Spectrosc.* **4** (1960) 342.

14. J.D. Louck, *J. Mol. Spectrosc.* **10** (1963) 163.

15. J.D. Louck, *J. Mol. Spectrosc.* **15** (1965) 83.

16. J.E. Wollrab, *Rotational spectra and molecular structure* (Academic Press, New York and London, 1967).

17. H.W. Kroto, *Molecular Rotation Spectra* (John Wiley & Sons, Great Britain, 1975).

18. E.T. Whittaker and G.N. Watson, *A Course of Modern Analysis* (Cambridge University Press, United Kingdom, 1927).

19. P.M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953).

20. M. Abramowitz and I.A. Stegun *Handbook of Mathematical Functions* (Dover, New York, 1965).

21. S. Mateos-Cortes, E. Ley-Koo, and S.A. Cruz, *Int. J. Quantum Chem.* **86** (2002) 376.

22. E. Ley-Koo and L. Chaos-Cador, *Rev. Mex. Fís.* **48** (2002) 67.

23. Press, H. William *et al.*, *Numerical Recipes* (Cambridge University Press, 1992) Vol. 1. Routine dgeev.f of LAPACK, http://www.netlib.org/lapack/.

24. E.G. Kalnins, W. Miller, and P. Winternitz, *SIAM J. of Math.* **30** (1976) 630.

25. E. Ley-Koo and A. Góngora, *Common generating function for the complete wave functions of the three dimensional hydrogen atom*, to be submitted.

26. L. Chaos-Cador and E. Ley-Koo, *Int. J. of Quantum Chem.* **97** (2004) 844.