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# ON THE BEHAVIOR OF VIBRATIONALLY-EXCITED MOLECULES

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In the present lecture several topics on the behavior of vibrationally-excited molecules are considered. The first is the translational energy distribution of products of molecular beam reactions proceeding via molecular complexes. The second is the behavior of vibrationally-excited molecules inferred from recent quantum, classical and semiclassical theoretical studies--a largely statistical behavior at high vibrational energies and a nonstatistical one at low energies.

The translational energy distribution of products of bimolecular reactions involving intermediate complexes, such as

$$F + CCl_2 = CH_2 \xrightarrow{\alpha} FCCl_2 - \dot{C}H_2 \xrightarrow{\beta} Cl + FCCl = CH_2 \qquad (1)$$

$$F + C(CH_3)_2 = CH_2 \xrightarrow{\alpha} FC(CH_3)_2 - \dot{C}H_2 \xrightarrow{\beta} CH_3 + FCCH_2 = CH_2 \ , \qquad (2)$$

depends on (a) the energy distribution in the transition state of step $\beta$ in these reactions, and on (b) subsequent coupling, if any, of the internal modes of motion to the translational motion of the separating products in step $\beta$. When that coupling is negligible, the energy distribution of the products can readily be related to that of the transition state.[1] Since RRKM theory attempts to describe the energy distribution in the transition state, it can then be tested by measurements of the energy distribution of reaction products. Some information on the coupling in (b) is obtained from the steric factor of the reaction for the reverse of step $\beta$. A steric factor of unity implies a loose transition state and so no such coupling. Probably the steric factors of (1) and of (2) are of the order of unity and $10^{-3}$, respectively. Data on (1) agreed well with the theoretical (e.g., RRKM) predictions[2] while (2) required a fuller analysis of the coupling effects in (b).[3] One treatment, which assumes the reverse of (2) to be translationally rather than vibrationally "driven", was given in Ref. 3.

Some examples of classical mechanical trajectory calculations for a system of anharmonically coupled oscillators are described next. For the Hamiltonian

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda x(y^2 + \eta x^2) \ , \qquad (3)$$

the classical mechanical equations of motion for coordinates x and y and for momenta $p_x$ and $p_y$ have been integrated numerically on a computer to yield these variables as a function of time.[4] A typical trajectory is given in Fig. 1 for the case of incommensurable $\omega_x$ and $\omega_y$.

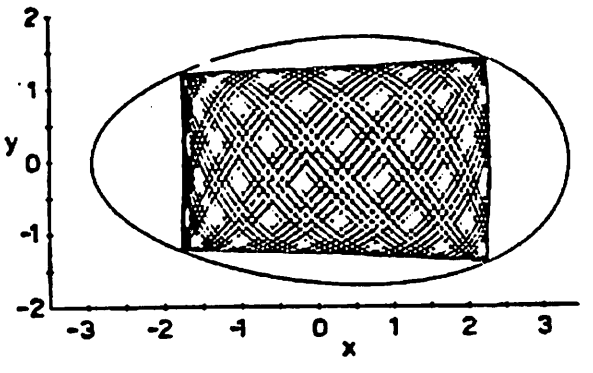


Fig. 1. A trajectory for Hamiltonian (1) with $\omega_x$ and $\omega_y$ incommensurable. The oval is the place where the potential energy equals the total energy E.

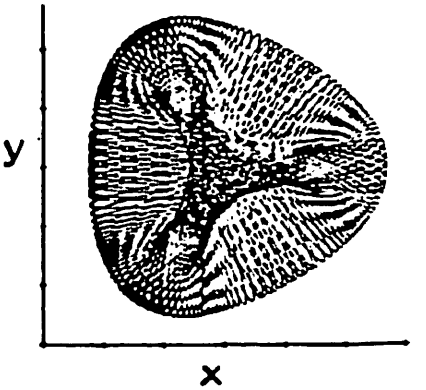


Fig. 2. As in Fig. 1 but $\omega_x = \omega_y$.

One sees from Fig. 1 that not all of the energetically accessible configuration space is occupied by the trajectory. In the four-dimensional phase space $(x, y, p_x, p_y)$ at a given energy E, the instantaneous value of $p_y$ is determined, apart from sign, by the instantaneous value of x, y, and $p_x$ of the trajectory, by energy conservation. Thus, the system moves on a three-dimensional surface in this phase space. However, for quasi-periodic trajectories, such as that in Fig. 1, it moves in a more restricted way--on a two-dimensional surface! It winds around a torus (doughnut), ultimately covering it uniformly when $\omega_x \neq \omega_y$.[5] A projection of the torus onto the (x, y) plane yields Fig. 1. One can plot $p_x$ versus x each time the trajectory in Fig. 1 crosses the plane y = 0, with $p_y > 0$, as in Fig. 4 of Ref. 4. By calculating the area $\oint p_x\, dx$ and setting it equal to

$$\oint p_x\, dx = (n_x + \tfrac{1}{2})h \quad , \tag{4}$$

where $n_x$ is an integer, and doing the same for a $p_y$ vs. y plot, composed of points noted each time the trajectory crosses the x = 0 axis, with, say, $p_x > 0$,

$$\oint p_y\, dy = (n_y + \tfrac{1}{2})h \quad , \tag{5}$$

one can "quantize" the trajectory, thereby making use of a semiclassical theory bridging classical and quantum mechanics.[4] The initial conditions of the trajectory, including the total energy E, are adjusted until the $n_x$ and $n_y$ determined by (4) and (5) are integers. The energy eigenvalues calculated in this way agree well with the quantum mechanical eigenvalues.[4]

Related remarks apply to the cases where $\omega_x$ and $\omega_y$ are commensurable, for example 1:1 or 2:1.[6,7] An example of the 1:1 case is given in Fig. 2.[6] One now has extensive energy exchange between the x and y coordinates, but the motion is still quasi-periodic rather than statistical: One again has simple patterns in the momentum versus coordinate plots, and eigenvalues can again be calculated reasonably accurately using curvilinear analogs of Eqs. (4) and (5).[6] Indeed, at low energies for these and other systems, one typically has this nonstatistical behavior of the vibrational motion of the molecules ("KAM" theorem).[5]

According to the semiclassical theory the vibrational wavefunction should be large (but oscillatory) in the region occupied by the trajectories, e.g., in Figs. 1 and 2. This expectation was verified by a large basis set variational calculation of the wavefunction.[7]

The spectral lines were also calculated from trajectories in this "quasi-periodic" regime (defined in the standard way as a Fourier transform of the autocorrelation function of a coordinate) and suitable semiclassical analysis.[8] They yielded a spectrum composed of a few lines, and these agreed well with the quantum mechanically calculated lines.[8]

At high energies the vibrationally-excited molecule behaves very differently. The trajectory now tends to occupy all of the energetically-accessible region as in Fig. 3.

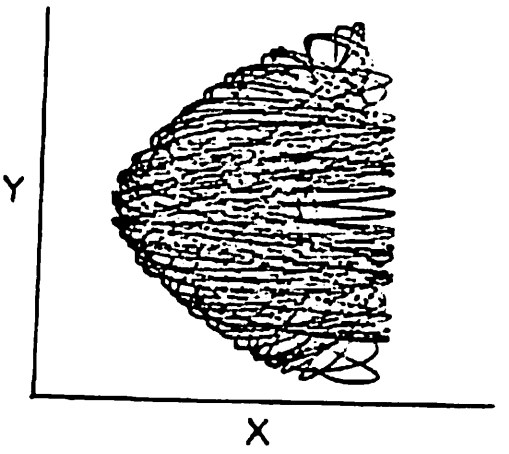


Fig. 3. As in Fig. 1 but for a high energy trajectory (statistical regime).

The $p_x$ vs. x plot at y = 0 and the $p_y$ vs. y plot at x = 0 now resemble a shotgun pattern,[5,7] and so no area can be calculated for Eq. (4) or (5). Similarly, the quantum mechanical wavefunction tends to occupy the energetically accessible space;[7] the classical

mechanical spectrum now contains many lines, and the quantum mechanical spectrum also contains various lines, fewer than those in the classical spectrum but in the same region as the classical lines.[9]

In the high energy ("statistical") regime each quantum state thus behaves as though it tries to occupy all of the relevant phase space and so a theory such as RRKM would be valid under such conditions. At low enough conditions the reverse is true and a different, more dynamical approach is required. The energy region where the statistical behavior sets in is given by Chirikov's theory of overlapping internal resonances:[10] The system can oscillate between two "modes" in a resonance, and continue to behave in a nonstatistical fashion, but when there are many overlapping resonances, it moves from one mode to many other modes and ultimately, for a sufficient number of overlapping resonances, occupies all of the energetically accessible phase space.

An internal resonance results in a slow energy exchange superimposed on the natural fast oscillations, and so contributes additional lines, displaced from the main frequencies by an amount equal to the frequency of this transfer. When there are many resonances, one would expect, on this basis, to have numerous lines, as observed. Thus, this observed result of Refs. 8 and 11 offers support for Chirikov's theory. Averaging over many trajectories converts the line classical spectrum in this statistical case to a continuous curve.

The semiclassical wavefunction for the quasi-periodic bound state systems can be written as[12]

$$\psi = \sum_b A \exp iS/\hbar \tag{6}$$

where A is determined from S by normalization (the Van Vleck determinant), S is $\int(p_x\,dx + p_y\,dy)$ and the sum b is over all four branches of S corresponding to the four possible combinations of signs of $p_x$ and $p_y$, and is such that the classical variables of the trajectory producing S correspond to the specified integer values of $n_x$ and $n_y$ in Eqs. (4) and (5). (A fuller discussion is given in Refs. 12, 6, and 7.)

In the statistical regime the semiclassical wavefunction is not yet known, since the $\oint p\,dq$ integrals no longer rigorously exist under these conditions. One possibility, a rather approximate one, is that $\psi$ now includes contributions from all zeroth order sets of integers n consistent with the given energy E (say, N sets):

$$\psi_E \approx \sum_n a_n \psi_n \ , \qquad |a_n| \approx 1/\sqrt{N} \tag{7}$$

where each $\psi_n$ is of the form in (6) and the sum is over all sets of integers n for that E, within some uncertainty $\delta E$ related to the rate of modal energy exchange between the $\psi_n$'s. Because of the large number of n's contributing, one expects destructive interference of cross-terms in computing averages with this $\psi_E$. (This interference would occur, for example, when there is a random distribution of signs of the $a_n$'s subject to the constraint imposed by orthogonality of the N $\psi_E$'s in the (E, E + $\delta$E) range.) The average of any function f in such a state is then

$$\int \psi_E^* f \psi_E \, dq \approx \frac{1}{N} \sum_n \int \psi_n^* f \psi_n \, dq \tag{8}$$

where dq denotes the volume element in coordinate space. One can show, when the semiclassical expression for $\psi_n$ in Eq. (6) is introduced, that this average effectively equals the microcanonical average:

$$\int \psi_E^* f \psi_E \, dq \approx \int\int dq\,dp\, \delta(E - H(q,p)) / \int dq\,dp\, \delta(E - H) \ . \tag{9}$$

Here, E is the energy eigenvalue of the exact wavefunction $\psi_E$. Eq. (9) can be, but has not yet been, tested by numerical comparison of both sides of the equation for various f's. $\delta$ is the Dirac delta function, ensuring a microcanonical average.

Related remarks may apply to the computation of off-diagonal matrix elements such as those involved in the calculation of spectra, e.g., for a spectral line of frequency $\nu = (E' - E)/h$, one calculates $|\int \psi_{E'}^* x \psi_E \, dq|^2$, which would become $\Sigma |\int \psi_m(E') x \psi_n(E)\, dq|^2 / N(E)N(E')$, with $\Sigma$ over m and n, when cross-terms are neglected. There are fewer lines in the quantum spectrum in the statistical case than in the classical spectrum,[9] perhaps because of the restriction in the former case on the allowed n's (integers) and not on the latter. Thereby, there are fewer resonances between the different modes in the quantum case and so a smaller number of lines.

In summary, we believe that a quantum state in the statistical regime already has statistical properties, with the excitation distributed among many zeroth-order modes of vibration, and RRKM behavior is then anticipated. Further calculations will test this possibility, e.g., via testing Eq. (9). At low enough energies ("quasi-periodic" regime) a quite different, highly nonstatistical behavior prevails.

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