CLASSICAL ESTIMATES OF THE NUMBERS OF NORMAL, LOCAL,
AND STOCHASTIC STATES OF POLYATOMIC MOLECULES AS
FUNCTIONS OF ENERGY: APPLICATIONS TO H₂O

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For a general polyatomic molecule, the classical phase space at some fixed energy and angular momentum is divisible into two regimes: a quasiperiodic and a stochastic (or chaotic) regime. In certain molecules--those having symmetrically equivalent X-H bonds, where X is any heavy atom--the classical trajectories comprising the quasiperiodic regime can be subdivided into two classes: "normal" trajectories, for which the time-averaged amplitudes in all the X-H stretching vibrations are equivalent, and "local" trajectories, which exhibit a permanent imbalance in the amplitudes of the various X-H stretching vibrations.

We report here the development of trajectory diagnostics for bound, nonseparable motion to distinguish "normal", "local", and stochastic types of motion in systems with more than two internal (coordinate) degrees of freedom, and the application of these diagnostics to determine the numbers of normal, local, and stochastic states of a realistic model of nonrotating H₂O as functions of energy. This application is the first such study for a real polyatomic molecule.

The diagnostics involve properties of an appropriate coordinate cross-correlation function and tests of the numerical stability of trajectories. The time-averaged values of the chosen correlation function distinguish normal from local trajectories; the time structure of the correlation function and tests of numerical stability distinguish quasiperiodic from stochastic trajectories. The procedure is summarized in the following six steps:

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(i) determine the appropriate correlation function for the molecule in question to distinguish normal and local motion--for the case of H_2O , an appropriate choice is

$$A(t) = a(t) / \langle |a(t)| \rangle$$

$$a(t) = [\delta r_1(t)]^2 - [\delta r_2(t)]^2$$

where the δr_i in the latter expression are the two O-H bond displacements and the demoninator in the former expression is the time-averaged value of $|a(t)|$;

(ii) employ the Monte Carlo method to determine the number of states of the molecule at or below some specified internal energy E_c using the semiclassical formula

$$N(E_c) = \frac{1}{h^n} \int_{Q_1} \dots \int_{Q_n} \int_{P_1} \dots \int_{P_n} \theta(E_c - H(\underline{Q}, \underline{P})) dQ_1 \dots dQ_n dP_1 \dots dP_n$$

where $\theta(x)$ is equal to unity for $x > 0$ and equal to zero for $x < 0$;

(iii) using the same sampling technique employed in (ii), calculate an ensemble of trajectories with starting conditions randomly selected from a uniform distribution in the allowed classical phase space at or below the energy E_c ;

(iv) from the results of (iii), in which the trajectory diagnostics are applied to determine the "type" of each member of the ensemble, calculate $\langle f_n \rangle$, $\langle f_\ell \rangle$, and $\langle f_s \rangle$, the ensemble-averaged fractions of the allowed classical phase space corresponding to normal, local and stochastic motion, respectively;

(v) using the results of (ii) and (iv), calculate the numbers of normal, local, and stochastic states at or below the energy E_c by $N_i(E_c) = N(E_c) \langle f_i \rangle$, $i=n, \ell, s$;

(vi) repeat steps (ii) through (v) for various choices of E_c .

The results of this procedure as applied to the modified Sorbie-Murell model of H_2O are given in Table 1.

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Table 1. Numbers of Total, Normal, Local, and Stochastic States
as Functions of Energy for a Nonrotating, Three-Dimensional Model of H₂O

Energy above minimum, E_c (cm ⁻¹) ^a	Total States, N (E)	Normal States $N_n (E_c)$	Local States, $N_l (E_c)$	Stochastic States, $N_s (E_c)$
6231	1.48 ± 0.02	1.32 ± 0.06	0.15 ± 0.04	0.01 ± 0.01
11265	9.96 ± 0.10	6.12 ± 0.32	3.19 ± 0.28	0.65 ± 0.14
16299	33.05 ± 0.07	12.71 ± 0.84	12.80 ± 0.84	7.54 ± 0.72
21333	81.33 ± 0.14	19.81 ± 1.64	21.20 ± 1.69	40.32 ± 1.95
26367	167.88 ± 0.28	30.62 ± 2.96	31.63 ± 2.99	105.65 ± 3.80
31401	312.43 ± 0.51	33.46 ± 4.68	42.71 ± 5.19	236.29 ± 6.79
36435	547.58 ± 1.25	39.04 ± 6.82	40.30 ± 6.94	468.29 ± 10.32

^a The dissociation energy is 38354 cm⁻¹ above the minimum.

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