

A Variational Procedure for Calculation of the Ro-vibrational Energy Levels of Triatomic Molecules Using Transformed Internal Coordinates

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Received: April 5, 1994; In Final Form: June 6, 1994*

In this paper, we present a two-step variational procedure to solve the ro-vibrational problems for triatomic molecules using the transformed internal valence coordinates. The first step is the solution of a series of secular problems depending on K , which is the projection of the total angular momentum onto the body-fixed z -axis. In the second step, we have used the N lowest eigenfunctions obtained in the first step to construct the ro-vibrational Hamiltonian matrix and suggested an efficient diagonalization method to diagonalize this matrix. The ro-vibrational energy levels of the H_2O molecule for $J \leq 20$ on the potential energy function fitted by Jensen have been calculated and compared with the observed values and some theoretical results to test the procedure.

I. Introduction

In recent years, there have been enormous advances¹ in the calculation of the ro-vibrational energy levels of triatomic molecules using variational techniques. Naturally, many calculations have been made using the traditional Eckart² Hamiltonian in its quantum mechanical form as given by Watson.³ However, the Eckart Hamiltonian was inappropriate for large amplitude vibrations. Usually, on higher ro-vibrational energy regions where all vibrational motions exhibit large amplitude vibrations, calculations have been performed by using specially constructed Hamiltonians which were particularly appropriate to the problems at hand. This has led to an increasing number of Hamiltonians and complementary solution strategies^{4–12} which take full account of anharmonicity and vibration–rotation coupling effects. Almost all of these theoretical procedures employ the two-step solution strategy suggested and developed by Carter and Handy,⁹ Chen et al.,¹³ Tennyson and Sutcliffe,¹⁴ and Choi and Light.¹⁵ The first step¹⁴ is the solution of a series of secular problems depending on J and K , where J is the total angular momentum and K is its projection onto the body-fixed z -axis. This is similar to the process of solving a pure $J = 0$ vibrational problem, but the vibrational molecular kinetic energy operator is modified by J and K . For a given J , one needs to solve $(J + 1)$ such problems. The second step is to choose an appropriate subset of the solutions obtained in the first step to form the full Hamiltonian matrix elements. The ro-vibrational energy levels and wave functions can be determined by diagonalizing this matrix. The difficulties in this problem arise from the fact that the size of the final Hamiltonian matrix increases as $(2J + 1)$. Although the partial symmetry of the rotation functions can be used to reduce this matrix into two separate blocks, the sizes of which increase as J and $(J + 1)$, respectively, the basic difficulties in large J calculations still remain to be overcome.

In this work, we suggest a two-step variational procedure to solve the ro-vibrational problems using the transformed internal valence coordinates. The first step is the solution of a series of secular problems depending on K , which is different from the procedures suggested by Chen et al.¹³ and by Tennyson and Sutcliffe,¹⁴ since Chen et al. simply use the solutions of the pure vibrational problem, while Tennyson and Sutcliffe¹⁴ solve the problems for (J, K) combination. In the second step, we have used the N lowest eigenfunctions obtained in the first step to construct the ro-vibrational Hamiltonian matrix and suggest an efficient diagonalization method to diagonalize this matrix. This two-step variational procedure can reduce the time of computation significantly.

In section II, the ro-vibrational Hamiltonian in the transformed internal coordinates is described. Section III is devoted to the description of the two-step variational procedure suggested by us. Section IV presents some theoretical results of the ro-vibrational energy levels of the H_2O molecule for $J \leq 20$ on the potential energy function fitted by Jensen.¹⁶

II. The Hamiltonian in the Transformed Internal Coordinates

The complete rotation–vibration Hamiltonian for a triatomic molecule in the internal valence coordinates can be written as^{6,8} (in atomic units)

$$H = V + K_v + K_{\text{rot}} + K_{\text{cor}} \quad (1)$$

where V is the potential energy function of the triatomic molecule, K_v is the pure vibrational ($J = 0$) triatomic molecular kinetic operator, K_{rot} and K_{cor} are the vibration–rotation coupling kinetic energy operators. The operators appearing in eq 1 can be expressed explicitly as follows:

$$K_v = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial r_2^2} - \frac{1}{2I} \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right) - \frac{\cos \theta}{m_b} \frac{\partial^2}{\partial r_1 \partial r_2} + \frac{1}{m_b} \left(\frac{1}{r_2} \frac{\partial}{\partial r_1} + \frac{1}{r_1} \frac{\partial}{\partial r_2} - \frac{1}{r_1 r_2} \right) \left(\sin \theta \frac{\partial}{\partial \theta} + \cos \theta \right) \quad (2)$$

$$K_{\text{rot}} = \frac{1}{2\mu_1 r_1^2} (J^2 - 2J_z^2) + \frac{1}{2I \sin^2 \theta} J_z^2 \quad (3)$$

$$K_{\text{cor}} = -\frac{1}{2} \left[\frac{\sin \theta}{m_b r_1 r_2} \left(r_2 \frac{\partial}{\partial r_2} - 1 \right) + \left(-\frac{1}{\mu_1 r_1^2} + \frac{\cos \theta}{m_b r_1 r_2} \right) \frac{\partial}{\partial \theta} \right] \times (J_+ - J_-) + \frac{1}{2 \sin \theta} \left(\frac{\cos \theta}{\mu_1 r_1^2} - \frac{1}{m_b r_1 r_2} \right) (J_+ + J_-) J_z \quad (4)$$

with

$$1/I = 1/\mu_1 r_1^2 + 1/\mu_2 r_2^2 - (2 \cos \theta)/m_b r_1 r_2 \quad (5)$$

where r_1 and r_2 are the bond lengths, θ is the enclosed bond angle, the atom B with mass m_b is assigned to be the central atom, and

$$1/\mu_1 = 1/m_a + 1/m_b, \quad 1/\mu_2 = 1/m_b + 1/m_c \quad (6)$$

where m_a and m_c are the masses of the atoms at the end of the

* Abstract published in *Advance ACS Abstracts*, August 1, 1994.

bonds 1 and 2, respectively. The operators J_+ and J_- are the lowering and raising operators respectively, which are defined by

$$J_{\pm} = J_x \pm iJ_y \quad (7)$$

The operators J_{α} ($\alpha = x, y, z$) are the components of the total angular momentum operator in the body-fixed (BF) frame, which is chosen^{6,8} such that the z -axis is along with the bond 1 so that the bond 2 lies in the positive x -half of the x - z plane. One finds the following commutation relations to hold (in atomic units):

$$[J_x, J_y] = -iJ_z, [J_y, J_z] = -iJ_x, [J_z, J_x] = -iJ_y \quad (8)$$

The internal part of the volume element corresponding to the Hamiltonian in eq 1 is $\sin \theta dr_1 dr_2 d\theta$.

In order to eliminate the coupling term $\partial^2/\partial r_1 \partial r_2$ in K_v and use the symmetry of an AB_2 molecule to simplify the computation, we have suggested using the transformed internal coordinates (Q_1, Q_2, θ) , which are defined by¹⁷

$$Q_1 = (r_1/C + r_2C)/2^{1/2}, \quad Q_2 = (-r_1/C + r_2C)/2^{1/2} \quad (9)$$

where C is the scaling factor, $C = (\mu_1/\mu_2)^{1/4}$. In the AB_2 case, $C = 1$, and (Q_1, θ) and Q_2 represent the symmetrical and antisymmetrical internal valence coordinates, respectively. This leads to simplification in the construction of the vibrational Hamiltonian matrix for an AB_2 molecule since the secular matrix can be divided into its A_1 and B_2 blocks in this case.

The total ro-vibrational wave function can be expanded as

$$\Psi^J(Q_1, Q_2, \theta, \Omega) = \sum_K \chi_K^J(Q_1, Q_2, \theta) F_{MK}^J(\Omega) \quad (10)$$

where Ω stands for the three Euler angles between the space-fixed frame and body-fixed frame and M is the projection of J onto the space-fixed z -axis. F_{MK}^J is a parity-adapted rotation function ($p = 0$ for even parity and $p = 1$ for odd parity) defined by

$$F_{MK}^J(\Omega) = [2(1 + \delta_{k0})]^{-1/2} [D_{MK}^J(\Omega) + (-1)^{J+K+p} D_{M-K}^J(\Omega)] \quad (11)$$

where the D_{MK}^J are the ordinary angular momentum eigenfunctions expressed in terms of the three Euler angles, the matrix elements of the angular momentum operator between which it can easily be written down. In the case of $k = 0$, $J + p$ must be even and F_{M0}^J is identical to D_{M0}^J . On use of eqs 7–11, the ro-vibrational coupled equations in the transformed internal coordinates can be written as

$$(H_{KK}^J - E)\chi_K^J + H_{KK+1}^J \chi_{K+1}^J + H_{KK-1}^J \chi_{K-1}^J = 0 \quad (12)$$

where

$$H_{KK}^J = V + K_v^T + \frac{K^2}{2I \sin^2 \theta} + [J(J+1) - 2K^2]A(Q_1, Q_2) \quad (13)$$

$$H_{KK+1}^J = b^+(J, K) B_k(Q_1, Q_2, \theta) \quad (14)$$

where

$$b^+(J, K) = (1 + \delta_{k0})^{1/2} (J(J+1) - K(K+1))^{1/2} \quad (15)$$

$$K_v^T = -\left(\frac{1}{2\mu} + \frac{1}{2m_b} \cos \theta\right) \frac{\partial^2}{\partial Q_1^2} - \left(\frac{1}{2\mu} - \frac{1}{2m_b} \cos \theta\right) \frac{\partial^2}{\partial Q_2^2} - \frac{1}{2I} \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta}\right) + \frac{2}{m_b(Q_1^2 - Q_2^2)} \left(Q_1 \frac{\partial}{\partial Q_1} + Q_2 \frac{\partial}{\partial Q_2} - 1\right) \left(\sin \theta \frac{\partial}{\partial \theta} + \cos \theta\right) \quad (16)$$

$$A(Q_1, Q_2) = 1/\mu(Q_1 - Q_2)^2 \quad (17)$$

$$B_k(Q_1, Q_2, \theta) = \frac{1}{m_b(Q_1^2 - Q_2^2)} \left\{ \cos \theta \left[\frac{\partial}{\partial \theta} + (K+1) \cot \theta \right] - \sin \theta \left[\frac{Q_1 + Q_2}{2} \left(\frac{\partial}{\partial Q_1} + \frac{\partial}{\partial Q_2} \right) + K \right] \right\} + \frac{1}{\mu(Q_1 - Q_2)^2} \left[\frac{\partial}{\partial \theta} + (K+1) \cot \theta \right] \quad (18)$$

In eq 15, δ_{k0} is the Kronecker delta. In eqs 16–18, μ is the reduced mass, $\mu = (\mu_1 \mu_2)^{1/2}$. The expression of H_{KK-1}^J is not given explicitly since the full ro-vibrational Hamiltonian matrix is a real symmetric matrix. It can be shown from eqs 13–18 that the rotational symmetrization does not affect both the operators and the potential energy function appearing in the vibration-rotation coupled eq 12; it only modifies the H_{KK+1}^J terms by introducing a factor of $2^{1/2}$ into the terms coupling $K = 0$ to $K = 1$ in the case of $(J+p)$ even. Therefore, the coupled equations are decoupled into two separate blocks: one block contains $(J+1)$ parity-adapted rotation functions with K values running from 0 to J ; another block is simply a submatrix of the former block matrix with the rows and columns containing $K = 0$ removed. The energy levels and the vibrational parts $\{\chi_K^J\}$ of the ro-vibrational wave functions can be obtained by solving the coupled eq 12. In the next section, a two-step variational procedure for solving eq 12 is presented and discussed.

III. A Two-Step Variational Procedure

A. Solution of the Vibrational Problems. It can be seen from eq 12 that for a direct solution of the ro-vibrational problem the size of the secular equation increases as J and $(J+1)$ for $(J+p)$ odd and $(J+p)$ even, respectively. Therefore, the direct solution is very difficult for larger J calculations. Two-step variational procedures have been suggested and developed by Tennyson and Sutcliffe,¹⁴ Carter and Handy,⁹ Choi and Light,¹⁵ and Chen et al.,¹³ which can reduce considerably the size of the ro-vibrational secular equation. In this paper, we present an alternative two-step variational procedure in order to reduce further the number of the vibrational problems and the computational effort.

In the first step, we have suggested solving the vibrational problems defined by

$$[H_k - \epsilon_i^K] \Phi_i^K(Q_1, Q_2, \theta) = 0 \quad (19)$$

with

$$H_K = K_v^T + V + \frac{K^2}{2I \sin^2 \theta} \quad (20)$$

It is easy to see that for the AB_2 molecule, the Hamiltonian in eq 20 is symmetrical for exchange between r_1 and r_2 (that is, change the sign of Q_2), so the secular problem (19) can be divided into its A_1 and B_2 blocks according to the symmetry of the basis

TABLE 1: Ro-vibrational Energy Levels (in cm⁻¹) of Water for $J = 20$ and for the Vibrational States (001) and (011) Using the 180, 190, and 200 Vibrational Functions^a

K_a	K_c	(001)				(011)			
		expt ²³	180	190	200	expt ²³	180	190	200
0	20	7740.7	5.9	5.8	5.6	9283.9	13.6	12.4	11.6
1	20	7740.7	6.0	5.8	5.7	9283.9	14.2	12.7	11.6
1	19	8095.9	6.0	5.9	5.8	9684.7	10.7	9.5	8.9
2	19	8095.9	6.0	5.9	5.8	9684.7	11.0	9.5	9.0
2	18	8415.0	6.3	6.3	6.2	10033.4	-8.5	-8.5	-8.5
3	18	8415.0	6.4	6.3	6.2	10033.4	-8.5	-8.5	-8.5
3	17	8702.4	6.8	6.7	6.7	10343.2	-4.8	-4.8	-4.8
4	17		8709.2	8709.2	8709.1		10338.4	10338.4	10338.4
4	16	8959.0	7.4	7.3	7.3	10615.5	7.2	6.5	6.1
5	16	8959.5	7.4	7.3	7.3		10625.8	10625.4	10624.8
5	15	9181.2	0.9	0.7	0.4		10853.8	10855.5	10854.4
6	15		9196.7	9196.6	9196.5		10872.7	10872.3	10871.7
6	14	9357.7	8.5	8.5	8.5		11030.1	11029.8	11029.5
7	14		9412.7	9412.5	9412.2		11091.5	11091.2	11090.8
7	13	9475.7	5.7	5.7	5.6		11158.5	11158.3	11158.1
8	13		9597.9	9597.9	9597.8		11310.9	11310.6	11310.2
8	12		9625.8	9625.8	9625.7		11328.1	11327.9	11327.6
9	12		9804.2	9804.2	9804.1		11543.3	11543.1	11543.9
9	11		9809.4	9809.4	9809.4		11552.6	11557.0	11553.2
10	11		10005.5	10005.2	10005.0		11794.0	11793.7	11793.4
10	10		10005.6	10005.3	10005.1	11784.0	10.3	10.0	9.7
11	10		10268.0	10267.9	10267.9		12061.0	12060.6	12060.4
11	9		10268.0	10268.0	10268.0	12051.3	9.7	9.4	9.1
12	9	10516.8	5.5	5.5	5.4	12331.6	8.9	8.6	8.4
12	8	10516.8	5.5	5.5	5.5	12331.6	8.9	8.6	8.4
13	8	10783.0	4.3	4.2	4.2		12619.8	12619.8	12619.8
13	7	10783.0	4.3	4.2	4.2		12619.8	12619.8	12619.8
14	7		11059.9	11059.8	11059.8		12924.0	12923.8	12923.7
14	6		11059.9	11059.2	11059.8		12924.0	12923.8	12923.7
15	6		11337.4	11337.4	11337.3		13222.6	13222.5	13222.4
15	5		11337.4	11337.4	11337.3		13222.6	13222.5	13222.4
16	5		11631.6	11631.5	11631.4		13519.9	13519.8	13519.7
16	4		11631.6	11631.5	11631.3		13519.9	13519.8	13519.7
17	4		11895.9	11895.8	11895.8		13816.7	13816.7	13816.6
17	3		11895.9	11895.8	11895.8		13816.7	13816.7	13816.6
18	3		12171.7	12171.6	12171.6		14108.0	14108.0	14108.0
18	2		12171.7	12171.6	12171.6		14108.0	14108.0	14108.0
19	2		12440.7	12440.7	12440.7		14390.4	14390.4	14390.4
19	1		12440.7	12440.7	12440.7		14390.4	14390.4	14390.4
20	1		12706.6	12706.6	12706.6		14664.8	14664.6	14664.6
20	0		12706.6	12706.6	12706.6		14664.8	14664.6	14664.6

^a For observed levels, the calculated values are given as calculated – observed; otherwise, the actual calculated values are given.

with respect to Q_2 . The solution of the vibrational problem in eq 19 is technically the same process as solving a pure $J = 0$ vibrational problem, but in the present case, the effective Hamiltonian (20) contains a term with K^2 so that it depends on K , which is the projection of J onto the BF z -axis. Recently, we have suggested an SCF-CI¹⁷ procedure to calculate the highly excited vibrational states of triatomic molecules in the transformed internal coordinates. In order to eliminate the singular term $K^2/\sin^2 \theta$ and simplify the integral over θ between the basis functions, a normalized associated Legendre polynomial $\Theta_j^K(\theta)$ which is defined by

$$\Theta_j^K(\theta) = \left(\frac{(2j+1)!(j-K)!}{2(j+K)!} \right)^{1/2} P_j^K(\cos \theta) \quad (21)$$

should be used as the primitive basis for the bending vibration. The harmonic oscillator functions are used as the primitive basis for the stretching vibrations for computational simplicity, as in the SCF-CI procedure.¹⁷ This primitive basis can be contracted to the optimal independent-mode wave functions $\{\phi_n^{(1)}(Q_1), \phi_n^{(2)}(Q_2), \phi_n^K(\theta)\}$ using the following effective independent-mode Hamiltonians,

$$h_1(Q_1) = \langle \phi_0^{(2)}(Q_2) \phi_0^{K=0}(\theta) | H_{K=0} | \phi_0^{(2)}(Q_2) \phi_0^{K=0}(\theta) \rangle \quad (22)$$

$$h_2(Q_2) = \langle \phi_0^{(1)}(Q_1) \phi_0^{K=0}(\theta) | H_{K=0} | \phi_0^{(1)}(Q_1) \phi_0^{K=0}(\theta) \rangle \quad (23)$$

$$h_3^K(\theta) = \langle \phi_0^{(1)}(Q_1) \phi_0^{(2)}(Q_2) | H_K | \phi_0^{(1)}(Q_1) \phi_0^{(2)}(Q_2) \rangle \quad (24)$$

In the case of $K = 0$, the three secular problems with the above three Hamiltonians are coupled to each other, so the SCF method should be utilized to determine the optimal three effective independent-mode Hamiltonians and the corresponding independent-mode wave functions. In the case of $K > 0$, only the Hamiltonian $h_3^K(\theta)$ and the wave functions $\phi_n^K(\theta)$ for bending vibrations need to be determined. This leads to considerable computational savings in the following calculations. After the functions $\{\phi_n^{(1)}(Q_1), \phi_n^{(2)}(Q_2), \phi_n^K(\theta)\}$ have been obtained, the eigenvalues $\{\epsilon_i^K\}$ and eigenfunctions $\{\Phi_i^K(Q_1, Q_2, \theta)\}$ of eq 19 can be calculated using the same CI procedure suggested in our previous paper.¹⁷

B. Construction and Diagonalization of the Ro-vibrational Hamiltonian Matrix. In the second step, we have taken a set of the N lowest vibrational eigenfunctions obtained in the first step for each K to expand the vibrational part of the total ro-vibrational wave function as

$$\chi_K^J(Q_1, Q_2, \theta) = \sum_{i=1}^N \Phi_i^K(Q_1, Q_2, \theta) C_{iK}^J \quad (25)$$

On substitution of eq 25 into eq 12, the ro-vibrational Hamiltonian matrix can be constructed. It is easy to show that the nonzero matrix elements are given by

$$\langle \Phi_i^K | H | \Phi_j^K \rangle = \epsilon_i^k \delta_{ij} + [J(J+1) - 2K^2] A_{ij}^K \quad (26)$$

$$\langle \Phi_i^K | H | \Phi_j^{K+1} \rangle = b_{jK}^+ B_{ij}^k \quad (27)$$

$$\langle \Phi_i^K | H | \Phi_j^{K-1} \rangle = \langle \Phi_j^{K-1} | H | \Phi_i^K \rangle \quad (28)$$

where

$$A_{ij}^K = \langle \Phi_i^K | A(Q_1, Q_2) | \Phi_j^K \rangle \quad (29)$$

$$B_{ij}^k = \langle \Phi_i^K | B_K(Q_1, Q_2, \theta) | \Phi_j^{K+1} \rangle \quad (30)$$

It should be noted that the matrices **A** and **B** are independent of the total angular momentum *J*. Therefore, the matrices **A** and **B** with *K* = 0, 1, 2, ..., *K*_{max} can be evaluated and stored in disk in the first step, then the ro-vibrational matrix with *J* ≤ *K*_{max} can be very easily constructed using eqs 26–28. This obviously leads to the substantial computational savings in the vibrational calculations and the construction of the final secular matrix, compared with the procedure of Tennyson and Sutcliffe.^{14,18}

Diagonalization of a symmetric matrix is a key problem in all variational procedures. The secular matrix obtained in the second step is a banded real symmetric matrix with half-width 2*N* and length *JN* or (*J* + 1)*N*. Diagonalization of this matrix with diagonalizers for a real symmetric matrix and a banded real symmetric matrix has been found¹⁴ to be very time consuming. In order to round this problem, we have suggested a modified diagonalization method which is modified from the TRED2 routine in the EISPACK¹⁹ package for a banded real symmetric matrix and described as follows. First, about *JN*(*N* − 1)/2 Givens transformations are performed in a suitable way to transform this banded matrix into a new banded real symmetric matrix with half-width (*N* + 1) and the same length. Second, about (*JN*)²/2 Givens transformations are performed to transform the new banded matrix into a tridiagonal matrix. All of the Givens transformations are not accumulated but stored on disk. Third, the TQL routine in the EISPACK package is employed to determine the eigenvalues of the matrix. Finally, an inverse-iteration method is used to determine the eigenfunctions of the tridiagonal matrix for the eigenvalues of interest; the back transformation of the Givens transformations is then carried out to obtain the ro-vibrational wave functions of interest. The largest matrix needed to be stored in memory is the banded real symmetric matrix with half-width (*N* + 1) and length (*J* + 1)*N*. This diagonalization strategy leads to the efficient savings both in storage and in CPU time.

IV. Application to H₂O

The ro-vibrational energy levels of the water molecule have been studied theoretically by many researchers, because of the wealth of experimental data and its importance for many applications. A number of potential energy surfaces (PESs) for H₂O have been constructed from the extensive spectroscopic data. Recently, Fernley, Miller, and Tennyson (FMT)²⁰ have shown that Jensen's PES is the most reliable one among those PESs. For the theoretical study of ro-vibrational energy levels for H₂O, Carter and Handy (CH)⁹ have evaluated levels for *J* ≤ 9, Chen et al.¹³ have evaluated levels for *J* ≤ 10, and Fernley, Miller, and Tennyson²⁰ have evaluated levels for *J* ≤ 2. In order to test the procedure described above, we have calculated the band origins for the ro-vibrational states for *J* ≤ 20 and compared them with the observed values and some theoretical results.

For H₂O, the transformed internal coordinates are identical to the symmetrized internal coordinates, in which *Q*₁ and *θ* denote symmetrical stretching and bending vibrations, respectively, and *Q*₂ denotes an antisymmetrical stretching vibration. Therefore,

TABLE 2: Ro-vibrational Energy Levels (in cm^{−1}) of Water for *J* = 20 and for the Vibrational States (000) and (100)^a

<i>K</i> _a	<i>K</i> _c	(000)		(100)	
		expt ²³	calc	expt ²³	calc
0	20	4048.3	−0.8	7627.5	3.7
1	20	4048.3	−0.8	7627.5	3.7
1	19	4412.3	−0.8	7985.1	3.4
2	19	4412.3	−0.8	7985.1	3.4
2	18	4738.6	−0.7	8305.9	3.6
3	18	4738.6	−0.7	8305.9	3.7
3	17		5031.3		8598.4
4	17	5032.0	−0.6		8598.6
4	16	5292.1	−0.1		8855.4
5	16	5294.0	−1.0		8857.3
5	15	5513.3	0.9		9074.9
6	15	5527.0	0.1		9087.4
6	14		5683.4		9245.0
7	14	5739.2	0.0		9294.7
7	13		5814.8		9376.1
8	13	5947.3	−0.8		9516.9
8	12		5967.3		9527.4
9	12	6167.9	−2.4		9733.7
9	11	6171.0	−2.1		9735.6
10	11		6403.1		9928.0
10	10		6403.5		9928.3
11	10	6664.1	−5.8	10180.9	1.6
11	9	6664.2	−5.9		10182.5
12	9	6935.4	−7.7	10445.6	1.2
12	8	6935.4	−7.7	10445.5	1.2
13	8	7217.6	−9.7	10719.7	0.9
13	7	7217.6	−9.7	10719.7	0.9
14	7	7507.6	−11.8	11001.3	0.4
14	6	7507.6	−11.8	11001.3	0.4
15	6	7802.7	−13.9	11287.8	0.0
15	5	7802.7	−13.9	11287.8	0.0
16	5	8100.3	−16.2	11576.7	−0.2
16	4	8100.3	−16.2	11576.7	−0.2
17	4	8397.6	−18.6	11865.7	−0.6
17	3	8397.6	−18.6	11865.7	−0.6
18	3	8691.9	−21.1		12151.4
18	2	8691.9	−21.1		12151.4
19	2	8979.9	−23.9		12432.6
19	1	8979.9	−23.9		12432.6
20	1	9257.4	−26.9		12698.9
20	0	9257.4	−26.9		12698.9

^a See Table 1 footnote.

the vibrational secular problem is naturally divided into its **A**₁ and **B**₂ blocks according to the symmetry of the independent-mode wave functions for the *Q*₂ mode.

In the first step of the procedure described above, we use 50 primitive basis functions to determine the optimal independent-mode wave functions and use *n*₁ + *n*₂ + *n*₃ ≤ 17 (where *n*_{*i*} denotes the quantum number of the independent-mode *i*) to generate 627 and 524 configurations for the **A**₁ and **B**₂ blocks, respectively. In this step, we have evaluated and stored the eigenvalues of eq 19 and the coupled matrices **A** and **B** in eqs 29 and 30 for *K* ≤ 20. The related integrals in the calculations are evaluated with the HEG quadrature.^{21,22}

In the second step, we have calculated the ro-vibrational energy levels of water for *J* ≤ 20 using the procedure described in part B of section III. In order to test the convergence of the energy levels, we have performed the calculations with the 180, 190, and 200 lowest vibrational eigenfunctions obtained in the first step for *J* = 20. The results for the vibrational states (001) and (011) are presented in Table 1 together with the observed values.²³ It can be seen from Table 1 that most of the energy levels are converged to better than 0.5 cm^{−1}. Therefore, we have used the 200 lowest vibrational eigenfunctions to perform the calculations for *J* ≤ 20.

For *J* = 1 and 2, our results are not listed here, since they are almost the same as the results of FMT²⁰ who used the same PES. Some of our results are given in Tables 2–4. The results for *J* = 20 and for the vibrational states (000) and (100) are listed in Table 2 together with the observed values.²³ The results for the

TABLE 3: Ro-vibrational Energy Levels (in cm^{-1}) of Water for $J = 9$ and for the Vibrational States (000), (100), (001), and (011)^a

K_a	K_c	(000)			(100)		
		expt ²³	CH ⁹	calc	expt ²³	CH ⁹	calc
0	9	920.2	-0.1	-0.2	4559.7	0.3	0.2
1	9	920.2	0.0	-0.1	4559.8	0.2	0.2
1	8	1079.1	0.9	-0.1	4716.0	0.0	0.4
2	8	1080.4	0.6	-0.2	4717.1	-0.1	0.4
2	7	1201.9	1.1	0.2	4837.7	0.3	0.7
3	7	1216.2	0.8	-0.1	4850.4	-0.4	0.6
3	6	1282.9	2.1	0.4	4918.2	0.8	0.9
4	6	1340.9	1.1	-0.4	4971.3	-0.3	0.7
4	5	1360.2	1.8	0.0	4992.1	3.9	3.5
5	5	1475.0	1.0	-1.0	5108.3	0.7	-0.6
5	4	1477.2	0.8	-0.8	5107.7	-0.7	-0.4
6	4	1631.3	-0.3	-1.8	5256.4	-2.4	-0.7
6	3	1631.4	0.6	-1.7	5256.4	-2.4	-0.7
7	3	1810.6	-0.6	-2.6	5430.2	-5.2	-1.1
7	2	1810.6	-0.6	-2.6	5430.2	-5.2	-1.1
8	2	2009.8	-0.8	-3.6	5624.4	-7.4	-1.6
8	1	2009.8	-0.8	-3.6	5624.4	-7.4	-1.6
9	1	2225.5	-1.5	-4.8	5837.0	-10.0	-2.5
9	0	2225.5	-1.5	-4.8	5837.0	-10.0	-2.5

K_a	K_c	(001)			(011)		
		expt ²³	CH ⁹	calc	expt ²³	CH ⁹	calc
0	9	4661.4	2.6	1.3	6234.0	12.0	2.1
1	9	4661.4	2.6	1.4	6234.0	12.0	2.1
1	8	4817.0	3.0	1.5	6406.0	10.0	3.6
2	8	4817.7	2.3	1.6	6407.5	9.5	2.2
2	7	4939.8	3.2	1.8	6537.1	8.9	2.4
3	7	4949.0	3.0	2.1	6553.2	7.8	2.8
3	6	5022.3	3.7	1.7	6624.6	7.4	1.9
4	6	5067.1	1.9	2.4	6687.5	6.5	3.2
4	5	5087.0	1.0	2.8	6706.1	5.9	3.2
5	5	5193.5	1.5	2.1	6833.2	4.8	3.3
5	4	5196.5	1.5	2.2	6835.4	4.6	3.2
6	4	5339.6	0.4	1.7	7001.8	2.2	3.4
6	3	5339.8	1.2	1.7	7001.9	3.1	3.4
7	3	5507.5	-0.5	1.1	7193.3	-0.3	3.4
7	2	5507.5	-0.5	1.1	7193.3	-0.3	3.4
8	2	5694.0	-2.0	0.6	7404.0	-3.0	3.4
8	1	5694.0	-2.0	0.6	7404.0	-3.0	3.4
9	1	5896.3	-3.3	-0.3	7630.0	-6.0	3.2
9	0	5896.3	-3.3	-0.3	7630.0	-6.0	3.2

^a See Table 1 footnote.

vibrational states (000), (100), (001), and (011) and for $J = 9$ and 15 are listed in Tables 3 and 4 together with the observed values²³ and the theoretical results of Carter and Handy⁹ for $J = 9$. It can be seen from Table 3 that our results are better than the results of Carter and Handy⁹ who used the PES which they fitted themselves; for example, their errors are 10 cm^{-1} for the (100) $K_a = 9$ and $K_c = 0$ state and 12 cm^{-1} for the (011) $K_a = 0$ and $K_c = 9$ state. The corresponding values in our results are 2.5 and 2.1 cm^{-1} , respectively. From Tables 2 and 4, it can be seen that most of the calculated values are within several wavenumbers of the experimental values, the largest discrepancies are -14.6 cm^{-1} for the (000), $K_a = 15$, and $K_c = 0$ state in the case of $J = 15$ and -26.9 cm^{-1} for the (000), $K_a = 20$, and $K_c = 0$ state in the case of $J = 20$. All calculations have been carried out on a SUN SPARC station 2.

It is shown from this application that the variational procedure described in this paper is efficient for the calculation of the higher ro-vibrational energy levels of a triatomic molecule, especially for an AB_2 molecule. This variational procedure is very suitable for a series of J calculations.

Acknowledgment. We wish to thank Professor Auchin Tang for the stimulation of this work. This work has been supported by the National Natural Science Foundation of China.

TABLE 4: Ro-vibrational Energy Levels (in cm^{-1}) of Water for $J = 15$ and for the Vibrational States (000), (100), (001), and (011)^a

K_a	K_c	(000)		(100)	
		expt ²³	calc	expt ²³	calc
0	15	2358.3	-0.4	5970.2	1.4
1	15	2358.3	-0.4	5970.2	1.4
1	14	2631.3	-0.5	6238.2	1.7
2	14	2631.3	-0.5	6238.2	1.7
2	13	2872.3	-0.4	6474.7	2.0
3	13	2872.6	-0.4	6475.4	2.0
3	12	3080.2	-0.1	6682.0	2.0
4	12	3083.9	-0.3		6685.6
4	11	3244.6	0.8		6849.2
5	11	3269.5	-0.2		6868.3
5	10	3360.6	1.3	6960.4	2.9
6	10	3443.2	-0.6		7040.0
6	9	3472.9	0.4	7070.6	2.2
7	9	3624.2	-1.5	7220.2	1.6
7	8	3629.1	-1.2	7223.0	0.8
8	8	3824.5	-2.7	7414.5	-0.3
8	7	3825.0	-2.7	7414.9	-0.3
9	7	4045.3	-4.1	7636.5	-2.2
9	6	4045.3	-4.0	7636.5	-2.1
10	6	4283.3	-5.5	7831.7	-0.8
10	5	4283.3	-5.5	7831.7	-0.8
11	5	4535.0	-7.1	8084.8	-0.3
11	4	4535.0	-7.1	8084.8	-0.3
12	4	4797.0	8.5	8341.9	-0.7
12	3	4797.0	-8.5	8341.9	-0.7
13	3	5066.2	-10.6	8604.6	-1.0
13	2	5066.2	-10.6	8604.6	-1.0
14	2	5339.7	-12.6	8871.1	-1.4
14	1	5339.7	-12.6	8871.1	-1.4
15	1	5614.1	-14.6	9139.0	-2.0
15	0	5614.1	-14.6	9139.0	-2.0

K_a	K_c	(001)		(011)	
		expt ²³	calc	expt ²³	calc
0	15	6077.1	-0.6	7636.6	-2.3
1	15	6077.1	-0.6	7636.5	-2.2
1	14	6343.4	3.5	7934.1	4.5
2	14	6342.5	2.3	7935.8	4.2
2	13	6578.9	2.8	8191.8	4.7
3	13	6579.7	3.9	8193.4	4.7
3	12	6784.7	4.2	8412.5	5.1
4	12	6786.7	4.4	8417.2	5.3
4	11	6952.2	4.8	8584.6	5.0
5	11	6966.6	5.2	8612.5	5.9
5	10	7074.3	4.4	8694.2	4.8
6	10	7131.6	5.7	8796.6	6.3
6	9	7167.3	6.6	8823.9	6.5
7	9	7302.7	4.7	8990.1	6.2
7	8	7309.5	5.2	8994.5	6.3
8	8	7489.3	4.7	9203.2	6.0
8	7	7490.1	4.7	9203.2	6.4
9	7	7696.2	3.8	9435.8	5.8
9	6	7696.3	3.8	9435.8	5.8
10	6	7919.7	2.9	9684.4	5.5
10	5	7919.7	2.9	9684.4	5.5
11	5	8156.3	1.9	9945.1	5.0
11	4	8156.3	1.9	9945.1	5.0
12	4	9402.9	0.7	10214.4	4.5
12	3	8402.9	0.7	10214.4	4.5
13	3	8656.3	-0.5	10489.1	3.7
13	2	8656.3	-0.5	10489.1	3.8
14	2	8913.6	-1.9	10765.9	3.0
14	1	8913.6	-1.9	10765.9	3.0
15	1	9171.5	-3.4		11024.5
15	0	9171.5	-3.4		11024.5

^a See Table 1 footnote.**References and Notes**

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