

ASPECTS OF INTRAMOLECULAR DYNAMICS IN CHEMISTRY

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ABSTRACT

The role of chaotic and quasiperiodic behavior of isolated molecules is discussed. The quantum analog of classical quasiperiodic states appears to be relatively well understood. A possible quantum analog of classical chaotic behavior is described, using overlapping quantum mechanical Fermi resonances as a way of generating irregularities. The relation of these Fermi resonances to avoided crossings in eigenvalue plots and to various treatments of intramolecular dynamics in the chemical literature is outlined.

INTRODUCTION

In this lecture we review several aspects of the role of chaos in the behavior of isolated molecules:

- (1) interests of chemists in the properties of isolated molecules
- (2) possible quantum analogs of classical chaotic and quasiperiodic motion, and the relation to quantum mechanical 'overlapping Fermi resonances' and overlapping avoided crossings,
- (3) relation of 'overlapping Fermi resonances' to theories of various experimental results.

Since we have discussed some of this material elsewhere¹⁻⁴ we shall abbreviate this written version of the lecture.

RELATION TO CHEMISTRY

The relation of chaotic and quasiperiodic nonlinear behavior to the properties of isolated molecules is twofold: (a) chemical reactive behavior, (b) spectral properties. As an example of (a), we note that the rate of dissociation of a molecule, such as



and isomerization of a molecule, such as



depends on the vibrational energy of the molecule and on whether the motion is quasiperiodic or chaotic. (More precisely it depends on the quantum mechanical analogs of these properties.) Spectral properties, absorption and fluorescence, will also depend on these properties.

A review of some of the experimental methods of excitation of the vibrations of molecules, the experimental results, and the relevant statistical theory of unimolecular dissociations and isomerizations are given in ref. 1-4. The statistical theory ("RRKM" theory) frequently used in interpretation of the experiments is in agreement with most of these data.¹⁻⁴

Recently, the possible ability of a heavy metal atom to partially isolate dynamically the parts of a molecule that are attached to it has been discussed.^{2, 5, 6} If this isolation can be accomplished it will offer a possibility of intramolecular laser selective chemistry, in which one selectively excites one part of a molecule and causes mainly that part to dissociate or isomerize. Normally, the vibrational energy of excitation would, at least in the absence of the heavy atom, rapidly redistribute between the various parts of the molecule (in ~ 1 picosecond). A discussion has been given elsewhere of the heavy metal atom studies, both experiment⁵ and theory.^{2, 6}

ON THE QUANTUM ANALOG OF QUASIPERIODIC AND CHAOTIC BEHAVIOR

We first recall that nonlinear classical resonances provide an effective way of exchanging energy between vibrational modes, a point stressed by many authors (e. g. , Chirikov, Ford). It offers a route to classical chaos. The role of these nonlinear resonances in coupling vibrational modes is very evident in refs. 2 and 6.

The semiclassical connection between classical quasiperiodic states and corresponding quantum states was treated in a practical

way for the first time for systems with hard-walled potentials by Keller⁷ and for systems with smooth potentials by Eastes⁸ and by Noid.⁹ Methods were presented there for calculating action integrals in nonseparable systems.⁷⁻⁹ Since that time a variety of semiclassical quantization procedures have been introduced and are complementary to the original trajectory method (cf. ref. 3 for review). The quantum analog of classical quasiperiodic behavior seems fairly clear (e. g., 1-3): (1) One expects regular eigenvalue sequences, each sequence corresponding to some mode being excited and each sequence with a smoothly varying spacing. In the terminology of Percival the spectrum is 'regular'.¹⁰ Of course, in a system with many coordinates and hence with many eigenvalue sequences it may be very difficult or impractical to determine if there are regular sequences of eigenvalues, even if the behavior is actually quasiperiodic. (2) Secondly, one expects that in this quantum analog the wavefunction ψ (or $|\psi|^2$) will have a regular pattern, e. g.³ Sometimes, as in the case of the 99-quasibound state Henon-Heiles system the wave pattern is rather complicated¹¹ but still regular.

In the quantum analog of classical chaotic states one expects irregular spectra, as Percival has noted¹⁰ (no recognizable regular sequences of eigenvalues), and irregular patterns for $|\psi|^2$. One mechanism for generating these irregularities, we have noted, lies in "Fermi resonances", illustrated by avoided crossings in plots of eigenvalues versus perturbation parameters.^{2, 4, 12, 13} We amplify on this point next:

We note that near-degeneracy of two eigenvalues in itself has no implications regarding energy transfer between two modes. However, if this near-degeneracy disappears when a suitable perturbation parameter is varied, i. e., if the two eigenvalues participate in an 'avoided crossing', a wavepacket constructed from a sum of two such states is associated with a quasiperiodic energy transfer between two modes. The two modes are reasonably well described by the two states away from the avoided crossing (e. g., of Figs 4 and 5 of ref. 12). As discussed elsewhere,²⁻⁴ isolated avoided crossings, like isolated classical resonances, do not yield chaos, but overlapping "avoided crossings" ("overlapping Fermi resonances") yield the two attributes of the chaotic behavior mentioned above--irregular spectra and irregular patterns for $|\psi|^2$. These avoided crossings are discussed in refs. 2-4 and 12-13.

We have also noted that classical chaos may be a necessary, but not a sufficient for "quantum chaos".² Sufficient conditions have been proposed (ref. 2 and references cited therein) for the case where a quantum Fermi resonance is generated by a classical resonance, (i. e., for a quantum resonance which occurs in a Hamiltonian having a classical resonance in the same phase space

region). These conditions have been phrased in quantitatively and are² (1) that the width of the classical resonances be larger than $\hbar$; otherwise the splitting at the avoided crossing becomes very small, (2) that the overlap of neighboring resonances in action space be greater than $\hbar$; otherwise there will not be a quantitatively significant overlap of the corresponding quantum Fermi resonances (avoided crossings), and (3) that the center of the resonance be sufficiently close^{4b} to a relevant quantum state.

Insight into quantum mechanical avoided crossings and thereby into the associated quantum Fermi resonances, when generated by classical resonances, has been obtained in a recent semiclassical analysis.^{12, 14} The splitting of the eigenvalues in the vicinity of the avoided crossing was calculated in this way from data on classical trajectories and was found to be in reasonable agreement with that calculated numerically by diagonalizing a large basis set.¹⁴ An interesting feature was that the classical trajectories themselves generated, in the 'primitive semiclassical' treatment, eigenvalue plots which intersect rather than avoid each other.^{12, 14} The quantum mechanical splitting was associated, thereby, with a classically-forbidden process.^{14, 15} Use of low order perturbation theory led to a functional form of a semiclassical Hamiltonian suitable for the latter analysis.¹⁴ The various parameters in this Hamiltonian were then evaluated from the phase integrals associated with the two sets of trajectories and with the separatrix separating the two types of trajectories. The Hamiltonian led to a Mathieu's differential equation of fractional order for the semiclassical wavefunction, whose eigenvalues yielded the eigenvalues for the system.¹⁴ A phase integral analysis of the problem has also been made.¹⁵ Such studies delineate further the relation between these aspects of quantum and classical behavior.

RELATION OF AVOIDED CROSSINGS (FERMI RESONANCES) TO THEORIES OF INTRAMOLECULAR ENERGY TRANSFER

The concept of overlapping avoided crossings (overlapping quantum mechanical Fermi resonances) is related to a number of concepts that are used to interpret various types of experimental data. For example, in interpreting data on the dependence of the infrared multiphoton absorption cross-section for molecules as a function of absorbed energy, a series of one-quantum exchanges to other vibrational modes has been proposed to model the absorption coefficient at higher energies.¹⁶ Such a model, involving the coupling of many modes by resonances, corresponds to 'overlapping Fermi resonances'.

A second example is in an interpretation of the linewidths in C_6H_6 in which a CH overtone vibration is excited and assumed to

lose its energy by coupling to an HCC mode in a 2:1 Fermi resonance, and that this HCC mode is in turn, coupled to other nearly resonant modes.¹⁷ Again, such a mechanism would correspond to the idea mentioned above of "overlapping Fermi resonances". If the linewidth of the high CH overtones is correctly modelled by this energy loss (T_1 -type) mechanism, and if indeed the line is not inhomogeneously broadened, then the linewidth indicates an energy loss rate from the excited CH vibration in the subpicosecond region.

A third example of overlapping Fermi resonances may occur in Jensen's discussion, in this symposium, of the multiphoton ionization of atom.

In summary, a picture is beginning to emerge in which the quantum analog of classical quasiperiodic motion is, we believe, reasonably clear. The many successful examples of semiclassical quantization, beginning with the cited work of Keller,⁷ Eastes⁸ and Noid,⁹ are consistent with this view. The quantum analog of classical chaotic behavior is also, we believe, becoming clearer, at least qualitatively. One route to this quantum chaos is that of 'overlapping' quantum mechanical Fermi resonances.

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