QUANTUM EFFECTS IN INTRAMOLECULAR ENERGY TRANSFER: THE ROLE OF OBSERVATIONS

Ronni KOSLOFF* and Stuart A. RICE
The Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637, USA

Received 29 August 1979; in final form 15 November 1979

We show that when the nature of the preparation and observation processes are included in the quantum mechanical description of intramolecular energy transfer, Heller's argument for the nonergodicity of isolated degenerate quantum systems must be modified The observation of nonergodic behavior in such systems is discussed.

Consider a system of coupled nonlinear oscillators. It is now well established [1] that the classical mechanical trajectories of such a system are quasiperiodic at low energy and stochastic at high energy; the transition between these domains of different behavior occurs over a small energy range, the location of which depends on the system hamiltonian The corresponding quantum mechanical behavior was studied by Nordholm and Rice [2], who examined the nature of the stationary states when represented in a suitable harmonic oscillator basis. They proposed that the quantum mechanical analogue of the transition from quasiperiodic to stochastic trajectories is a dramatic change in the distribution of amplitude amongst the basis functions; at low energy only a few basis functions contribute to the wavefunction, whereas at high energy all equienergetic combinations of basis functions contribute to the wavefunction. Although this criterion is basis dependent, and to some extent subjective, it has been verified by studies of the nodal distribution of the wavefunction [3], and by studies of the nature of the representation of the system wavefunction in the natural orbital basis [3].

Heller [4], in an important contribution, has pointed out the existence of interference effects that lead to a fundamental difference between the quantum mechanical and classical mechanical behavior of systems of coupled nonlinear oscillators. He showed, using only group theoretical arguments, that nonlinear oscillator systems which have symmetries leading to degenerate quantum states do not transfer energy equivalently to rigorously equivalent phase space locations. In particular, if the initial state is a wave packet, Heller shows that the time averaged probability of finding the system in the initial state is larger than that of finding the system in states which are symmetrically equivalent. This behavior, which is independent of energy, contradicts the behavior expected when the corresponding classical mechanical trajectory is stochastic, since in the latter case the time averaged probabilities for finding the system in symmetrically equivalent states are equal.

The interference effects, destructive in some regions of phase space and constructive in other regions, represent only one of the fundamental differences between the quantum mechanical and classical mechanical descriptions of a system. An equally important difference arises from the nature of the observation process. In this note we demonstrate that the means that must be used to prepare the system in an initial state of the type discussed by Heller, or to verify the prediction that the time averaged probabilities of finding the system in symmetrically equivalent states are not the same, destroy the basis for the lack

* Chaim Weizman Postdoctoral Fellow.

of equality of time averaged amplitudes. Thus the complete quantum mechanical description, including the nature of the observation, must be used to determine if there is asymptotic behavior which is necessarily different from that of the classical mechanical description.

Heller's argument can be summarized as follows. Let ψ_a be the wavefunction of the initial state. The time averaged probability of finding the system in the state ψ_b is [2]

$$P(a|b) = \lim_{T\to\infty} \left[T^{-1} \int_0^T \mathrm{Tr}[\hat{\rho}_a(t)\hat{\rho}_b]\,dt \right], \quad (1)$$

where $\hat{\rho}_a = |a\rangle\langle a|$, and $\hat{\rho}_b = |b\rangle\langle b|$ are the density operators corresponding to ψ_a and ψ_b Suppose the eigenfunctions of the system hamiltonian are ϕ_{ni}, where n labels the energy and i the degeneracy. Then

$$\psi_a = \sum_{n\,i} a_{ni}\phi_{ni}, \quad \psi_b = \sum_{m\,i} b_{mi}\phi_{mi}, \quad (2)$$

so that (1) can be rewritten in the form

$$P(a|b) = \sum_n \sum_m \left| \sum_i a_{ni} b_{mi} \right|^2 = \sum_n |\boldsymbol{a}_n \cdot \boldsymbol{b}_n|^2. \quad (3)$$

Heller now compares $P(a|a)$ with $P(a|Ra)$, where R is a symmetry operation Because R is represented by a unitary matrix which preserves length, it is found that

$$|\boldsymbol{a}_n \cdot \boldsymbol{b}_n|^2 = |\boldsymbol{a}_n \cdot \Gamma(R)\boldsymbol{a}_n|^2 \leqslant |\boldsymbol{a}_n \cdot \boldsymbol{a}_n|^2, \quad (4)$$

which implies

$$P(a|a) \geqslant P(a|Ra). \quad (5)$$

The prediction implied by (5) is not meaningful unless the means of preparation of the initial state and of observation are both specified. We now note that in order to differentiate between symmetry equivalent states of an isolated system it is necessary to break the isolation and the symmetry. i e both the preparation and the measurement process necessarily introduces into the total hamiltonian for the system and the measuring apparatus a term which lifts the degeneracy of the states of the isolated system hamiltonian. When that degeneracy is lifted Heller's argument ceases to be valid. For simplicity, only the influence of observation will be analyzed below, a parallel argument can be used to describe the preparation process.

Consider, as an example, the Henon–Heiles hamiltonian. The potential energy surface in this case has three fold symmetry and belongs to the group C_{3v}.

$$v(r, \theta) = \tfrac{1}{2} r^2 + \tfrac{1}{3} \lambda r^3 \sin 3\theta. \quad (6)$$

We imagine using a two level system as a measuring apparatus to differentiate the three equivalent states [5,6]. the spin up state of the measuring apparatus will be correlated with ψ_a and spin down position with ψ_b. The initial state of the measuring apparatus is, then, spin up. The interaction between the system and the measuring apparatus is taken to be

$$\hat{H}_I = g(t) \sin(\tfrac{1}{2}\theta)(\hat{\sigma}_x - \tfrac{1}{2}), \quad (7)$$

where $g(t)$ specifies the time dependence of the probing interaction and $\hat{\sigma}_x$ is the appropriate angular momentum operator of the two level measurement apparatus A measurement is made as follows: the system is probed, subject to the interaction hamiltonian (7), for a period such that

$$\int_0^t g(t)\,dt = 2\pi/3^{1/2}. \quad (8)$$

As a result of this probing, the final state of the measuring apparatus records the time averaged probability $P(a|b)$ in a system in which the threefold degeneracy has been lifted. Although the form chosen for $\hat{H}_I$ in (7) is specific, the principle implied is generally valid; we conclude that eq (5) describes a situation which is necessarily disturbed by the observation process.

The result of this analysis of the influence of observations on the asymptotic distribution of amplitude in a quantum mechanical system only shows that the interference effects in a system with degenerate states that would prohibit quasi-ergodic behavior are perturbed by observation, the result does not show that quasi-ergodic behavior must be observed, nor does it show that it is impossible to observe the consequences of (5). Imagine an ensemble of systems with interaction (6) prepared in a coherent state. Suppose the measurement process is carried out, at different times $t_1 < t_2 < ...$ on different replicas of the ensemble. Although each measurement on one replica alters the amplitude distribution in that replica, rendering it useless for further measurements, we imagine that in the absence of measurements (5) holds so that measurements on different replicas will yield behavior different from that predicted if (5) does not hold. The validity of this interpretation will depend on the nature of the preparation process and of the observation made, and each case must be examined for special characteristics. For example, one way of observing interference effects that prevent attainment of ergodicity, and to avoid having the measuring process lift the degeneracy of the isolated system, is to determine the values of a set of operators that commute with the symmetry operators of the isolated system. In the case of the Henon–Heiles system one such operator is the angular momentum. Because the potential energy operator (6) has C_{3v} symmetry, possible changes in the angular momentum must satisfy selection rules and therefore, the angular momentum will not change in an ergodic fashion.

This research was supported by grants from the NSF CHE78-01573 and AFOSR F49620-76-C-0017. Discussions of the contents of this note with Professor R A. Harris and with Professor R. Heller were helpful in focusing our thoughts.

References

[1] M. Henon and C Heiles, Astron. J. 69 (1964) 73; J. Ford, Advan. Chem. Phys. 24 (1975) 155.
[2] K S.J. Nordholm and S A. Rice, J. Chem. Phys. 61 (1974) 203, 61 (1974) 768.
[3] R M Stratt, N.C. Handly and W H. Miller, J. Chem. Phys., to be published.
[4] E.J. Heller, Chem. Phys. Letters 60 (1979) 338.
[5] A Peress, Am. J. Phys 42 (1974) 886.
[6] R Kosloff, Advan Chem. Phys, to be published.