

## SEMICLASSICAL ROTATION-VIBRATION ENERGIES FOR A TRIATOMIC MOLECULE: $\text{H}_2\text{O}$

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We report primitive semiclassical rotation-vibrational energy levels for a triatomic molecule,  $\text{H}_2\text{O}$ , with inclusion of all three vibrational degrees of freedom. Both the Lai-Hagstrom and Hoy-Bunker potential surfaces are used. Vibrational and rotational actions are calculated using the fast Fourier transform Sorbie-Handy method. Overall, encouraging agreement with the quantum variational results of Chen, Maessen, and Wolfsberg is found.

### 1. Introduction

Much effort has been devoted in recent years to the problem of semiclassical quantization of energy eigenvalues for non-separable molecular potential-energy surfaces [1], with the aim of providing practical alternatives to quantum-mechanical variational calculations [2]. Most studies in this area have focused on vibrational states in the absence of rotations. Nevertheless, incorporation of rotational degrees of freedom is essential for elucidation of the spectroscopic and dynamical consequences of the interaction between rotation and vibration (for a recent review, see ref. [3]).

Work on the semiclassical quantization of the rigid asymmetric top [4-8] provides a foundation for subsequent efforts to extend semiclassical methods to the full rotation-vibration problem (for wave-packet-based approaches, see refs. [9,10]). A key ingredient is the canonical transformation of Augustin and Miller [11] (see also ref. [12]), which explicitly reduces the rigid-rotor Hamiltonian to a system with one degree of freedom. Exploiting the Augustin-Miller transformation, Frederick and McClelland have calculated both primitive [13] and uniform [13,14] semiclassical energy levels for a rigid-bender [15] model of  $\text{H}_2\text{O}$ , in which stretching motions were frozen out. Good agreement was obtained with the

quantum results of Bunker [13] in a regime where the usual perturbation theory of rotation-vibration interaction [16] is inapplicable. The rigid-bender model for  $\text{H}_2\text{O}$  is effectively a two-dimensional system, whose phase-space dynamics can be explored using the Poincaré surface-of-section method [17,18].

In this paper we report primitive EBK [1] semiclassical rotation-vibration energies for a triatomic molecule,  $\text{H}_2\text{O}$ , with inclusion of all three vibrational degrees of freedom. The full rotation-vibration problem for a triatomic is effectively four dimensional, and requires a method suitable for quantizing systems with several degrees of freedom. We have applied the FFT SH method [19] (see also ref. [20]) to calculate good vibrational and rotational action variables. The semiclassical results reported here are obtained using the potential-energy surfaces of Lai-Hagstrom [21,22] and Hoy-Bunker [23], and are compared with the quantum variational results of Chen, Maessen and Wolfsberg [22].

### 2. Method

Classical equations of motion for the rotating-vibrating triatomic are integrated in lab-fixed Cartesian coordinates, with the potential surface expressed in terms of geometrically defined bond lengths and interbond angles [24]. Both the Lai-

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Hagstrom [21] and Hoy-Bunker [23] potentials are Taylor expansions in bend and stretch displacement coordinates containing terms up to quartic, with slightly different equilibrium geometries (see table 1 of ref. [22]). A transformation to molecule-fixed (Eckart) coordinates [25] is made to follow the time evolution of vibrational (normal-mode coordinates and momenta) and rotational (molecule-fixed components of the total angular momentum vector  $J$ ) variables.

The orientation of the rotating Eckart frame is calculated using a symmetric orthonormalization procedure [25,26]. Let the  $3N$  components  $\{a_i^\alpha\}$ ,  $\alpha=1, \dots, N$ ,  $i=x, y, z$ , define the static molecular model (equilibrium structure) for an  $N$ -atom system [25,26]. For an arbitrary distorted configuration of nuclei  $\{r^\alpha\}$ , define the three Eckart vectors

$$F_i = \sum_{\alpha} m^{\alpha} a_i^{\alpha} r^{\alpha}, \quad (1)$$

and the associated Gram matrix  $\Gamma$ ,

$$\Gamma_{ij} = F_i \cdot F_j. \quad (2)$$

The three unit vectors  $\{f_i\}$  defining the Eckart frame are then given by

$$f_i = \sum_j F_j (\Gamma^{-1/2})_{ji}, \quad (3)$$

where the positive definite square root of  $\Gamma$  is used. This method involves only numerical matrix algebra, and avoids use of the Euler angle parameterization of the direction cosine matrix. (For a planar molecule such as  $H_2O$ , one of the Eckart vectors is identically zero. The corresponding  $2 \times 2$  Gram matrix is used in this case.)

Normal-mode coordinates are obtained by linear transformation of molecule-fixed Cartesian displacements [24]. Instantaneous values of the canonical pair of variables  $(k_a, \chi_a)$  associated with  $A$ -type rotation about the axis of least inertia are calculated from the body-fixed components of the total angular momentum vector  $J$ , with the replacement  $J(J+1) \rightarrow (J+\frac{1}{2})^2$  [5,7]:

$$J_x = -[(J+\frac{1}{2})^2 - k_a^2]^{1/2} \sin(\chi_a), \quad (4a)$$

$$J_y = -[(J+\frac{1}{2})^2 - k_a^2]^{1/2} \cos(\chi_a), \quad (4b)$$

$$J_z = k_a. \quad (4c)$$

A corresponding pair of variables  $(k_c, \chi_c)$  can be defined for  $C$ -type motion.

The FFT SH method [19] is used to calculate good action variables from the normal-mode and rotational variable time series. The FFT SH approach is an approximate procedure, in which it is necessary to identify a set of coordinates in which the motion is approximately separable. For the states reported here, the good actions are assumed to be topologically equivalent to the uncoupled vibrational and rotational actions, i.e. it is assumed that there are no strong vibration-vibration or rotation-vibration resonances. A lack of low-order rotation-vibration resonances is consistent with the quantum calculations of Chen, Maessen and Wolfsberg [22], in which only a limited amount of centrifugal mixing of  $J=0$  vibrational eigenstates is found for  $(0, 0, 0)$  and  $(0, 1, 0)$  states with  $J=10$ . Also, for the vibrational

Table 1

Rotational energies for  $J=10$  ( $\text{cm}^{-1}$ ) for the Lai-Hagstrom potential-energy surface of water. The energies are given with respect to the rotationless vibrational state  $(0, 0, 0)$ . The dashed line divides  $A$ - from  $C$ -type states

$k_a$	$k_c$	$\Delta E^{a)}$	QM <sup>b)</sup>	FFT SH <sup>c)</sup>
10	0	3.76	2672.964	2669.20
10	1	3.76	2672.964	2669.20
9	1	-0.480	2451.850	2452.33
9	2	-0.480	2451.850	2452.33
8	2	0.178	2243.318	2243.14
8	3	0.177	2243.317	2243.14
7	3	-2.51	2051.021	2053.51
7	4	-2.53	2050.981	2053.51
6	4	-7.61	1879.253	1886.49
6	5	-7.98	1878.511	1886.49
5	5	0.216	1736.246	1736.03
5	6	-7.95	1728.075	1736.03
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4	6	-2.38	1635.853	1638.23 <sup>d)</sup>
4	7	22.3	1593.975	1571.71
3	7	-13.4	1558.337	1571.71
3	8	3.49	1458.701	1455.21
2	8	-2.49	1452.721	1455.21
2	9	-0.108	1304.352	1304.46
1	9	-0.524	1303.936	1304.46
1	10	2.07	1123.481	1121.41
0	10	2.06	1123.470	1121.41

<sup>a)</sup>  $\Delta E = \text{QM} - \text{FFT SH}$ .

<sup>b)</sup> Quantum-mechanical energies from ref. [22].

<sup>c)</sup> Present work.

<sup>d)</sup> Eigenvalue obtained by interpolation from the higher-energy  $A$ -type states.

quantum numbers considered, the rotationless states have normal-mode character, and no transition to local-mode dynamics is evident. Our assumption of quasiseparability is further supported by examining plots of zeroth-order actions (for the vibrations, harmonic normal-mode energies) versus time for quantizing trajectories; although the zeroth-order actions exhibit fluctuations due to anharmonic and vibration-rotation couplings, there are no large-scale oscillations characteristic of low-order resonances. Nevertheless, some trajectories with  $k$ -values in the vicinity of the  $A$ - to  $C$ -type separatrix (see below) appear to be weakly chaotic on a 16 ps timescale (the FFT SH algorithm will still yield values for "actions" in such cases). A detailed classical trajectory study of rotation-vibration interactions in three-mode  $H_2O$  is in progress. For quasiperiodic trajec-

tories, use of the FFT EBK [19,20] method rather than FFT SH would allow more accurate calculation of good actions or treatment of strong low-order resonant motions.

Initial conditions are iterated to find trajectories satisfying the primitive EBK quantization conditions:

$$N_i = (n_i + \frac{1}{2})\hbar, \quad i=1,2,3, \quad \text{vibrations}, \quad (5a)$$

$$N_i = n_i\hbar, \quad i=A \text{ or } C, \quad \text{rotation}. \quad (5b)$$

As discussed in detail by Duchovic and Schatz for the case of a rigid asymmetric top [7], the appropriate quantization condition (5b) for rotational motion depends on which side of the separatrix dividing  $A$ - from  $C$ -type motion the trajectory lies. The primitive quantization procedure used here is unable to obtain the  $k$ -splittings of the rotational levels;

Table 2

Rotational energies for  $J=10$  ( $\text{cm}^{-1}$ ) for the Hoy-Bunker potential-energy surface of water. The energies are given with respect to the rotationless vibrational state (0, 0, 0). The dashed line divides  $A$ - from  $C$ -type states

$k_a$	$k_c$	$\Delta E$ <sup>a)</sup>	QM <sup>b)</sup>	FFT SH <sup>c)</sup>
10	0	-0.088	2710.710	2710.79
10	1	-0.088	2710.710	2710.79
9	1	1.31	2478.836	2477.53
9	2	1.31	2478.836	2477.53
8	2	-0.026	2260.733	2260.76
8	3	-0.025	2260.732	2260.76
7	3	-2.81	2059.779	2056.99
7	4	-2.78	2059.775	2056.99
6	4	-5.68	1879.999	1885.68
6	5	-6.17	1879.512	1885.68
5	5	2.51	1728.485	1725.98
5	6	-3.46	1722.509	1725.98
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4	6	13.0	1619.653	1606.64 <sup>d)</sup>
4	7	5.72	1584.526	1578.81
3	7	-37.8	1541.021	1578.81
3	8	-4.03	1448.839	1452.87
2	8	-12.3	1440.598	1452.87
2	9	-0.66	1295.952	1296.61
1	9	-1.28	1295.328	1296.61
1	10	-2.17	1116.621	1118.79
0	10	-2.19	1116.603	1118.79

<sup>a)</sup>  $\Delta E = \text{QM} - \text{FFT SH}$ .

<sup>b)</sup> Quantum-mechanical energies from ref. [22].

<sup>c)</sup> Present work.

<sup>d)</sup> Eigenvalue obtained by interpolation from the higher-energy  $A$ -type states.

Table 3

Rotational energies for  $J=10$  ( $\text{cm}^{-1}$ ) for the Lai-Hagstrom potential-energy surface of water. The energies are given with respect to the rotationless vibrational state (0, 1, 0). The dashed line divides  $A$ - from  $C$ -type states

$k_a$	$k_c$	$\Delta E$ <sup>a)</sup>	QM <sup>b)</sup>	FFT SH <sup>c)</sup>
10	0	3.06	2829.225	2826.17
10	1	3.06	2829.225	2826.17
9	1	0.92	2590.400	2589.48
9	2	0.92	2590.400	2589.48
8	2	-0.25	2362.718	2362.97
8	3	-0.25	2362.718	2362.97
7	3	1.34	2150.503	2149.16
7	4	1.31	2150.471	2149.16
6	4	1.30	1958.681	1957.38
6	5	0.67	1958.054	1957.38
5	5	-1.42	1795.943	1797.36
5	6	-8.68	1788.678	1797.36
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4	6	2.64	1678.624	1675.95 <sup>d)</sup>
4	7	29.09	1637.899	1608.81
3	7	-16.96	1591.850	1608.81
3	8	6.84	1487.755	1480.91
2	8	-1.81	1479.098	1480.91
2	9	-1.61	1317.366	1318.98
1	9	-2.28	1316.698	1318.98
1	10	4.32	1116.360	1112.04
0	10	4.10	1116.339	1112.04

<sup>a)</sup>  $\Delta E = \text{QM} - \text{FFT SH}$ .

<sup>b)</sup> Quantum-mechanical energies from ref. [22].

<sup>c)</sup> Present work.

<sup>d)</sup> Eigenvalue obtained by interpolation from the higher-energy  $A$ -type states.

Table 4

Rotational energies for  $J=10$  ( $\text{cm}^{-1}$ ) for the Hoy-Bunker potential-energy surface. The energies are given with respect to the rotationless vibrational state  $(0, 1, 0)$ . The dashed line divides A- from C-type states

$k_a$	$k_c$	$\Delta E$ <sup>a)</sup>	QM <sup>b)</sup>	FFT SH <sup>c)</sup>
10	0	0.148	2915.048	2914.90
10	1	0.148	2915.048	2914.90
9	1	-0.160	2656.970	2657.13
9	2	-0.160	2656.970	2657.13
8	2	1.67	2411.744	2410.07
8	3	1.67	2411.744	2410.07
7	3	-2.19	2183.339	2185.53
7	4	-2.20	2183.325	2185.53
6	4	2.38	1976.248	1973.87
6	5	2.07	1975.939	1973.87
5	5	-2.83	1797.621	1800.45
5	6	-7.07	1793.383	1800.45
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4	6	3.91	1663.377	1659.47 <sup>d)</sup>
4	7	21.5	1633.731	1612.19
3	7	40.8	1571.396	1612.19
3	8	12.1	1481.055	1468.96
2	8	-2.20	1466.760	1468.96
2	9	1.38	1312.081	1310.70
1	9	0.097	1310.801	1310.70
1	10	1.50	1112.713	1111.21
0	10	1.46	1112.670	1111.21

<sup>a)</sup>  $\Delta E = \text{QM} - \text{FFT SH}$ .

<sup>b)</sup> Quantum-mechanical energies from ref. [22].

<sup>c)</sup> Present work.

<sup>d)</sup> Eigenvalue obtained by interpolation from the higher-energy A-type states.

for  $k_a \approx J$  or  $k_c \approx J$ , each primitive energy level corresponds to a pair of near-degenerate quantum levels. For quantum states in the vicinity of the separatrix, there can either be two primitive quantizing trajectories corresponding to the same state, or none. Duchovic and Schatz discuss several interpolation schemes for quantizing states near the separatrix [7]. For the results reported below, we use a simple extrapolation scheme to determine primitive semiclassical energies for such states. More accurate treatment requires a uniform quantization procedure [5,7,13,14].

Total trajectory integration time was 16 ps. Good actions were converged to  $10^{-2}$ , while quantizing energies, as corrected by linear extrapolation [27], were converged to  $10^{-4}$ .

### 3. Results

Rotation-vibration energies for total angular momentum  $J=10$  are given in tables 1 and 2 for the ground  $(0, 0, 0)$  vibrational state of  $\text{H}_2\text{O}$  using the Lai-Hagstrom [21] and Hoy-Bunker [23] potentials, respectively. The energies shown are relative to the corresponding semiclassical eigenvalue for the  $J=0$  vibrational ground state. Results for the excited bending  $(0, 1, 0)$  state are given in tables 3 and 4. The quantum variational levels of Chen, Maessen and Wolfsberg [22] are shown for comparison. The overall level of agreement is very encouraging, as can be seen from figs. 1 and 2, where differences between the quantum and semiclassical eigenvalues are plotted against the quantum variational energies. There is however a noticeable deterioration in the quality of the primitive semiclassical eigenvalues in the vicinity of the separatrix. This disagreement is a consequence of the use of primitive quantization conditions, and also possibly the presence of weak chaos for states with rotational motion near the A/C separatrix.

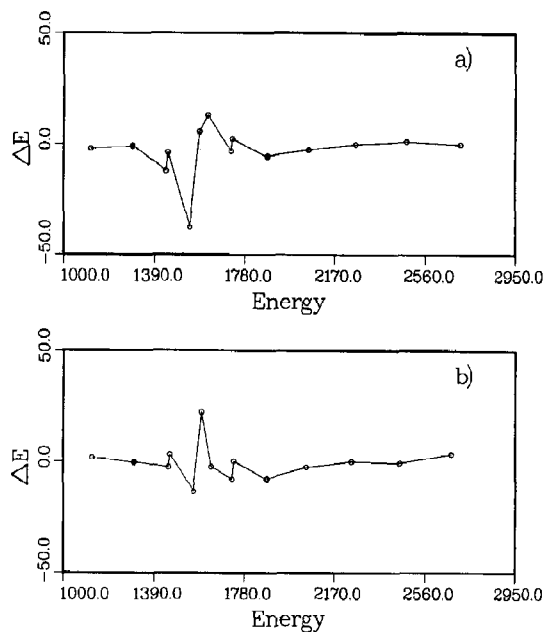


Fig. 1. Difference  $\Delta E$  between primitive semiclassical rotation-vibration energies and quantum variational eigenvalues versus quantum energies for  $J=10$ ,  $(0, 0, 0)$  states of  $\text{H}_2\text{O}$ . (a) Hoy-Bunker potential. (b) Lai-Hagstrom potential. All energies in  $\text{cm}^{-1}$ .

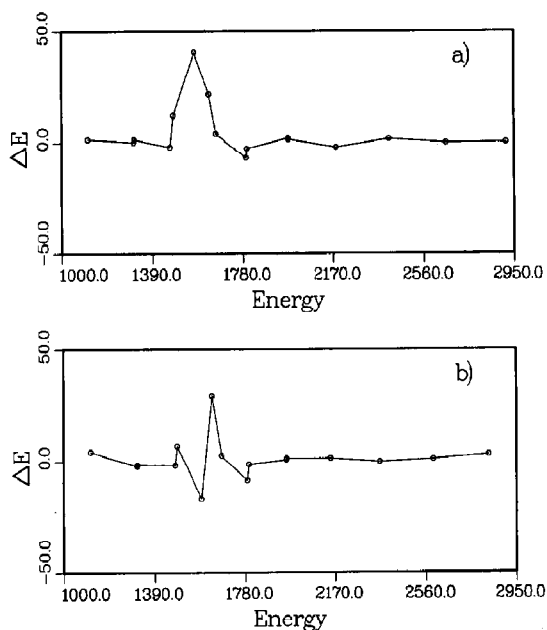


Fig. 2. Difference  $\Delta E$  between primitive semiclassical rotation-vibration energies and quantum variational eigenvalues versus quantum energies for  $J=10$ ,  $(0, 1, 0)$  states of  $H_2O$ . (a) Hoy-Bunker potential. (b) Lai-Hagstrom potential. All energies in  $cm^{-1}$ .

#### 4. Conclusion

The work reported here establishes the feasibility of semiclassical quantization of rotation-vibration levels for triatomic molecules with inclusion of all vibrational degrees of freedom. Improvements currently under investigation are accurate calculation of actions using the FFT EBK method [20], and uniform quantization of rotation-vibration levels using, for example, the method suggested by Frederick [14].

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