

Calculating pure rotational transitions of water molecule with a simple Lanczos method

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Abstract. We have calculated pure rotational transitions of water molecule from a kinetic energy operator (KEO) with the z -axis perpendicular to the molecular plane. We have used rotational basis functions which are linear combinations of symmetric top functions so that all matrix elements are real. The calculated spectra agree well with the observed values.

Keywords. Pure rotational spectra; Lanczos method; H₂O.

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1. Introduction

The rovibrational spectrum of water molecule is of considerable interest for a number of applications. These areas include astronomy and astrophysics, studies involving the atmosphere of planets, and simulations involving combustion. Consequently, there is a large amount of experimental data. However, the spectrum of water is very complicated, being dominated by many overlapping molecular bands containing typically 10^4 – 10^7 lines each [1]. For oxygen rich stars, water can be a major absorber, and the very large number of very weak lines can be an important factor governing the predicted size of the stellar atmosphere [2,3]. In contrast to the experimental situation, theoretical calculation of energy levels is rather straightforward. The energy levels are obtained by deriving an exact kinetic energy operator (KEO), choosing basis functions, calculating matrix elements, and computing eigenvalues. Theoretical spectra have been generated for astrophysical applications, but the existing spectra for high J values faces the problem of better convergence and hence accuracy [4–6]. The challenge is then to obtain sufficient accuracy in the data through better convergence. The most widely used method of computing eigenvalues is the simplest product-basis iterative method uses the Lanczos algorithm and ideas of Cullum and Willoughby (CW).

In general, all numerically exact calculations of rovibrational energy levels of triatomics have been done with a KEO with the y axis perpendicular to the plane of the molecule. Recently Sarkar *et al* [7] have used simple Lanczos method for calculating rovibrational energy levels of a triatomic molecule from a KEO with the z axis perpendicular to the

molecular plane. For any molecule the KEO with the z axis perpendicular to the plane has the advantage that it facilitates the term by term evaluation of matrix-vector products. The motivation for the present work was to calculate the pure rotational transitions of water molecule using the newly designed method by us and to compare the data with those of experimental values [8].

2. Theory

The details of the methodology has been described elsewhere [7]. Here we briefly outline the salient features of the method.

We use the Radau coordinate bisector kinetic energy operator (KEO) with the z axis perpendicular to the molecular plane [9–11]. The KEO with the z axis perpendicular to the molecular plane facilitates an iterative calculation of energy levels because it reduces the number of sums over vibrational indices required to compute Hamiltonian matrix-vector products. To use z axis perpendicular to the plane one must (i) deal with complex matrix elements or choose rotational basis functions which are not symmetric top functions to obtain real matrix elements; and (ii) cope with the singularities which are more difficult to handle than the singularities one obtains with the y axis perpendicular to the molecular plane.

The vibration-rotational KEO (in atomic units) we use is

$$T = T^{\text{vib}} + T^{\text{rot}} + T^{\text{cor}}, \quad (1)$$

where

$$T^{\text{vib}} = -\frac{1}{2m_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial R_2^2} - \left(\frac{1}{2m_1 R_1^2} + \frac{1}{2m_2 R_2^2} \right) \frac{\partial}{\partial c} (1 - c^2) \frac{\partial}{\partial c}, \quad (2)$$

$$T^{\text{rot}} = \frac{1}{2} [G_{xx} J_x^2 + G_{yy} J_y^2 + G_{zz} J_z^2 + G_{xy} (J_x J_y + J_y J_x)], \quad (3)$$

$$T^{\text{cor}} = -\frac{i}{2} \sum_{v=R_1, R_2, c} \left[G_{vz} \frac{\partial}{\partial v} + \frac{\partial}{\partial v} G_{vz} \right] J_z, \quad (4)$$

$c = \cos \theta$, R_1 and R_2 are the lengths of the two Radau vectors, θ is the angle between them, m_1 and m_2 are the masses of the two terminal nuclei, and J_x , J_y and J_z are total angular momenta operators in the molecule-fixed frame which obey the anomalous commutation relations. The coefficients are

$$G_{R_1 z} = G_{R_2 z} = 0, \quad (5)$$

$$G_{cz} = (1/2)(1 - c^2)^{1/2} \left[\frac{1}{m_1 R_1^2} - \frac{1}{m_2 R_2^2} \right], \quad (6)$$

$$G_{xx} = \frac{1}{2(1 + c)} \left[\frac{1}{m_1 R_1^2} + \frac{1}{m_2 R_2^2} \right], \quad (7)$$

$$G_{yy} = \frac{1}{2(1-c)} \left[\frac{1}{m_1 R_1^2} + \frac{1}{m_2 R_2^2} \right], \quad (8)$$

$$G_{zz} = \frac{1}{4} \left[\frac{1}{m_1 R_1^2} + \frac{1}{m_2 R_2^2} \right], \quad (9)$$

$$G_{xy} = \frac{1}{2(1-c^2)^{1/2}} \left[-\frac{1}{m_1 R_1^2} + \frac{1}{m_2 R_2^2} \right]. \quad (10)$$

3. The basis functions

We have used the rotational basis functions as suggested by Huber [12] instead of symmetric top functions to avoid complex matrix elements so that we can calculate eigenvalues using the simple Lanczos procedure. For a given value of J there are $2J + 1$ rotational basis functions. We write them as $H_{JK}^{l=0} = R_{JK}^+ H_{JK}^{l=1} = R_{JK}^-$, where

$$R_{JK}^+ = (1/\sqrt{2})(Y_{JK} + (-1)^K Y_{J,-K}), \quad (11)$$

$$R_{JK}^- = (1/\sqrt{2})(Y_{JK} - (-1)^K Y_{J,-K}), \quad (12)$$

Y_{JK} is a symmetric top function with $m = 0$. There are no R_{JK}^- functions for $K = 0$. For $K = 0$ the norm of the R_{JK}^+ functions is two. For $K > 0$ the norm of the $R_{JK}^{+/-}$ functions is one. When operating on a $R_{JK}^{+/-}$ function with $K \geq 0$ one sometimes obtains a $R_{JK'}^{+/-}$ function with $K' < 0$. It is then necessary to use the relation

$$R_{J,-K}^{+/-} = (+/-)(-1)^K R_{JK}^{+/-}. \quad (13)$$

Matrix elements of the KEO with the z axis perpendicular to the molecular plane are all real in this basis.

In the Huber basis, for each value of J , the matrix elements (which are functions of the vibrational coordinates) of the KEO are

$$\begin{aligned} \langle R_{JK}^+ | H | R_{JK'}^+ \rangle &= (T^{\text{vib}} + V) \delta_{KK'} \\ &+ \left[\frac{G_{xx} + G_{yy}}{4} (J(J+1) - K^2) + \frac{K^2}{2} G_{zz} \right] \delta_{KK'} \\ &+ \left[\frac{G_{xx} - G_{yy}}{8} \right] C_K^J C_{K-1}^J \delta_{KK'+2} \\ &+ \left[\frac{G_{xx} - G_{yy}}{8} \right] C_{K'}^J C_{K'-1}^J \delta_{K+2,K'}, \end{aligned} \quad (14)$$

$$\begin{aligned} \langle R_{JK}^- | H | R_{JK'}^- \rangle &= (T^{\text{vib}} + V) \delta_{KK'} \\ &+ \left[\frac{G_{xx} + G_{yy}}{4} (J(J+1) - K^2) + \frac{K^2}{2} G_{zz} \right] \delta_{KK'} \\ &+ \left[\frac{G_{xx} - G_{yy}}{8} \right] C_K^J C_{K-1}^J \delta_{KK'+2} \\ &+ \left[\frac{G_{xx} - G_{yy}}{8} \right] C_{K'}^J C_{K'-1}^J \delta_{K+2,K'}, \end{aligned} \quad (15)$$

$$\begin{aligned} \langle R_{JK}^+ | H | R_{JK}^- \rangle &= (T^{\text{vib}} + V) \delta_{KK'} + Q C_K^J C_{K-1}^J \delta_{KK'+2} \\ &\quad - Q C_{K'}^J C_{K'-1}^J \delta_{K+2,K'} - \frac{1}{2} F K \delta_{KK'}, \end{aligned} \quad (16)$$

$$\begin{aligned} \langle R_{JK}^- | H | R_{JK}^+ \rangle &= (T^{\text{vib}} + V) \delta_{KK'} - Q C_K^J C_{K-1}^J \delta_{KK'+2} \\ &\quad + Q C_{K'}^J C_{K'-1}^J \delta_{K+2,K'} + \frac{1}{2} F K \delta_{KK'}, \end{aligned} \quad (17)$$

where

$$Q = -G_{xy}/4, \quad (18)$$

$$C_K^J = [J(J+1) - K(K+1)]^{1/2}, \quad (19)$$

$$F = \frac{\partial}{\partial c} G_{cz} + G_{cz} \frac{\partial}{\partial c}. \quad (20)$$

The Huber functions for even (odd) values of K are coupled only to Huber functions with even (odd) values of K . The parity of a Huber function is $(-1)^K$. The KEO with z -axis perpendicular to the molecular plane are singular at both $c = \pm 1$. We have treated the singularities by using Jacobi functions as bending basis functions. For the details of the treatment see ref. [7].

For the Radau lengths we use discrete variable representation (DVR) functions (the Morse-type DVR functions of ref. [13]) $\alpha(R_1)$ and $\beta(R_2)$. The parameters, all in atomic units, of the Morse type functions are: $\alpha = 1.157$, $D_e = 0.197696$, $\gamma = 8.28696$. We use the Radau equilibrium length, $R_e = 1.772724$ bohr.

4. Exploiting symmetry

We have chosen the following symmetry adapted basis functions for our final calculations,

$$\begin{aligned} T_{\alpha\beta,n,K}^{J,s,l} &= \frac{1}{\sqrt{2}} [\alpha(R_1)\beta(R_2) + (-1)^{s+l}\beta(R_1)\alpha(R_2)] J_n^{a,b} H_{JK}^l; \quad \alpha > \beta \\ &= \alpha(R_1)\beta(R_2) J_n^{a,b} H_{JK}^l; \quad \alpha = \beta. \end{aligned} \quad (21)$$

The $\alpha = \beta$ functions are symmetric with respect to permuting the two hydrogen nuclei. If J is even (odd) and $s = 0$, an $\alpha \neq \beta$; $T_{\alpha\beta,n,K}^{J,s,l}$ function is symmetric (antisymmetric) with respect to permuting the two hydrogen nuclei. If J is even (odd) and $s = 1$, an $\alpha \neq \beta$; $T_{\alpha\beta,n,K}^{J,s,l}$ function is antisymmetric (symmetric) with respect to permuting the two hydrogen nuclei. This basis separates the matrix into four blocks. Using the Lanczos method we can converge eigenvalues of different blocks separately.

5. Calculating eigenvalues

We have calculated eigenvalues using the Lanczos method of Cullum and Willoughby [14]. This method has two advantages: it requires very little memory and it is very simple. The KEO with the z axis perpendicular to the plane of the molecule has terms which couple

values of K which differ by two. The KEO with the y (or the x) axis perpendicular to the plane of the molecule has terms which couple values of K which differ by two and also terms which couple values of K which differ by one. As a result, for a single Hamiltonian matrix-vector multiplication there are fewer sums over vibrational indices if one uses the KEO with the z axis perpendicular to the plane of the molecule.

6. Results

We have calculated the rovibrational spectra of water molecule for high J values using the method outlined above. We use the recent potential energy surface of Polyansky *et al* [10]. All the results presented in several tables are computed with a basis with 14 Morse-type DVR functions for R_1 and R_2 and 15 Jacobi functions for the bend. We used 22 Jacobi quadrature points to converge potential integrals for each value of K . We need 7000 Lanczos iterations to converge the reported energy. We have checked the convergence of our energy levels by increasing both the number of basis functions and the number of Lanczos iterations. In tables 1–6 we have reported the calculated pure rotational transitions

Table 1. Pure rotational transitions for the (000) vibrational state in cm^{-1} .

J'	K'_a	K'_b	J	K_a	K_b	Exptl.	Calc.
23	7	16	22	8	15	449.370	449.230
25	4	21	24	5	20	518.787	518.799
24	6	19	23	5	18	520.140	520.120
24	7	18	23	6	17	549.541	549.560
24	9	16	23	8	15	698.470	698.560
23	9	15	22	8	14	698.770	698.840
21	13	8	20	12	9	771.409	771.436
24	12	12	23	11	13	817.210	817.230
25	11	14	24	10	15	819.932	819.933
24	17	8	23	16	7	865.929	865.943
19	6	14	18	3	15	872.971	872.913

Table 2. Pure rotational transitions for the (010) vibrational state in cm^{-1} .

J'	K'_a	K'_b	J	K_a	K_b	Exptl.	Calc.
17	6	12	16	5	11	496.14	496.08
20	6	15	19	5	14	496.40	496.27
17	7	11	16	6	10	576.619	576.553
20	7	14	19	6	13	579.53	579.32
18	7	12	17	6	11	581.01	580.90
20	8	13	19	7	12	661.13	660.95
19	9	11	18	8	10	690.63	690.95
22	9	14	21	8	13	733.79	733.56
21	8	13	20	7	14	736.184	736.278
21	9	12	20	8	13	736.649	736.575
21	11	10	20	10	11	770.09	769.92
20	14	6	19	13	7	783.29	783.00

for different vibrational state. These are then compared with the observed values in the same table. The observed values are from ref. [8]. In each case the two sets of data agree well.

Table 3. Pure rotational transitions for the (010) vibrational state in cm^{-1} .

J'	K'_a	K'_b	J	K_a	K_b	Exptl.	Calc.
21	12	10	20	11	9	784.19	783.99
21	12	9	20	11	10	784.21	784.02
23	10	13	22	9	14	791.98	792.68
22	11	12	21	11	10	804.19	803.99
22	12	10	21	11	11	804.27	804.07
21	14	8	20	13	7	804.867	805.829
22	13	10	21	12	9	816.16	815.93
22	13	9	21	12	10	816.19	815.96
23	13	11	22	12	10	835.89	835.68
23	13	10	22	12	11	836.39	835.78
18	6	13	17	3	14	864.048	864.051
19	5	14	18	4	15	864.62	864.82

Table 4. Pure rotational transitions for the (001) vibrational state in cm^{-1} .

J'	K'_a	K'_b	J	K_a	K_b	Exptl.	Calc.
13	7	7	12	6	6	473.66	473.44
13	7	6	12	6	7	480.06	479.91
14	7	8	13	6	7	490.72	490.39
13	8	6	12	7	5	498.08	498.22
13	8	5	12	7	6	489.65	498.80
14	7	7	13	6	8	504.94	504.79
14	8	7	13	7	6	519.65	519.15
14	8	6	13	7	7	521.23	521.47
13	9	5	12	8	4	517.189	517.164
13	9	4	12	8	5	517.224	517.198
14	9	6	13	8	5	540.131	540.120
14	9	5	13	8	6	540.249	540.240

Table 5. Pure rotational transitions for the (100) vibrational state in cm^{-1} .

J'	K'_a	K'_b	J	K_a	K_b	Exptl.	Calc.
13	7	7	12	6	6	480.206	480.242
13	7	6	12	6	7	482.172	482.105
14	7	7	13	6	8	502.16	501.86
13	8	6	12	7	5	505.696	505.598
14	8	7	13	7	6	527.790	527.717
14	10	5	13	9	4	528.3	531.3
13	9	5	12	8	4	529.39	528.74
13	9	4	12	8	5	529.41	528.73
14	9	5	13	8	6	553.29	552.63

Table 6. Pure rotational transitions for the (020) vibrational state in cm^{-1} .

J'	K'_a	K'_b	J	K_a	K_b	Exptl.	Calc.
14	5	10	13	4	9	447.94	447.36
13	6	7	12	5	8	523.95	525.08
13	7	7	12	6	6	549.13	548.76
13	7	6	12	6	7	549.796	549.742
14	7	8	13	6	7	570.13	569.67
13	8	6	12	7	5	570.27	570.49
13	8	5	12	7	6	570.38	570.61
14	7	7	13	6	8	572.93	572.82
13	9	4	12	8	5	584.86	585.35
14	8	7	13	7	6	592.71	592.96
14	9	6	13	8	5	607.53	607.93
14	4	11	13	1	12	783.8735	783.8721

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